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Synthesis of dyes derived from 1-aryl-5-amino-4-cyanopyrazoles

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Abstract

Eight dyes were prepared by diazotisation of substituted aminocyanopyrazoles and coupling to anilines or 2-naphthol. The dyes were fully characterized by spectroscopic techniques. The cyano group of the pyrazoles was found to be susceptible to hydrolysis during preparation.

Keywords: Cyanopyrazole; Azo dyes; Diazotisation

1. Introduction

Heterocycles are extensively used in disperse dye chemistry for textile or non-textile applications including their application in reprography, functional dye and non-linear optical systems, photodynamic therapy and lasers [1].

Azo dyes containing heterocyclic rings lead to brighter and often deeper shades than their benzene analogues [2] and they are still very important for applications such as disperse dyes for polyester fibres [3].

Following previous interest in our group for heterocyclic textile dyes [4] and also for pyrazole derivatives [5] for various purposes, it was decided to prepare dyes derived from arylpyrazoles, containing electron withdrawing groups, such as carboxyl and nitro groups.

2. Results and discussion

The preparation of pyrazoles involved the reaction of the required hydrazines with ethoxymethylenemalononitrile in ethanol at room temperature [6]. The 5-amino-4-cyano-*N*-phenylpyrazoles **1** were obtained in 94% (**1b**) and 43% (**1a**) yields and were fully characterized.

The pyrazole containing the nitro group (**1a**) had previously been used as starting material for the preparation of dyes [6]. Aminocyanopyrazoles **1** were evidenced on IR by signals at 2215–2243 cm^{-1} and in the NMR spectra by a singlet for proton 3 (e.g. at 7.64 ppm for compound **1a**) and the pair of doublets expected for the *para*-substituted phenyl ring.

The preparation of the dyes was started by diazotization of the amino group on the pyrazole ring by the nitrosylsulfuric method. The coupling reaction was performed in dilute H_2SO_4 when *N*,*N*-diethylaniline and *meta*-*N*,*N*-diethylbenzanilide were the coupling components (Scheme 1). In three cases (**3**–**5**), the cyano group was hydrolysed during the preparation of the dye to the corresponding amide, even when the nitrosylsulfuric acid was diluted with a mixture of acetic and propionic acids.

Coupling with 2-naphthol was always performed under alkaline conditions (NaOH).

For the sake of simplicity in the discussion, the dyes were organized on the basis of the coupling components.

2.1. Dyes obtained with anilines

When the respective diazotized pyrazoles were coupled either with *N*,*N*-diethylaniline or with *m*-*N*,*N*-diethylbenzanilide, the reaction proceeded smoothly in 19–38% yields.

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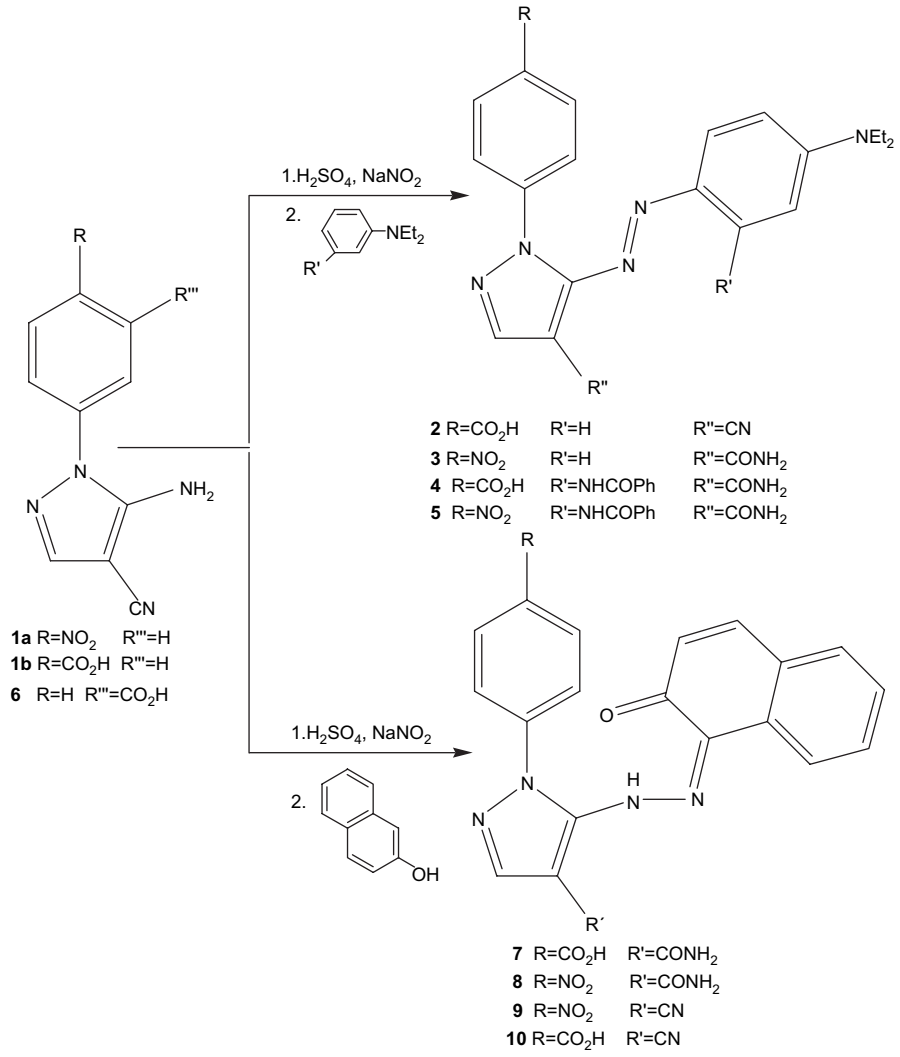

