SYNTHESIS OF 3-AMINO-1-PHENYL-1H-PYRAZOLE-4,5-DIONE-4-ARYLHYDRAZONES AS FAST DYES

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ازدواج ديازو للمركب ٣-أمينو-١-فينيل-٢-بيرازولين-٥-أون مع أملاح آريل ديازونيوم في البريدين أعطى مركبات ٣-أمينو-١-فينيل-1H- بيرازول-٤,٥-داي اون-٤-آريل هيدرازونات التي تم استخدامها بصورة واسعة كأصباغ سريعة على منسوجات الصوف والحرير والقطن والبوليستر.

Diazocoupling of 3-amino-1-phenyl-2-pyrazolin-5-one (**1**) with aryldiazonium salts in pyridine afforded the coloured 3-amino-1-phenyl-1H-pyrazole-4,5-dione-4-arylhydrazones (**2**), which are, extensively, employed as fast dyes for wool, silk, cotton and polyesters.

INTRODUCTION

5-Pyrazolones are very important class of heterocycles due to their biological and pharmacological activities [1,2] which exhibit an anti-inflammatory [3], herbicidal plant growth [4], fungicidal [5], bactericidal [5], plant growth regulator [4], antipyretic [6,7] and protein kinase inhibitors [8,9]. Also, they are used as key starting material for the synthesis of common commercial arylazopyrazolone dyes, which are used as good fastness dyestuffs for wool, cotton, silk, leather, rubber and synthetic polymers (Nylons).

On the other hand, many azopyrazolone dyes have been utilized as chromogenic reagents for colourimetric determinations [10,11] and as indicator for complexometric titrations [12]. Also, there are some arylazopyrazolone dyes having potent antimicrobial activities [13].

EXPERIMENTAL

All melting points reported are uncorrected. IR spectra were recorded using Perkin Elmer's Spectrum RXIFT-IR spectro-photometer (υ in cm^{-1}). The NMR spectra were recorded on Bruker Avance DPX400 spectrometer using TMS as internal standard (chemical shifts as δ values in ppm). The UV spectra were recorded by Shimadzu, Carry 50 (λ in nm, in absolute ethanol as solvent). Elemental analyses were preformed on Perkin Elmer 2400, series II micro-analyzer.

3-amino-1-phenyl-2-pyrazolin-5-one (**1**) is an Aldrich product, which is used without further purification.

General procedure:

Diazocoupling of 3-amino-1-phenyl-2-pyrazolin-5-one (1):

Synthesis of 3-amino-1-phenyl-1H-pyrazole-4,5-dione-4-arylhydrazones (2a-j):

The desired aromatic amine (0.015 mol) was treated with conc. HCl (5 ml) and cooled at 5°C in ice-bath. An aqueous cold solution of sodium nitrite (0.017 mol in 10 ml water) was added to the prepared aromatic amine hydrochloride to give the desired aromatic diazonium chloride solution which is added drop-wise during 30 min with stirring to an ice-cold solution of 3-amino-1-phenyl-2-pyrazolin-5-one (**1**, 0.012 mol) in pyridine (50 ml). After complete addition the coloured precipitant was filtered, washed with hot water (3 x 25 ml), dried and crystallized from the proper solvent to give the coloured arylhydrazones (**2a-j**). The physical data of dyes (**2**) are listed in **Table 1**.

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Table 1: The physical data of 3-amino-1-phenyl-1H-pyrazole-4,5-dione-4-arylhydrazones (2a-j).

