SYNTHESIS OF SOME NEW HETEROARYLBISAZO DYES DERIVED FROM p-AMINOAZOBENZENE

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Several novel arylbisazopyrazolo[1,5-*a*]pyrimidines were synthesized from diazotization of 4-aminoazobenzene and coupling with malononitrile and then refluxed with hydrazine hydrate to give 3,5-diamino-4-arylbisazo-1*H*-pyrazole.The later compound was diazotized and coupled with bifunctional reagents to produce novel heteroarylbisazo dyestuffs. Structural characterization of these novel dyes was carried out using IR, ^{1}H NMR, and mass spectroscopy.

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Introduction

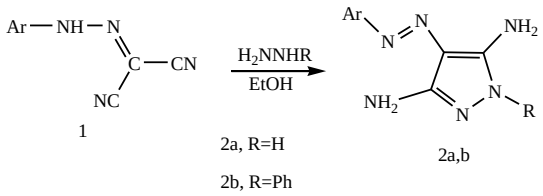
It has been known for many years that the azo compounds are the most widely used class of dyes due to their versatile applications in various fields such as dyeing of textile fibers, coloring of different materials, biological medical studies and advanced applications in organic synthesis.[1,2] Azo dyes with heterocyclic diazo components have been intensively investigated to produce bright and strong colour shades ranging from red to greenish blue on synthetic fabrics.[3,4]

5-Aminopyrazoles are very important class of heterocycles due to their biological and pharmacological activities.[5,6] These compounds often exhibit anti-inflammatory, herbicidal, fungicidal, bactericidal, and antipyretic activities.[6-12] The aminopyrazole compounds have been easily obtained by the reaction of nitrile derivatives with hydrazine, and are very useful as precursors for the synthesis of fused heterocyclic ring systems.[13,14] Reactions of aminopyrazoles with electrophilic reagents give rise to various fused annulated heterocyclic systems, including pyrazolo[1,5-*a*]pyrimidines which are synthetic analogs of purines. These compounds exhibit a wide spectrum of biological activity, in particular enzymatic, antibacterial, antiphlogistic and antiparasitic activities.[15,16] They are also used as intermediates in the dyestuff industry.[17-19]

In continuation of these studies, we report here the synthesis of some new bisazopyrazolo[1,5-*a*]pyrimidine, pyridazin, isoxazol, and 1,3,5-triazine thione dyes starting with *p*-aminoazobenzene.

Results and Discussion

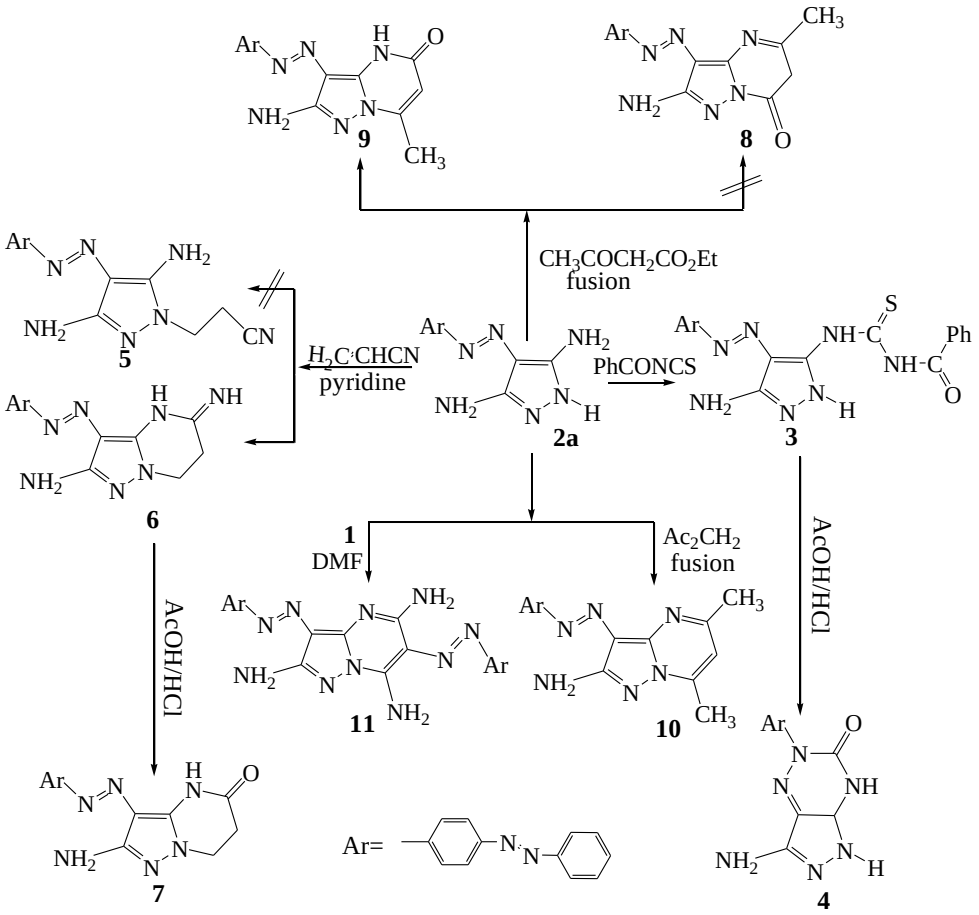
The dye intermediate 2-[4-phenylazo-phenylhydrazono]-malononitrile (**1**) was prepared by the general route[20] involving diazotization of the *p*-aminoazobenzene and coupling of its diazonium salt with malononitrile. 2-[4-Phenylazo-phenylhydrazono]- malononitrile (**1**) was reacted with hydrazine hydrate and phenyl hydrazine yielding the corresponding pyrazole derivatives (**2a, b**) (Scheme 1).