Scheme 1. Synthesis of dyes.

On perusal of the proton NMR spectra of dyes (**3**, **4**, and **5**) apart from expected signals, two broad well-separated singlets (e.g. δ 7.26 and 7.91 in **4**), accounting for one proton each, were found. Also in the ^{13}C NMR spectra, the resonance corresponding to the CN group (δ 114.64) at position C3 of the pyrazole was found missing, and an additional carbonyl signal was found at 163.58 ppm. The IR spectra of dye **4** showed no presence of the peak at 2243 cm^{-1} corresponding to the cyano group.

Hence, on the basis of the spectroscopic data, it could be rationalized that the cyano group was susceptible to hydrolysis and the dyes were obtained as the corresponding amides. The only exception was observed with dye **2**, where the CN group remained intact.

The amount of H_2SO_4 used for the diazotization was varied and even under the optimized conditions (for both diazotization and coupling) the hitherto produced results were obtained. When the concentration of H_2SO_4 was significantly decreased, no diazotization occurred.

It is reported that the diazotization of amino-nitropyrazole can be performed under conditions [6], where after the formation of nitrosylsulfuric acid, the medium is diluted by the addition of a mixture of acetic and propionic acids (5:1 v/v). Even though the solubility of the pyrazoles **1a** and **1b** in that mixture was marginal, the experiments were carried out in a lower molar scale.

Even in this method, the cyano group (with the exception of dye **2**) of the pyrazoles was found to be converted into the respective amides.

2.2. Dyes obtained with 2-naphthol

The diazotization of the pyrazoles for coupling with 2-naphthol was performed by both ways mentioned above (nitrosylsulfuric method with or without the addition of a mixture of acetic and propionic acids (5:1 v/v). The coupling proceeded in sodium hydroxide solution.

When the diazotization conditions did not involve dilution with the organic acid mixture, the cyano group was found hydrolysed to amide, in the resulting dyes **7**, **8**.

In our previous work of dyes from aminopyrazole **6** and 2-naphthol, nitrosylsulfuric method with the addition of

a mixture of acetic and propionic acids (5:1 v/v) for diazotization, evolved an orange dye with the cyano group intact on the pyrazoles [4a].

Consequently it was decided to obtain dyes from aminopyrazoles (**1a** and **1b**) by nitrosylsulfuric method with the addition of a mixture of acetic and propionic acids (5:1 v/v) in the conditions previously described. The preparations were successful and products isolated were the nitriles **9** and **10**.

In Table 1 yields, melting points, visible and IR absorption characteristics of the products are shown. All the compounds were characterized by spectroscopic methods and elemental analysis or high resolution mass spectrometry. Other techniques such as ^{13}C NMR, HMQC and HMBC were also used.