Compd. No.	Mol. Formula (M.wt)	m.p. (°C) (Colour)	Solvent of cryston (yield %)	Elemental analysis Calculated/Found		
				C	H	N
2a	$C_{15}H_{12}BrN_5O$ (358.19)	204-206 (brown)	Benzene (62)	50.30 50.17	3.38 3.33	19.55 19.42
2b	$C_{15}H_{13}N_3O_2$ (295.30)	222-224 (red)	Ethanol (91)	61.01 60.86	4.44 4.41	23.72 23.60
2c	$C_{16}H_{15}N_5O_2$ (309.32)	168-170 (red)	Ethanol (89)	62.13 61.97	4.89 4.83	22.64 22.53
2d	$C_{17}H_{15}N_5O_2$ (321.33)	201-203 (brown)	Acetic acid (81)	63.54 63.37	4.71 4.66	21.79 21.65
2e	$C_{16}H_{13}N_5O_3$ (323.31)	293-295 (violet)	Dioxan (74)	59.44 59.32	4.05 4.00	21.66 21.54
2f	$C_{19}H_{22}N_6O$ (350.42)	> 300 (brown)	Ethanol (93)	65.12 65.01	6.33 6.30	23.98 23.79
2g	$C_{21}H_{17}N_5O$ (355.39)	223-225 (brown)	Ethanol (90)	70.97 70.82	4.82 4.78	19.71 19.53
2h	$C_{19}H_{15}N_5O_4S$ (409.42)	> 300 (orange)	Ethanol (51)	55.74 55.63	3.69 3.64	17.11 16.97
2i	$C_{20}H_{19}N_7O_2$ (389.41)	206-208 (brown)	Ethanol (89)	61.69 61.54	4.92 4.87	25.18 25.03
2j	$C_{18}H_{15}N_7O_2$ (361.36)	201-203 (violet)	Ethanol (53)	59.83 59.66	4.18 4.13	27.13 27.00

General methods of dyeing:

Method A: For arylhydrazones containing an acidic groups OH in **2b**, COOH in **2e** and SO_3H in **2h**.

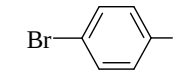
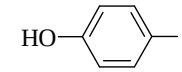
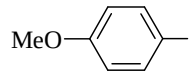
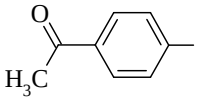
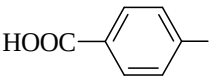
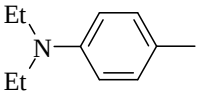
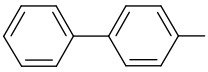
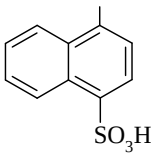
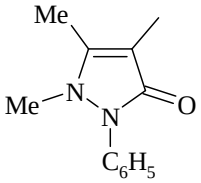
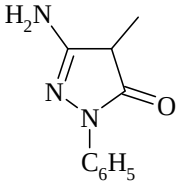
Textile sample (2.0 g) was immersed in NaOH solution (5.0 %) for 30 min, then the sample was taken and immersed in the dyeing solution containing 0.5 g of arylhydrazone in 50.0 ml of NaOH (5.0 %). The mixture was left for 1h at 60°C. The solution was adjusted to pH 5 by adding glacial acetic acid with stirring for 15 min, then solution of 20.0 g of Na_2SO_4 in 250 ml water was added with stirring. The temperature of the mixture was raised to 90°C for 1h with stirring. Finally, the textile sample was taken, rinsed 3 times with 100 ml cold water and dried.

Method B: For arylhydrazones containing basic groups NH_2 in all synthesized arylhydrazones except **2b**, **2e** and **2h**.

Textile sample (2.0 g) was immersed in acetic acid (50 %) for 30 min. The dyeing solution was prepared by dissolving 0.5 g of arylhydrazone in 2.0 ml conc. HCl and then diluted to 50 ml by adding acetic acid (50 %). The textile sample was taken and immersed in the dyeing solution for 30 min at room temperature and 30 min at 60°C, then sodium sulphate (10 g) was added with stirring. The temperature of the mixture was raised and kept at 90°C for 30 min. The textile sample was taken and rubbed, then immersed in Na_2CO_3 solution (30%) and kept at 60°C for 30 min. The sample was taken, rinsed with water (3 x 100 ml) and then with hot water and dried.

All dyed fabrics by arylhydrazones (**2a-j**) are exposed to direct sunlight in open air for 15 days, washed by hot water and dried to give fabrics with bright, fast and stable colour. The UV spectra and the colour of the dyed textiles by the synthesized arylhydrazones (**2a-j**) are listed in **Table 2**.