Scheme 1. Synthesis of pyrazole derivatives.

The treatment of compound **2a** with benzoyl isothiocyanate furnished the pyrazol-5-yl-thiourea (**3**). Compound **3** was converted into pyrazolo[3,4-e]as-triazines (**4**) on treatment with acetic acid- hydrochloric acid mixture. Structures of both **3** and **4** were proposed for this reaction product on the basis of analytical and spectral data. Moreover, the reaction of **2a** with acrylonitrile was investigated as a possible route for the synthesis of pyrazolo[1,5-*a*]pyrimidines. Compound **2a,** treated with acrylonitrile in boiling pyridine, afforded directly the iminopyrazolo[1,5-*a*]pyrimidine (**6**) and not the cyano ethylation product (**5**). Compound **6** could be readily converted to the corresponding 5-ketopyrazolo[1,5-*a*]pyrimidine derivative (**7**) by refluxing it in a mixture of acetic acid–hydrochloric acid or by heating with conc. sulfuric acid. On the other hand, the reaction of compound **2a** with ethyl acetoacetate afforded the condensation product **9** not **8**. The *m/z* fragmentation showed the base beak at 360 (M^+-72) due to the cleavage of amide bond The first step of the mechanism involves the condensation of the NH group of the pyrazole ring with the carbonyl group, followed by dehydration, subsequent nucleophilic cyclization, with the loss of ethanol molecule.

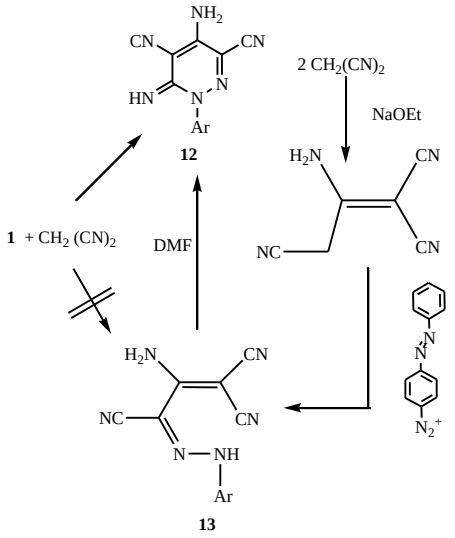
Similarly, compound **2a** reacted with acetylacetone to furnish pyrazolo[1,5-*a*]pyrimidine derivative (**10**), which was confirmed from analytical and spectral data. In a similar manner, aminopyrazole **2a** also reacted with 2-[4-phenylazo-phenylhydrazono]-malononitrile **1** in boiling DMF to furnish pyrazolo[1,5-*a*]pyrimidine (**11**). The ^{1}H NMR spectrum of structure **11** showed three singlets at δ = 2.75, 2.85 and 6.92 ppm corresponding to the three NH_2 groups. IR spectrum showed peaks at 3411, 3275 and 3150 cm^{-1} for the NH_2 and MS (*m/z* 581, M^+) (Scheme 2).