3. Conclusion

Eight dyes were prepared, in low yields, by diazotisation of substituted aminocyanopyrazoles and coupling to anilines or 2-naphthol. It was observed that the cyano group on the pyrazole ring was labile under nitrosylsulfuric diazotization conditions. When this solution was diluted with a mixture of acetic and propionic acids (5:1 v/v) and the coupling took place in base, as it was the case for the naphthol derivatives, the cyano group remained intact.

4. Experimental

4.1. General

Melting points are uncorrected, IR spectra were determined on a Perkin Elmer FTIR-1600 and UV spectra were determined on a Hitachi U-2000. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were determined at 75.4 MHz both on a Varian Unity Plus Spectrometer. Mass spectra were obtained by electron impact except for compounds **7** and **8** where FAB$^+$ was applied. High resolution mass spectra were obtained on an AutoSpec E Spectrometer. Elemental analyses were obtained on a Leco CHNS-932 instrument. TLC was carried out on plates coated with silica gel 60 F_{254}. Column chromatography was performed on silica gel (<230 mesh) with mixtures of light petroleum and ethyl acetate of increasing polarity, unless other conditions are described. Light petroleum refers to the fraction boiling in the range 40–60 °C.

4.2. General method of preparation of aminocyanopyrazoles

The mixture of arylhydrazine (33 mmol) and ethoxymethylenemalononitrile (33 mmol) was stirred for 30 min and then ethanol (20 mL) was added. The mixture was stirred at room temperature for 24 h. The precipitated product was filtered off and recrystallized from an appropriate solvent.

4.2.1. 5-Amino-1-(4′-nitrophenyl)-1H-pyrazole-4-carboxamide (*1a*)

The title compound was obtained as a yellowish solid after recrystallization from acetone–water (isolated yield 43%), m.p. = 221.8–223.5 °C (lit. m.p. 224–225 °C [6,7]).

^{1}H NMR (DMSO-d_6) δ (ppm): 7.06 (2H, br s, NH_2); 7.83 (2H, d, $J = 9.0$ Hz, H-2′ and H-6′); 7.90 (1H, s, H-3); 8.35 (2H, d, $J = 9.3$ Hz, H-3′ and H-5′).

^{13}C NMR (DMSO-d_6) δ (ppm): 74.35 (C-4); 114.43 (CN); 124.22 (C-2′ and C-6′); 125.01 (C-3′ and C-5′); 142.82 (C-4′); 143.10 (C-3); 145.74 (C-1′); 151.99 (C-5).

IR (Nujol mull) (ν_{max}, cm^{-1}): 3445, 3316, 3230, 3210, 2230, 2218 (weaker, side band), 1650, 1598.

HRMS calcd for $C_{10}H_7N_5O_2$: 229.0600; found: (M^+) 229.0603.

4.2.2. 5-Amino-1-(4′-carboxyphenyl)-1H-pyrazole-4-carbonitrile (*1b*)

It was obtained as an orange solid (yield 94%), recrystallized from ethanol–water (yield 89%), m.p. 275–277 °C.

^{1}H NMR (DMSO-d_6) δ (ppm): 6.88 (2H, br s, NH_2); 7.65 (2H, d, $J = 8.7$ Hz, H-2′ and H-6′); 7.84 (1H, s, H-3); 8.06 (2H, d, $J = 8.7$ Hz, H-3′ and H-5′); 13.15 (1H, br s, COOH).

Table 1
Yields, melting points and UV/vis and IR spectroscopic data for dyes **2–5** and **7–10**