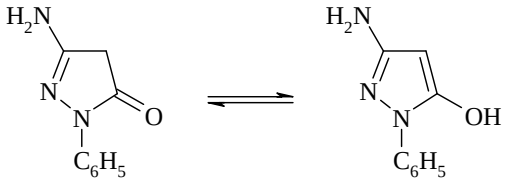
Table 2: The UV spectral data and dyeing textile of 3-amino-1-phenyl-1H-pyrazole-4,5-dione-4-arylhydrazones (2a-j).

Compd. No.	Ar	Method of dyeing	UV λ_{max} in nm	Fabric dyeing colour wool	silk	cotton	polyester
2a		B	354, 230, 215	pale yellow	pale yellow	weak yellow	weak yellow
2b		A	415, 270, 230	deep yellow	yellow	pale yellow	weak yellow
2c		B	420, 260, 235, 210	yellow	yellow	pale yellow	pale yellow
2d		B	395, 230, 215	buff	buff	buff	weak buff
2e		A	395, 235, 225, 215	pale brown	weak brown	deep buff	buff
2f		B	485, 270, 250, 235, 225	deep red	red	pink	deep pink
2g		B	410, 260, 240, 225	yellow	yellow	weak yellow	pale yellow
2h		A	420, 240	weak brown	orange	weak yellow	weak yellow
2i		B	430, 420, 405, 265, 255, 245, 230,220	yellow	deep yellow	pale yellow	pale yellow
2j		B	490, 285, 275, 250, 224	pale brown	brown	weak brown	beige

RESULTS AND DISCUSSION

In continuation to our interest in pyrazolone chemistry [14-18], we have reported here the synthesis of some new intensively coloured 3-amino-1-phenyl-1H-pyrazole-4,5-ione-4-arylhydrazones (**2a-j**) that are used for dyeing of silk, wool, cotton and polyesters. The 3-amino-1-phenyl-2-pyrazolin-5-one (**1**) existed in two tautomeric forms (I-II) due to their keto-enol

tautomerism, which are confirmed by IR absorption spectrum (**Scheme 1**).



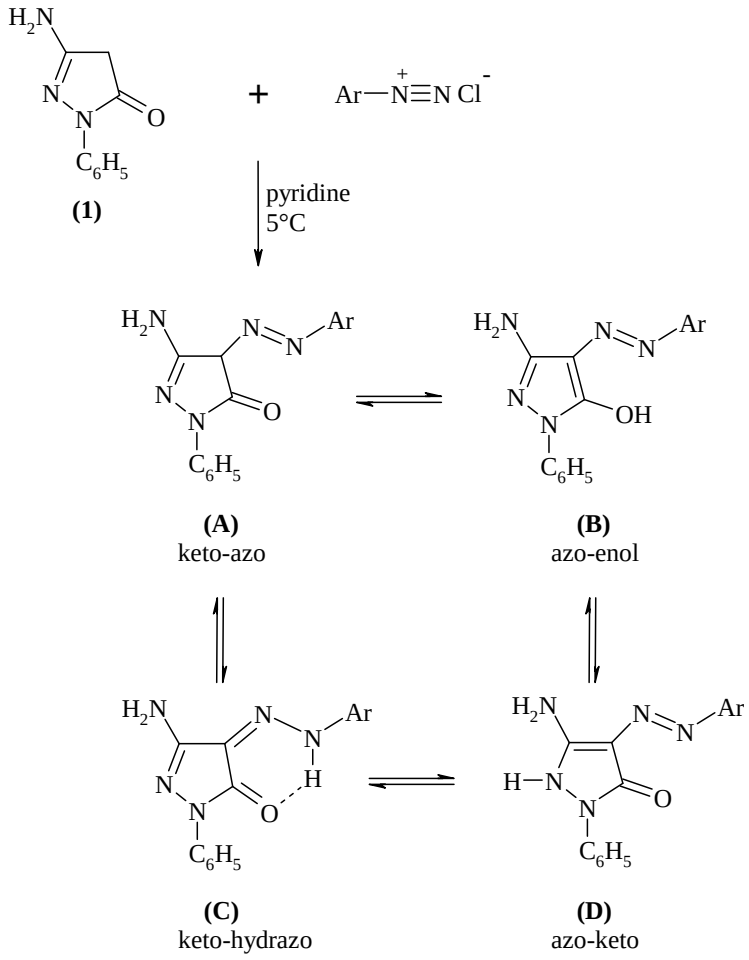
I II

(1)