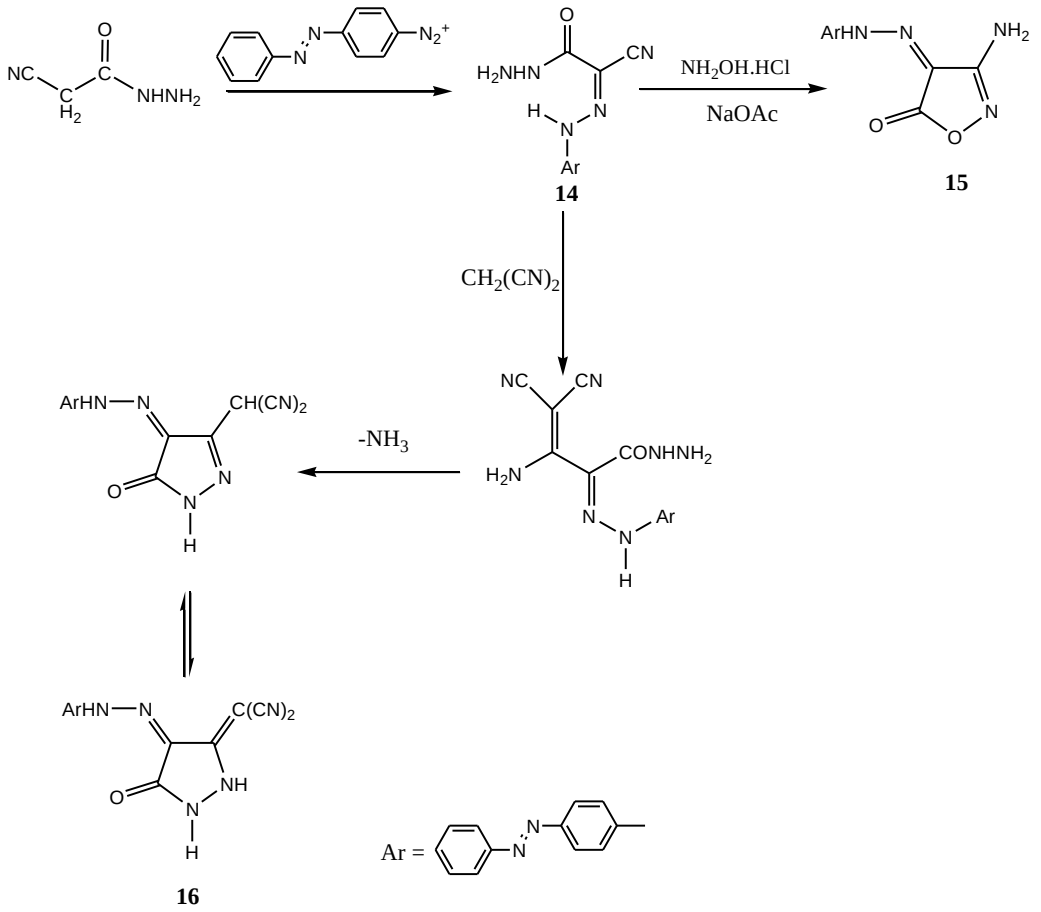
Scheme 2. Reactions of compound (**2a**).

Compound **1** reacted with malononitrile to yield compound **12**. The analytical and spectral data confirmed that the reaction product was compound **12** not **13**. In order to establish the structure of compound **12**, 2-amino-1,1,3-tricyanopropene was coupled with the diazonium salt of *p*-aminoazobezene to afford a product which was considered to have the structure of compound **13**. When compound **13** was boiled for a short period of time in DMF, a product was obtained that was identical in all respects with the product of the reaction of compound **1** with malononitrile, thus establishing structure **12** for the latter product.[21] The IR spectrum of compound **12** revealed a broad CN absorption in the region 2180–2200 cm^{-1}. This large frequency shift may be attributed to the presence of amino and imino groups adjacent to the cyano function. Baldwin and co-workers[22] reported CN absorption for o-aminonitriles in the range 2160–2200 cm^{-1} (Scheme 3).