Dye	Yield (%)	M.p. (°C)	UV/vis (in EtOH),[b] λ_{max} (nm) (ε (dm^3 mol^{-1} cm^{-1}))	IR[c] (cm^{-1})
2	38[a]	249–250	543.5 (3.4×10^4); 396.0 (2.1×10^3); 304.0 (7.9×10^3); 283.0 (6.8×10^3); 246.5 (1.7×10^4)	3463; 2453; 2249; 1723; 1677; 1658; 1607; 1418; 1327; 1288
3	33[a]	264–266	465.0 (3.9×10^3); 401.5 (2.4×10^3); 306.5 (1.7×10^4); 253.5 (1.0×10^4)	3464; 3120; 2996; 2938; 1693; 1595; 1522; 1496; 1337; 1276; 1177
4	24[a]	298–299	512.5 (1.6×10^4); 381.0 (1.9×10^3); 318.0 (5.0×10^3); 298.0 (4.1×10^3); 253.5 (1.4×10^4)	3425; 2977; 2925; 2237; 1694; 1682; 1620; 1556; 1536; 1393; 1367; 1336; 1268; 1214; 1173
5	19[a]	257–259	522.5 (3.3×10^4); 398.0 (4.6×10^3); 267.0 (1.7×10^4)	3406; 2977; 2938; 1706; 1664; 1595; 1553; 1521; 1498; 1469; 1406; 1332; 1288; 1267; 1167
7	29	310–312	470.0 (8.3×10^3)	3462; 1694; 1632; 1563; 1332; 1255; 1158; 1169
8	23	>300	472.0 (6.9×10^3); 284.0 (8.1×10^3)	3450; 1721; 1695; 1568; 1462; 1432; 1329; 1259; 1154; 1171
9	21	252–254	541 (1.6×10^4); 339 (1.58×10^4); 292 (1.4×10^4)	3460; 2736; 2671; 2229; 1710; 1613; 1594; 1249
10	19	292–94	522.5 (1.5×10^4); 330 (9.9×10^3); 274 (1.6×10^4)	3468; 2726; 2670; 2230; 1692; 1608; 1312; 1168

[a] Yields for method A; for method B the values were comparable.
[b] Dyes **9**, **10** in DMF.
[c] KBr pellets for dyes **2–5**; Nujol mull for dyes **7–10**.

^{13}C NMR (DMSO-d_6) δ (ppm): 72.94 (C-4); 114.64 (CN); 123.55 (C-2′ and C-6′); 129.61 (C-1′); 130.65 (C-3′ and C-5′); 141.08 (C-4′); 142.44 (C-3); 151.58 (C-5); 166.64 (C=O).

IR (Nujol mull) (ν_{max}, cm^{-1}): 3457, 3297, 3180, 2243 1688, 1639, 1608, 1537.

Anal. calcd for $C_{11}H_8N_4O_2$: C, 57.89; H, 3.51; N, 24.56. Found: C, 58.16; H, 3.69; N, 24.44.

HRMS calcd for $C_{11}H_8N_4O_2$: 228.0647; found: (M^+) 228.0647.

4.3. General method of preparation of dyes **2–5**

4.3.1. Method A

Sodium nitrite (2 mmol) was dissolved in concentrated H_2SO_4 (4 g) at room temperature followed by the addition of the aminocyano derivative (2 mmol). The mixture was stirred for 2 h at room temperature.

To a cooled solution (0–5 °C) of *N*,*N*-diethylaniline derivative (1.5 mmol) in water (300 mL) and concentrated H_2SO_4 (2 mL) was added dropwise, the previous diazonium solution and the mixture was stirred for 30 min. The precipitated product was collected and purified by column chromatography and recrystallization.

4.3.2. Method B

$NaNO_2$ (35 mg, 0.5 mmol) was added to concentrated H_2SO_4 (1.5 mL) with external cooling (ice–acetone bath). The suspension was heated to 60 °C and again cooled to 0–5 °C. To this cooled solution the mixture (3 mL) of acetic and propionic acids (5:1 v/v) was added and it was stirred for 10 min. The pyrazole (0.5 mmol) dissolved (or dispersed) in acetic and propionic acid mixture (5:1 v/v, 3 mL) was carefully added in portions and the mixture was stirred continuously for 120 min with external cooling (0–5 °C).

To a cooled solution of *N*,*N*-diethylaniline derivative (1.5 mmol) in a mixture of acetic and propionic acids (5:1 v/v, 2 mL) the prepared diazonium solution was added dropwise and the mixture was stirred for 30 min at reaction pH 7 (neutralized with solid anhydrous sodium acetate). The precipitated product was collected and purified by column chromatography and recrystallization.

4.3.3. 4-[4′-Cyano-5′-(4″-diethylamino-phenylazo)-pyrazol-1′-yl]-benzoic acid (**2**)

Both methods afforded the title compound as a dark red solid.