Scheme 1

A cold solution of aryldiazonium chlorides of primary aromatic amines, namely, 4-bromoaniline, 4-hydroxyaniline, 4-methoxyaniline, 4-acetylaniline, 4-carboxyaniline, 4-N,N-diethylaniline, 4-aminobiphenyl, 1-aminonaphthalene-4-sulphonic acid, 4-aminoantipyrine and 3-amino-1-phenyl-2-pyrazolin-5-one (**1**), which are prepared by treatment of sodium nitrite solution with the hydrochloride solution of the previous primary aromatic amines are coupled at C4 with a cold solution of 3-amino-1-phenyl-2-pyrazolin-5-one (**1**) in pyridine to give a tautomeric mixture of 3-amino-4-arylazo-1-phenyl-2-pyrazolin-5-one (**2a-j**).

The dyes may exist in four possible tautomeric forms, namely, two azo-keto forms **A** and **D**, the azo-enol form **B** and the hydrazone-keto form **C** as shown in **Scheme 2**. The deprotonation of the four tautomers (**A-D**) leads to a common anion.



(1)

pyridine
5°C

(A) keto-azo

(B) azo-enol

(C) keto-hydrazo

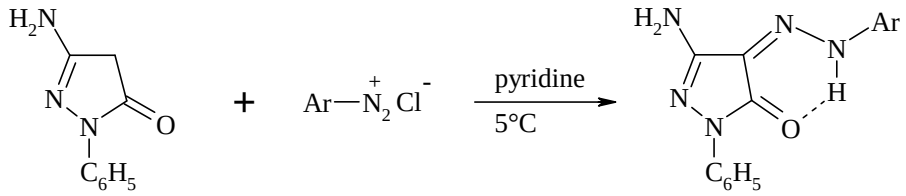
(D) azo-keto

Scheme 2

Numerous investigations were carried out to establish the tautomeric structures of 4-arylazo-5-pyrazolones both in the solid state and in solution using a variety of spectroscopic techniques. The spectral data, generally, leads to the conclusion that the tautomeric equilibrium of the arylazo-pyrazolone dyes is in favor of the hydrazone form in the solid state and also in $CHCl_3$, DMSO and pyridine [19-21].

Our spectral data listed in **Table 3** proved that the 4-arylhydrazopyrazolones (**C**) are the existed structure of the all synthesized dyes due to their stabilization by interamolecular hydrogen bonding (**Scheme 3**). The colour of the synthesized arylhydrazopyrazolones (**2a-j**) ranges from yellow to deep red crystals (**Table 1**).

The structures of arylhydrazopyrazolones (**2a-j**) have been confirmed by IR and ^{1}H-NMR spectral data which are listed in **Table 3**.



(1) **(2)**

a) Ar = C_6H_4-Br,4-

b) Ar = C_6H_4-OH,4-

c) Ar = C_6H_4-OCH_3,4-

d) Ar = C_6H_4-$COCH_3$,4-

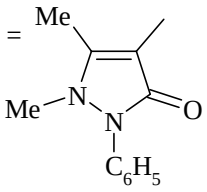
e) Ar = C_6H_4-COOH,4-

f) Ar = C_6H_4-$N(C_2H_5)_2$,4-

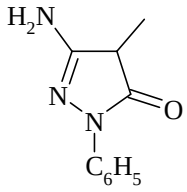
g) Ar = C_6H_5-C_6H_4,4-

h) Ar = 1-naphthyl-SO_3H,4-

i) Ar =

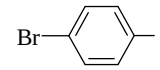
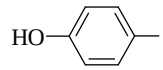
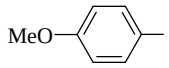
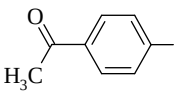
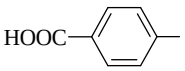
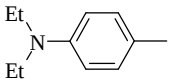
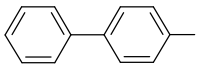
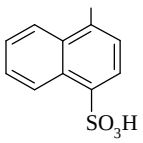
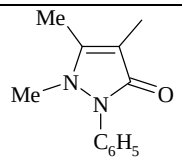
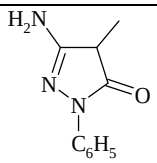


j) Ar =



Scheme 3

Table 3: The spectral data of 3-amino-1-phenyl-1H-pyrazole-4,5-dione-4-arylhydrazones (2a-j).