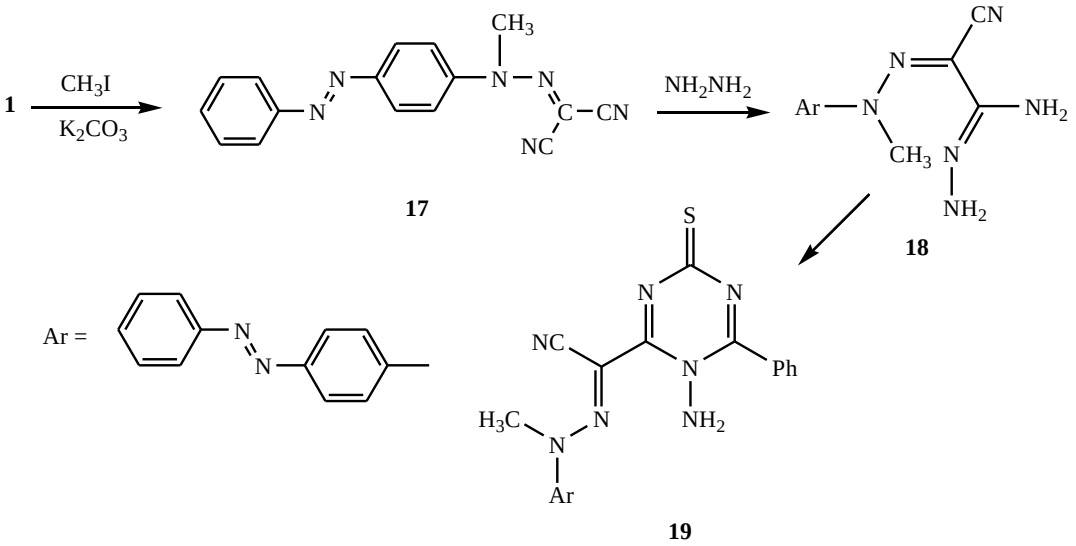
Compound **14** was synthesized via coupling of cyanoacethydrazide with the diazonium salt of p-aminoazobezene. Compound **14** reacted with hydroxylamine hydrochloride in cold in the presence of sodium acetate to afford 3-amino-4-[4-phenylazophenylhydrazono]-2-isoxazolin-5-one (**15**). The cyano group of compound **14** was condensed with malononitrile in refluxing DMF to yield a product which was considered to have the structure of compound **16**. Structures **14-16** were established on the basis of analytical and spectral data (Scheme 4).



Scheme 3. Synthesis of compounds (**12**) and (**13**).



Scheme 4. Synthesis of compounds (**14**) – (**16**).



Scheme 5. Synthesis of compounds (**18**) and (**19**).

Compound **18** could be obtained via the action of hydrazine hydrate on N-methylphenylazo-phenylhydrazono-malononitrile (**17**), the latter was synthesized via the action of methyl iodide on **1**. The IR spectra of compound **18** showed the strong absorption band at3440-3340 $cm^{-1}$for the amino group (NH_2), at 2210 cm^{-1} for the cyano group (CN), and 1600 cm^{-1} for (N=N). ^1H NMR spectrum of structure **18** revealed a singlet at δ 3.8 (s, 3H) assigned to methyl group, and (s, 4H) assigned for the 2-amino groups, and at δ 7.1-7.7, (m, 9H) for aromatic protons. The reaction of comound **18** with benzoyl isothiocynate, in refluxing acetone gives the corresponding aminotriazine derivative **19**. The IR spectra of compound **19** showed the strong absorption band at 3190-3000 $cm^{-1}$for the amino group (NH_2), at 2200 cm^{-1} for the cyano group (CN) and MS (*m/z* 420, M^+-45) (Scheme 5).