^{1}H NMR (DMSO-d_6) δ (ppm): 13.70 (1H, br s, OH); 8.20 (1H, s, H-3′); 8.10 (2H, d, $J = 8.4$ Hz, H-2 and H-6); 7.81 (2H, d, $J = 8.7$ Hz, H-3 and H-5); 7.66 (2H, d, $J = 9.6$ Hz, H-2″ and H-6″); 6.92 (2H, d, $J = 9.6$ Hz, H-3″ and H-5″); 3.52 (4H, q, $J = 7.2$ Hz, $2 \times CH_2$); 1.16 (6H, t, $J = 6.9$ Hz, $2 \times CH_3$).

^{13}C NMR (DMSO-d_6) δ (ppm): 12.55 ($2 \times CH_3$); 44.70 ($2 \times CH_2$); 105.14 (CN); 112.43 (C-3″ and C-5″); 124.97 (C-3 and C-5); 126.84 (C-2″ and C-6″); 130.07 (C-2 and C-6); 140.46 (C–N=N); 133.24 (C-1); 141.74 (C-4); 144.23 (C-3′); 150.72 (C-5′); 152.97 (C-4″); 121.77 (C-4′); 166.66 (C=O).

HRMS calcd for $C_{21}H_{20}O_2N_6$: 388.1648; found: 388.1631.

4.3.4. 5-(4″-Diethylamino-phenylazo)-1-(4′-nitro-phenyl)-1H-pyrazole-4-carboxamide (**3**)

A dark red solid was obtained by both methods.

^{1}H NMR ($CDCl_3$) δ (ppm): 9.73 (1H, br s, CON–H); 8.38 (2H, dd, $J = 7.1$ and 1.8 Hz, H-3′ and H-5′); 8.41 (1H, s, H-3); 7.90 (2H, dd, $J = 6.9$ and 2.1 Hz, H-2′ and H-6′); 7.67 (2H, dd, $J = 7.2$ and 1.8 Hz, H-2″ and H-6″); 6.74 (2H, dd, $J = 7.2$ and 1.8 Hz, H-3″ and H-5″); 5.99 (1H, br s, CON–H); 3.52 (4H, d, $J = 9.6$ Hz, $2 \times CH_2$); 1.28 (6H, t, $J = 6.9$ Hz, $2 \times CH_3$).

^{13}C NMR ($CDCl_3$) δ (ppm): 12.63 (CH_3); 45.20 (CH_2); 107.83 (C-4); 111.78 (C-3″ and C-5″); 124.05 (C-3′ and C-5′); 126.13 (C-2′ and C-6′); 126.69 (C-2″ and C-6″); 142.24 (C-1″); 144.41 (C-1′); 145.85 (C-3); 146.42 (C-4′); 149.07 (C-5); 152.32 (C-4″); 162. 44 (C=O amide).

MS-EI (*m*/*z*, %) 408.15 ($M^+ + 1$, 8); 258.05 (100). The molecule was unstable under EI conditions and it was only possible to obtain HRMS for the base peak. Calculated for $C_{10}H_7N_6O_3$ 259.0580; found: 259.0522 (corresponds to elimination of *N*,*N*-diethylaniline from the molecular ion).

4.3.5. 4-[5′-(2″-Benzoylamino-4″-diethylamino-phenylazo)-4′-carbamoyl-pyrazol-1′-yl]-benzoic acid (**4**)

The title compound was obtained as a dark red solid by both methods.

^{1}H NMR (DMSO-d_6) δ (ppm): 13.70 (1H, very br s, OH); 10.50 (1H, s, NH); 8.13 (1H, s, H-3′); 8.02 (1H, d, $J = 2.7$ Hz, H-3″); 7.94 (2H, dd, $J = 1.8$ and 8.7 Hz, H-2 and H-6); 7.91 (1H, br s, NH); 7.80 (2H, d, $J = 7.0$ Hz, *ortho*-Phe); 7.69 (2H, dd, $J = 2.1$ and 8.7 Hz, H-3 and H-5); 7.61 (1H, d, $J = 9.6$ Hz, H-6″); 7.58 (1H, t, $J = 7.2$ Hz, *para*-Phe); 7.49 (2H, t, $J = 7.2$ Hz, *meta*-Phe); 7.26 (1H, s, NH); 6.69 (1H, dd, $J = 2.7$ and 9.6 Hz, H-5″); 3.52 (4H, q, $J = 6.9$ Hz, $2 \times CH_2$); 1.20 (6H, t, $J = 6.9$ Hz, $2 \times CH_3$).