Compd. No.	Ar	IR (KBr) (ν in cm^{-1})				^{1}H-NMR (δ in ppm)
		C=C, C=N	C=O	CH	OH, NH	
2a		1564	1652	3069	3182 3302 3435	($CDCl_3$): 7.49 (m, 5H, Ar-H), 7.75 (d, 2H, Ar-H), 7.92 (s, 2H, Ar-H), 8.21-8.23 (d, 3H, N-H and NH_2).
2b		1562	1692	3071	3376 3478	(CD_3COOD): 6.88 (d, 2H, Ar-H), 7.16 (t, 1H, Ar-H), 7.39 (m, 4H, Ar-H), 7.71 (d, 2H, Ar-H), 8.65-8.68 (m, 4H, O-H, N-H and NH_2).
2c		1571	1695	2928 3077	3168 3427	(CD_3COOD): 3.76 (s, 3H, OCH_3), 6.93 (d, 2H, Ar-H), 7.14 (m, 1H, Ar-H), 7.34 (t, 2H, Ar-H), 7.47 (d, 2H, Ar-H), 7.71 (d, 2H, Ar-H), 8.41-8.43 (d, 3H, N-H and NH_2).
2d		1583	1652 1674	2912 3065	3199 3330	(CD_3COOD): 2.63 (s, 3H, CH_3), 7.22 (t, 1H, Ar-H), 7.43 (t, 2H, Ar-H), 7.66 (d, 2H, Ar-H), 7.78 (d, 2H, Ar-H), 8.08 (d, 2H, Ar-H), 8.50-8.52 (d, 3H, N-H and NH_2).
2e		1574	1629 1682	3061	3336 3439	(CD_3COOD): 7.21 (t, 1H, Ar-H), 7.43 (t, 2H, Ar-H), 7.57 (d, 2H, Ar-H), 7.76 (d, 2H, Ar-H), 8.13 (d, 2H, Ar-H), 9.51-9.54 (m, 4H, O-H, N-H and NH_2).
2f		1552	1649	2972 3070	3164 3441	($CDCl_3$): 1.13 (t, 6H, 2× CH_3), 3.39 (q, 4H, 2× N-CH_2), 7.13-7.94 (m, 9H, Ar-H), 8.55-8.57 (d, 3H, N-H and NH_2).
2g		1563	1637	3066	3180 3310 3484	(CD_3COOD); 7.16 (t, 1H, Ar-H), 7.29 (t, 1H, Ar-H), 7.38 (q, 4H, Ar-H), 7.60 (q, 4H, Ar-H), 7.66 (d, 2H, Ar-H), 7.72 (d, 2H, Ar-H), 8.39-8.42 (d, 3H, N-H and NH_2).
2h		1567	1629	3049	3339 3458	($CDCl_3$): 6.98 (b, 2H, NH_2), 7.19-8.75 (m, 11H, Ar-H), 9.07 (b, 1H, NH), 9.16 (s, 1H, SO_3H).
2i		1562	1652	2968 3071	3356 3458	($CDCl_3$): 2.47 (s, 3H, CH_3), 3.11 (s, 3H, N-CH_3), 7.13-7.94 (m, 10H, Ar-H), 8.09-8.12 (d, 3H, N-H and NH_2).
2j		1552	1698	2877 3074	3114 3298 3464	(CD_3COOD): 3.80 (d, 1H, C4`-H), 7.13–7.95 (m, 10H, Ar-H), 9.55-9.58 (m, 5H, N-H and 2x NH_2).

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