Experimental

General

All melting points were determined using Gallenkamp electric melting point apparatus and were uncorrected. The IR spectra cm^{-1} (KBr) were recorded on Perkin Elmer Infrared Spectrophotometer Model 157, Grating. The ^1H NMR spectra were recordedon a Varian Spectrophotometer at 200 MHz. using DMSO as a solvent and TMS as internal standard (chemical shift in δppm). The mass spectra (EI) and purity were recorded on 70 eV with Kratos MS equipment and/or a Varian MAT 311 ASpectrometer. The chemicals used were of laboratory grade.

Synthesis of the dyes

2-(4-Phenylazophenylhydrazono)malononitrile (1).

To a solution of malononitrile (6.606 g, 0.1 mol) in ethanol (100 mL), 5.0 g of anhydrous sodium acetate was added. The solution was then treated with diazonium salt of *p*-aminoazobenzene (prepared from p-aminoazobenzene (19.724 g, 0.1 mol) and the appropriate quantities of acetic acid and sodium nitrite). The reaction mixture was stirred for 1 h and the resulting solid was filtered off, washed with H_2O and recrystallized from ethanol. Yield 80 %, m.p. 155 ºC. IR (KBr/m) 3100 (NH), 2220 (conjugated CN), 1620 (C=N) and 1600, 1590 (N=N) cm^{-1}. Anal. Calcd for $C_{15}H_{10}N_6$ (274.28): C, 65.7; H, 3.70; N, 30.6. Found: C, 65.2; H, 4.00; N, 30.5.

3,5-Diamino-4-(4-phenylazophenylazo)-1H-pyrazole (2).

A mixture of **1** (2.743 g, 0.01 mol) and hydrazine hydrate 98 % (0.501 g, 0.01 mol) was heated on a boiling water bath for 1 h. The reaction mixture was then triturated with ethanol and the resulting solid product was filtered off and recrystallized from acetic acid. Yield 90 %, m.p. 245 ºC. IR (KBr/m) 3350–3380 (NH_2), 3280 (NH) and 1600–1550 (N=N) cm^{-1}. MS *m/z* 307 (M^+), 306, 201, 156, 125 and 91. Anal. Calcd for $C_{15}H_{14}N_8$ (306.33): C, 58.8; H, 4.60; N, 36.9. Found: C, 59.0; H, 4.8; N, 37.0.

3,5-diamino-4-(4-phenylazophenylazo)pyrazol-3-yl-benzoylthiourea(3)

To a solution of benzoyl isothiocyanate in acetone (50 mL), **(2)** (30.63 g, 0.1 mol) was added. The reaction mixture was refluxed for 2 h and then poured into water, the resulting solid product was filtered off and recrystallized from ethanol. Yield 70 %, M.p. 190 ºC. IR (KBr/m) 3350–3380 (NH2), 3280, 3330 (NH), 1680 (CO) and 1300 (C=S) cm^{-1}. ^1H NMR (DMSO, 200 MHz) δ = 5.1 (s,2H, NH2), 7.3–8.0 (m, 14H, Ar-H), 8.4 (s, 1H, NH), 9.0 (s, 1H, NH) and 9.3 (s, 1H, NH). Anal. Calcd for $C_{23}H_{19}N_9$ (421.4): C, 65.7; H,4.50; N, 29.9. Found: C, 65.4; H, 4.0; N, 29.8.

7-Amino-2-(4-phenylazophenylazo)-2,3-dihydro-3-oxo-4H-pyrazolo[3,4-*e*]-*as*-triazine (4)

To a suspension of **3** (4.695 g, 0.01 mol) in acetic acid (20 mL), concentrated HCl (2 mL) was added. The reaction mixture was refluxed for 30 min., and then poured into water. The solid product was collected by filtration and crystallization from acetic acid. Yield 60 %, m.p. 175 ºC. IR (KBr/m) 3450 (NH_2), 3320 (NH), 1700 (CO) and 1600 (N=N) cm^{-1}. ^1H NMR (DMSO, 200 MHz) δ = 5.2 (s, 2H, NH_2), 7.3–8.0 (m, 9H, Ar-H) and 9.0 (s, 1H, NH). MS *m/z* 335 (M+), 329, 323, 271, 237, 208, 167 and 57. Anal. Calcd for $C_{16}H_{13}N_8O$ (333.33): C, 57.8; H, 3.90; N, 33.7. Found: C, 58.0; H, 3.4; N, 33.8.