^{13}C NMR (DMSO-d_6) δ (ppm): 12.64 ($2 \times CH_3$); 44.84 ($2 \times CH_2$); 100.57 (C-3″); 108.34 (C-4′); 108.65 (C-5″); 121.67 (C-6″); 124.37 (C-3 and C-5); 127.26 (2C-*o*-Phe); 128.86 (2C-*m*-Phe); 129.52 (C-1); 130.12 (C-2 and C-6); 131.52 (C-1″); 132.09 (C-*p*-Phe); 133.85 (C-1‴); 140.25 (C-4″); 142.21 (C-3′); 142.44 (C-4); 150.72 (C-5′); 152.97 (C-2″); 163.58 (C=ONH$_2$); 165.24 (C=O-Phe); 166.53 (C=OOH).

Anal. calcd for $C_{28}H_{27}N_7O_4 \cdot \frac{1}{2}H_2O$: C, 62.91; H, 5.28; N, 18.34. Found: C, 62.46; H, 5.23; N, 17.93.

HRMS calcd for $C_{28}H_{27}O_4N_7$: 525.2125; found: 525.2150.

4.3.6. 5-(2″-Benzoylamino-4″-diethylamino-phenylazo)-1-(4′-nitro-phenyl)-1H-pyrazole-4-carboxamide (**5**)

The title compound was obtained as a dark red solid, by methods A and B.

^{1}H NMR (DMSO-d_6) δ (ppm): 10.60 (1H, s, NH); 8.17 (1H, s, H-3); 8.16 (2H, d, $J = 9.3$ Hz, H-3′ and H-5′); 8.05 (1H, d, $J = 2.4$ Hz, H-3″); 7.95 (1H, br s, NH); 7.86 (2H, d, $J = 9.0$ Hz, H-2′ and H-6′); 7.77 (2H, d, $J = 7.2$ Hz, *ortho*-Phe); 7.66 (1H, d, $J = 9.6$ Hz, H-6″); 7.55 (1H, t, $J = 7.5$ Hz, *para*-Phe); 7.45 (2H, t, $J = 7.5$ Hz, *meta*-Phe); 7.31 (1H, s, NH); 6.72 (1H, dd, $J = 2.7$ and 9.6 Hz, H-5″); 3.53 (4H, q, $J = 6.9$ Hz, $2 \times CH_2$); 1.21 (6H, t, $J = 7.2$ Hz, $2 \times CH_3$).

^{13}C NMR (DMSO-d_6) δ (ppm): 12.63 ($2 \times CH_3$); 44.90 ($2 \times CH_2$); 100.54 (C-3″); 108.80 (C-5″); 108.76 (C-4) 123.09 (C-6″); 124.48 (C-3′ and C-5′); 124.86 (C-2′ and C-6′); 127.15 (2C-*o*-Phe); 128.80 (2C-*m*-Phe); 131.41 (C-1″); 131.99 (C-*p*-Phe); 133.87 (C-1‴); 140.10 (C-2″); 143.12 (C-3); 143.83 (C-1′); 145.48 (C-4′); 150.83 (C-5); 153.18 (C-4″); 163.37 (C=ONH$_2$); 165.32 (C=O-Phe).

Anal. calcd for $C_{27}H_{26}N_8O_4 \cdot H_2O$: C, 59.55; H, 5.18; N, 20.58. Found: C, 60.09; H, 5.04; N, 20.03.

HRMS calcd for $C_{27}H_{26}O_4N_8$: 526.2077; found: 526.2099.

4.4. Method of preparation of dyes **7** and **8**

$NaNO_2$ (35 mg, 0.5 mmol) was added to concentrated H_2SO_4 (5 mL) with external cooling (ice–acetone bath) the suspension was stirred for 10–15 min at 20 °C and again cooled to 0–5 °C. To this cooled solution the pyrazole (0.5 mmol) was carefully added in portions and the mixture was stirred continuously for 120 min with external cooling.