2-Amino-5-imino-4,5,6,7-tetrahydro-3-(4-phenylazophenylazo)-pyrazolo[1,5-*a*]pyrimidine (6)

A solution of **2a** (30.63 g, 0.1 mol), in pyridine (40 mL) and water (10 mL), was treated with ethyl acrylate (10.01 g, 0.1 mol). The mixture was refluxed for 4 h. The reaction mixture was then poured into water and the solid product was collected by filtration and recrystallized from ethanol. Yield 90 %, m.p. 240 ºC. IR (KBr/m) 3390– 3330 (NH_2), 3120 (NH) and 1600 (N=N) cm^{-1}. ^1H NMR (DMSO, 200 MHz) δ = 2.1 (t, 2H, CH_2), 2.7 (t, 2H, CH_2), 5.1 (s, 2H, NH_2), 7.1–8.0 (m, 9H, Ar-H) and 8.8 (s, 1H, NH). Anal. Calcd for $C_{18}H_{17}N_9$ (359.4): C, 60.2; H, 4.80; N, 35.1. Found: C, 60.3; H, 5.0; N, 35.4.

2-Amino-4,5,6,7-tetrahydro-3-(4-phenylazophenylazo)-pyrazolo[1,5-*a*]pyrimidin-5-one (7)

To a suspension of **6** (35.94 g, 0.1 mol) in acetic acid (30 mL) conc. HCl (5 mL, 37.5%) was added. The reaction mixture was refluxed for 2 h and then poured into water. The product was filtered off and recrystallized from ethanol. Yield 80 %, Mp: 210 ºC. IR (KBr/m) 3390, 3330 (NH_2), 3120 (NH), 1670 (ring CO) and 1600 (N=N) cm^{-1}. ^1H NMR (DMSO, 200 MHz) δ = 2.5 (t, 2H, CH_2), 2.9 (t, 2H, CH_2), 4.9 (s, 2H, NH2), 7.1–8.0 (m, 9H, Ar-H) and 8.4 (s, 1H, NH). MS *m/z* 360 (M^+), 306, 255, 217, 197, 167, 92 and 77. Anal. Calcd for $C_{18}H_{16}N_8O$ (360.4): C, 60.0; H, 4.50; N, 31.1. Found: C, 59.9; H, 4.2; N, 31.0.

General procedure for the synthesis of (9) and (10)

Equimolar amounts of **2a** (3.063 g, 0.01 mol) and ethyl acetoacetate (1.301 g, 0.01 mol) or acetylacetone (1.001 g, 0.01 mol) were heated at 160 °C (bath temperature) for 8 h. The solid product was filtered and crystallized from the proper solvent.

Compound **9:** Yield 80 %, m.p. >300 °C. IR (KBr/m) 3400 (NH_2), 3330 (NH) and 1700(CO) cm^{-1}. ^1H NMR (DMSO, 200 MHz) δ = 2.5 (s, 3H, CH_3), 5.6 (s, 1H, CH ring), 7.0–8.0 (m, 9H, Ar-H) and 11.1 (s, 1H, NH). Anal. Calcd for $C_{19}H_{16}N_8O$ (372.4): C, 61.3; H, 4.30; N, 30.1. Found: C, 61.1; H, 4.2; N, 30.0.

Compound **10**: Yield 70 %, m.p. 220 °C. IR (KBr/m) 3420, 3380 (NH_2), 3310 d (NH), 1600 (N=N) and 1580 (C=C) cm^{-1}. ^1H NMR (DMSO, 200 MHz) δ = 2.2 (s, 3H, CH_3), 2.3 (s, 3H, CH_3), 5.5 (s, 1H, H6-ring), 5.7 (s, 2H, NH_2), 7.1–8.0 (m, 9H, Ar-H). Anal. Calcd for$C_{20}H_{18}N_8$ (370.4): C, 64.8; H, 4.90; N, 30.3. Found: C, 65.0; H, 4.6;N, 30.6.