The coupling component, 2-naphthol (72 mg, 0.5 mmol), was dissolved in 2 mL water and NaOH (20 mg, 0.5 mmol) and the solution was externally cooled. To this the diazonium solution was added dropwise, keeping the temperature at 5 °C and reaction pH at 10 (5 N NaOH was added when necessary). The solution was either neutralized to pH 7 (for compound **7**) or stirred continuously at room temperature (for compound **8**). A precipitate which came out was filtered off, washed and dried.

4.4.1. 4-{4′-Carbamoyl-5′-[N′-(2″-oxo-2H-naphthalen-1″-ylidene)-hydrazino]-pyrazol-1′-yl}-benzoic acid (**7**)

Recrystallization from acetone yielded the orange dye **7**.

^{1}H NMR (acetone-d_6) δ (ppm): 15.49 (1H, s, N*H*–N); 13.20 (1H, br s, CO_2H); 8.26 (1H, s, H-3″); 8.07 (2H, dd, $J = 6.6$ and 1.8 Hz, H-2 and H-6); 8.01 (1H, br s, CO–NH); 7.82 (1H, d, $J = 9.6$ Hz, H-4″); 7.65 (2H, dd, $J = 6.9$ and 1.8 Hz, H-3 and H-5); 7.59 (1H, d, $J = 7.2$ Hz, H-5″); 7.43 (1H, br s, CO–NH); 7.31 (1H, pt, $J = 7.5$ and 1.2 Hz, H-6″); 6.94 (1H, pt, $J = 7.8$ and 1.2 Hz, H-7″); 6.68 (1H, d, $J = 9.6$ Hz, H-3″); 6.36 (1H, br d, $J = 8.1$ Hz, H-8″).

^{13}C NMR (DMSO-d_6) δ (ppm): 105.69 (C-5′ or C-4′); 121.77 (C-8″); 130.58 (C-1); 130.42 (C-2 and C-6); 130.25 (C-4a″); 125.58 (C3″); 125.93 (C-3 and C-5); 127.05 (C-6″); 128.26 (C1″); 128.47 (C-7″); 129.02 (C-5″); 131.92 (C-8a″); 139.71 (C-3′); 142.21 (C4″); 143.84 (C-4′ or C-5′); 144.38 (C-4); 175.49 (C-2″); 166.70 (CO_2H); 163.79 (C=O amide).

HRMS calcd for $C_{21}H_{16}N_5O_4$: 402.1202; found: $(M+1)^+$ 402.1186.

4.4.2. 1-(4′-Nitro-phenyl)-5-[N′-(2″-oxo-2H-naphthalen-1″-ylidene)-hydrazino]-1H-pyrazole-4-carboxamide (**8**)

The precipitated solid was purified by column chromatography (eluted with 2% MeOH–$CHCl_3$) and dye **8** was obtained as an orange solid.

^{1}H NMR (DMSO-d_6) δ (ppm): 15.50 (1H, s, NH–N); 8.36 (2H, dd, $J = 7.1$ and 2.1 Hz, H-3′ and H-5′); 8.30 (1H, s, H-3); 8.01 (1H, br s, CO–NH); 7.85 (2H, dd, $J = 6.8$ and 2.1 Hz, H2′ and H-6′); 7.83 (1H, d, $J = 9.3$ Hz, H-4″); 7.60 (1H, d, $J = 6.9$ Hz, H-5″); 7.46 (1H, br s, CO–NH); 7.32 (1H, td, $J = 8.1$ and 1.2 Hz, H-6″); 6.97 (1H, td, $J = 7.8$ and 1.2 Hz, H-7″); 6.67 (1H, d, $J = 9.6$ Hz, H-3″); 6.40 (1H, d, $J = 6.9$ Hz, H-8″).

^{13}C NMR (DMSO-d_6) δ (ppm): 105.69 (C-5 or C-4); 121.33 (C-8″); 124.65 (C-3′ and C-5′); 125.67 (C-3″); 126.91 (C-2′ and C-6′); 127.34 (C-6″); 128.37 (C-4a″); 128.63 (C-7″); 129.20 (C-5″); 130.39 (C-1″); 131.80 (C-8a″); 140.22 (C-3); 142.50 (C4″); 144.04 (C-4 or C-5); 145.91 (C1′); 146.68 (C-4′); 163.64 (C=O amide); 176.19 (C-2″).

HRMS calcd for $C_{20}H_{15}N_6O_4$: 403.1155; found: $(M+1)^+$ 403.1149.