3,6-Bis(4-phenylazophenylazo)-2,5,7-triaminopyrazolo[1,5-*a*]-pyrimidine (11)

A mixture of **2a** (30.63 g, 0.1 mol) and **1** (27.43 g, 0.1 mol) was refluxed in DMF for 1 h. The reaction mixture was then poured into water, the solid product was collected by filtration and recrystallized from DMF/H_2O mixture. Yield 60 %, m.p. >300 °C. IR (KBr/m) 3411, 3275, 3150 (NH_2, NH), and 1600–1550 (N=N) cm^{-1}. ^1H NMR (DMSO, 200 MHz) δ = 2.75 (s, 2H, NH_2), 2.85 (s,2H, NH_2), 6.92 (s, 2H, NH_2), 7.4–8.1 (m, 18H, Ar-H). MS *m/z* 581(M^+), 522, 391, 337, 256, 201, 128 and 77. Anal. Calcd for$C_{30}H_{24}N_{14}$ (580.6): C, 62.1; H, 4.20; N, 33.8. Found: C, 62.4; H,4.0; N, 33.5.

4-Amino-3,5-dicyano-6-imino-1-(4-phenylazophenyl)pyridazine (12)

A solution of **1** (2.743 g, 0.01 mol) and malononitrile (0.661 g, 0.01 mol) in pyridine (30 mL) was refluxed for 10 h. It was then cooled and poured into water. The solid product so formed was collected by filtration and crystallized from DMFYield 80 %, m.p. >300 °C. IR (KBr/m): 3340–3000 (NH_2, NH), 2180, 2220 (CN), 1600 and 1550 (N=N) cm^{-1}. MS *m/z* 340 (M^+), 159. Anal. Calcd for $C_{18}H_{12}N_8$ (340.3): C, 63.5; H, 3.60; N, 32.9. Found: C, 63.2; H, 3.8; N, 33.0. Compound **12** was also obtained in 70 % yield via cyclization of **13** by refluxing in DMF for 10 min and working up the reaction mixture.

2-Amino-1,1,3-tricyano-3-(4-phenylazophenylhydrazono)propene (13)

To a solution of 2-amino-1,1,3-tricyanopropene (prepared by dimerization of malononitrile by the reported method[23]) (0.1 mol) in ethanol (100 mL), (5.0 g) of anhydrous sodium acetate was added. The solution was then treated with a solution of diazonium salt of 4-aminoazobenzene (prepared from (19.724 g, 0.1 mol) *p*-aminoazobenzene, acetic acid and the appropriate quantities of sodium nitrite). The reaction mixture was stirred for1 h. The resulting solid product was collected by filtration, washed several times with water and recrystallized from ethanol. Yield 82 %, m.p. >300 °C. IR (KBr/m) 3380–3066 (NH_2, NH-bands, broad), 2216, 2203 (two conjugated CN group), 1641 (C=N) and 1534(N=N) cm^{-1}. Anal. Calcd for $C_{18}H_{12}N_8$ (340.3): C, 63.5; H, 3.6; N, 32.9.Found: C, 63.8; H, 3.3; N, 33.1.

Phenylazophenylhydrazonocyanoacethydrazide (14)

To a solution of (2.09 g, 0.01 mol) diazonium salt of p-aminoazobenzene, a solution of (0.89 g, 0.01 mol), acethydrazide containing 2 g sodium acetate was added. The solid product so formed was collected by filtration and crystallized from etanol. Yield 90 %, m.p. 137 °C. IR (KBr/m) 3340–3000 (NH_2, NH), 2180, 2220 (CN), 1678 (CO) and 1550 (N=N) cm^{-1}. Anal. Calcd for $C_{15}H_{13}N_7O$ (307.3): C, 58.6; H, 4.3; N, 31.9. Found: C, 58.4; H, 4.0; N, 32.1.

5-Amino-4-(4-phenylazophenylazo)-3-isoxazolone (15)

A solution of **14** (3.07g, 0.01 mol) in ethanol (50 mL) was treated with hydroxylamine hydrochloride (0.71g, 0.01 mol) and 2 g sodium acetate. The reaction mixture was stirred for 4 h. The resulting solid product was collected by filteration and recrystallized from methanol**.** Yield 50 %, m.p. 190 °C. IR (KBr/m) 3340–3000 (NH_2, NH-band, broad), 1690 (CO) and 1600 (N=N) cm^{-1}. ^1H NMR (DMSO, 200 MHz) δ = 6.75 (s, 2H, NH_2), 8.4 (s, 1H, NH), 7.4–8.1 (m, 9H, Ar-H). Anal. Calcd for $C_{15}H_{12}N_6O_2$ (308.3): C, 58.4; H, 3.9; N, 27.3. Found: C, 58.5; H, 4.0; N, 27.5.

4-(4-Phenylazophenylazo)-5-oxo-2-pyrazolin-3-ylmalononitrile (16)

A solution of (3.07g, 0.01 mol) of **14** in 50 mL DMF was treated with (0.56g, 0.01 mol) of malononitrile. The reaction mixture was stirred for 30 min and then poured into water. The resulting solid product was collected by filtration and recrystallized from methanol-water mixture**.** Yield 70 %, m.p. 295 °C. IR (KBr/m) 3250–3000 (NH-band, broad), 2200 (CN), 1680 (CO) and 1500 (N=N) cm^{-1}. MS *m/z* 356 (M^+). Anal. Calcd for $C_{18}H_{12}N_8O_2$ (372.3): C, 58.1; H, 3.2; N, 30.1. Found: C, 58.4; H, 3.5; N, 30.6.

N-Methylphenylazophenylhydrazonomalononitrile (17)

To a solution of (2.74g, 0.01 mol) phenylazo-phenylhydrazono malononitrile in acetone (50 mL), methyliodide (1.42g, 0.01 mol) and 2 g of anhydrous potassium carbonate was added. The reaction mixture was refluxed for 90 min, the solvent was evaporated, the solid product was collected by filtration and recrystallized from methanol. Yield 70 %, m.p. 145 °C. IR (KBr/m) 3440–3340 (NH-band, broad), 2200 (CN), and 1500 (N=N) $cm^{-1.}$ ^1H NMR (DMSO, 200 MHz) δ = 3.8 (s, 3H, CH_3), δ 5.5, 5.3 (s, 4H, $2NH_2$), 7.7–8.1 (m, 9H, Ar-H). Anal. Calcd for $C_{16}H_{12}N_6$ (288.3): C, 66.7; H, 4.2; N, 29.2. Found: C, 66.4; H, 4.0; N, 30.2.

N-Methylphenylazophenylhydrazonocyanoacetamidrazone (18)

A solution of (2.9g, 0.01 mol) of **17** in ethanol (50 mL) was treated with 98 % hydrazine hydrate (0.501 g, 0.01 mol). The reaction mixture was refluxed for 90 min, then the solvent was evaporated, the solid product was collected by filtration and recrystallized from ethanol. Yield 70 %, m.p. 172 °C. IR (KBr/m) 3440–3340 (NH_2, broad), 2216 (CN), 1680 (CO), and 1550 (N=N) cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_8$ (320.4): C, 60.0; H, 5.0; N, 35.0. Found: C, 60.2; H, 4.8; N, 35.2.

Reaction of (18) with benzoylisothiocyanate

To a solution of benzoylisothiocyanate (1.31g, 0.01 mol) in acetone, **18** (3.2g, 0.01 mol) was added. The reaction mixture was refluxed for 2 h., the solvent was evaporated, the solid product was collected by filtration and recrystallized from DMF-water mixture to give 1-amino-1,3,5-triazine derivative (**19**). Yield 40%, m.p. 145 °C. IR (KBr/m) 3190–3000 (NH_2), 220 (CN), and 1570 (N=N) cm^{-1}. MS *m/z* 420 (M^+- 59). Anal. Calcd for $C_{24}H_{19}N_9S$ (465.5): C, 61.9; H, 4.1; N, 27.1 S, 6.9. Found: C, 61.4; H, 3.9; N, 28.5.S, 6.68

Conclusions

In this work, a series of bisazopyrazolo[1,5-*a*]pyrimidine, pyridazine, isoxazole, and triazine dyes have been synthesized. IR, ^{1}H NMR, and mass spectroscopy for the prepared compounds are in good agreement with the proposed structures.

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