4.5. Method of preparation of dyes **9** and **10**

$NaNO_2$ (35 mg, 0.5 mmol) was added to concentrated H_2SO_4 (1.5 mL) with external cooling (ice–acetone bath). The suspension was heated to 60 °C and again cooled to 0–5 °C. To this cooled solution the mixture (3 mL) of acetic and propionic acids (5:1 v/v) was added and the reaction mixture was stirred for 10 min. The pyrazole (0.5 mmol) in acetic and propionic acid mixture (5:1 v/v, 3 mL) was carefully added in portions and the mixture was stirred continuously for 120 min with external cooling.

The coupling was done as in the case of dyes **6** and **7**.

4.5.1. 1-(4′-Nitro-phenyl)-5-[N′-(2″-oxo-2H-naphthalen-1″-ylidene)-hydrazino]-1H-pyrazole-4-carbonitrile (**9**)

The precipitated solid was recrystallized from acetone.

^{1}H NMR (DMSO-d_6) δ (ppm): 13.65 (1H, br s, N*H*–N); 8.67 (1H, d, $J = 8.1$ Hz, H-8″); 8.57 (1H, s, H-3); 8.48 (2H, dd, $J = 7.2$ and 2.1 Hz, H-3′ and H-5′); 8.21 (2H, dd, $J = 6.9$ and 2.1 Hz, H-2′ and H-6′); 8.14 (1H, d, $J = 9.3$ Hz, H-4″); 7.91 (1H, d, $J = 7.8$ Hz, H-5″); 7.67 (1H, td, $J = 6.9$ and 1.2 Hz, H-7″); 7.53 (1H, td, $J = 6.9$ and 1.2 Hz, H-6″); 7.14 (1H, d, $J = 9.0$ Hz, H-3″).

^{13}C NMR (DMSO-d_6) δ (ppm): 81.35 (C-4); 114.28 (CN); 120.89 (C-3″); 122.00 (C-8″); 125.03 (C-3′ and C-5′); 125.89 (C-2′ and C-6′); 126.09 (C-6″); 128.33 (C-4a″); 129.65 (C-7″); 129.03 (C-5″); 131.52 (C-1″); 132.47 (C-8a″); 145.11 (C-3); 140.73 (C4″); 153.26 (C-5); 142.27 (C1′); 147.10 (C-4′); 158.66 (C-2″).

HRMS calcd for $C_{20}H_{12}O_3N_6$: 384.0971; found: 384.0984.

4.5.2. 4-{4′-Cyano-5′-[N′-(2″-oxo-2H-naphthalen-1″-ylidene)-hydrazino]-pyrazol-1′-yl}-benzoic acid (**10**)

Recrystallization from ethanol yielded a dark brown orange dye.

^{1}H NMR (DMSO-d_6) δ (ppm): 13.80 (1H, br s, NH); 9.44 (1H, s, COOH); 8.67 (1H, d, $J = 8.1$ Hz, H-8″); 8.54 (1H, s, H-3′); 8.18 (2H, dd, $J = 6.9$ and 1.8 Hz, H-2 and H-6); 8.15 (1H, d, $J = 9.0$ Hz, H-4″); 7.97 (1H, dd, $J = 7.2$ and 1.5 Hz, H-3 and H-5); 7.92 (1H, d, $J = 7.8$ Hz, H-5″); 7.67 (1H, pt, $J = 8.1$ and 1.2 Hz, H-6″); 7.54 (1H, pt, $J = 8.1$ and 1.2 Hz, H-7″); 7.14 (1H, d, $J = 9.0$ Hz, H-3″).

^{13}C NMR (DMSO-d_6) δ (ppm): 81.29 (C-4′); 114.21 (CN); 120.52 (C-3″); 121.98 (C-8″); 125.25 (C-3 and C-5); 126.23 (C-6″); 131.48 (C-4a″); 129.07 (C-5″); 129.71 (C-7″); 130.70 (C-2 and C-6); 128.42 (C1″); 132.30 (C-8a″); 135.25 (C-1); 140.52 (C-4); 140.84 (C-4″); 144.78 (C-3′); 152.24 (C-5′); 158.37 (C-2″); 166.38 (CO_2H).

HRMS calcd for $C_{21}H_{13}O_3N_5$: 383.1018; found: 383.1023.

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