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Synthesis, Characterization and Color Fastness Studies of Some New 1, 4,-Di-Azophenyl-(1/-Phenyl-3/-Aryl-4/-Substituted Phenyl)-Pyrazoles

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Abstract: *A series of novel 1, 4,-Di-Azophenyl-(1/-phenyl-3/-Aryl-4/-Substituted phenyl)-pyrazoles **(4a-m)** were synthesized by coupling reaction of 1-phenyl-3-(2/-hydroxy phenyl)-4-substituted phenyl-pyrazoles **(3a-m)** with diazotized 1,4-Diamino phenyl **(2)**. These dyes have been prepared in good yield and were characterized by UV-Visible, FT-IR and ^{1}H-NMR Spectroscopic techniques. The effect of solvent polarity and various PH on dyes in the visible absorption spectra were evaluated.*

Keywords: *Pyrazole, azo compounds, chalcones.*

1. Introduction

Azo compounds have been found to possess wide spectrum of biodynamic properties. Many of them have been reported as antibacterial[5], antimicrobial[6], diagnostic aid[7], antineoplastic[8], urinary antiseptic[9] and topical dermatologic activities[10]. Several azo compounds have been proved useful for the colouration of cellulose acetat fibres. Pyrazole derivatives possess wide range of pharmacological activities like antioxidant[9], antiinvasive[10], antivitral[11], antipyretic[12], antiinflammatory[13], antidepressant[14], blood pressure lowering[15]etc.

2. Resultt and Discussion

In view of these observations, it was thought worth-while to synthesize and investigate the 1, 4,-Di-Azophenyl-(1/-phenyl-3/-Aryl-4/-Substituted phenyl)-pyrazoles (4a-m) and 1-phenyl-3-(2/-hydroxy phenyl)-4-substituted phenyl-pyrazoles (3a-m) in which azo group have been linked with pyrazole moiety.

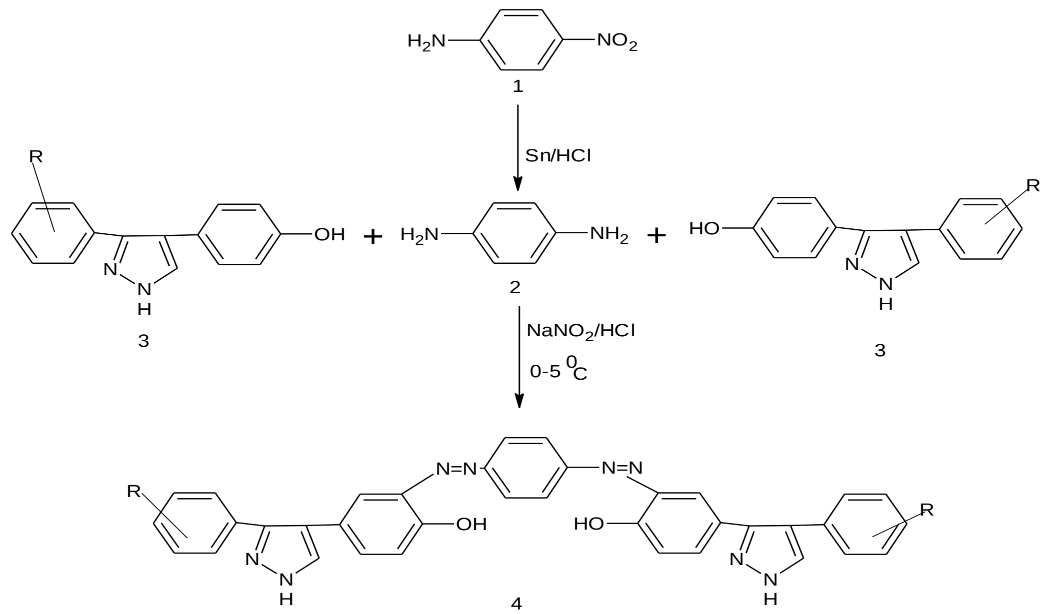
The reaction sequence leading to the formation of desired heterocyclic compounds are outlined in Scheme-I. The starting material 1, 4-Diamino phenyl **(2)** was prepared by the reduction of 4-nitro aniline in the presence of Sn/HCl. Which undergo diazotization with 1-phenyl-3-(2/-hydroxy phenyl)-4-substituted phenyl-pyrazoles **(3)** in presence of in presence of $NaNO_2$ and HCl at 0-5^{0}C yielded 1, 4,-Di-Azophenyl-(1/-phenyl-3/-Aryl-4/-Substituted phenyl)-pyrazoles (4a-m). The UV-Vis-spectra of the azo dyes **(4a-m)** were recorded and the values of absorptions (λ max) and fastness properties are shown in Table –I. It is apparent that the wavelength of maximum absorptions azo compound was observed at 200-500nm in EtOH solutions. Variation in λmax is being attributed to structural variation of electron–rich aromatic compounds with N=N linkage used for the preparation of these azo compounds.

Table I- *UV-VIS spectral data of 1, 4,-Di-Azophenyl-(1′-phenyl-3′-Aryl-4′-Substituted phenyl)-pyrazoles (4a –m) and color fastness properties.*

Code	Colour	λ max	Fastness properties			
			Silk		**Wool**	
			Light[a]	**wash[b]**	**Light[a]**	**Wash[b]**
4a	Red	475	2	3	2-3	3 -4
4b	Brown	456	3-4	2-3	3-4	2
4c	Red	442	2	4	2	3
4d	Brown	411	2-3	3-4	2-3	2 -3
4e	Red	422	4	2-3	3	3-4
4f	Orange	445	2-3	3-4	2-3	2 -3
4g	Red	470	3-4	2-3	3-4	2
4h	Red	474	2	4	3	2-3
4i	Red	473	3	2-3	3-4	3
4j	Orange	457	3-4	3	2-3	2 -3
4k	Red	420	4	3	4	2-3
4l	Red	420	2	4	4	2-3
4m	Purple	483	4	3-4	2-3	3

- IN EtOH solution(4a-m)
- Light-fastness: 1-minimum, 2-poor, 3-moderate, 4-fairly good, 5-good, 6-very good.
- Wash-fastness: 1-poor, 2-fair, 3-good, 4-very good, and 5-excellent.

Structure proof for the synthesized compounds (**4a-m)** was illusidated by IR and ^{1}HNMR studies. IR spectrum shows the presence of NH- group at 3333cm^{-1}, 1643cm^{-1}, N =N group at 1580cm^{-1}, OH group at 3345cm^{-1}, 1654, 755cm^{-1}, 738. ^{1}HNMR spectrum showed be presence 8.1 (s, 1H, NH-pyrazole), 6.8 - 7.0(Ar- H), 5.3 (s, 1H, OH).



Where,

	R
1)	H
2)	2-OH
3)	3-OH
4)	4-OH
5)	2-NO_2
6)	3-NO_2
7)	4-NO_2
8)	2-CL
9)	3--CL
10)	3-OCH_3
11)	4-OCH_3
12)	3, 4, 5-$(OCH_3)_3$
13)	-$N(CH_3)_2$

Scheme-I

3.EXPERIMENTAL SECTION

The melting points are uncorrected. Purity of the compounds was checked on silica gel G plates using iodine vapour as visualizing agent. Synthesized compound was characterized by IR spectra, run in KBr on a Perkin – Elmer infrared spectrophotometer. ^{1}H NMR spectra on Brucker AC–300F (300Hz) NMR spectrometer using DMSO-d_6 as a solvent and tetra methyl silane as internal standard.

Table II. *Characterization data of 1, 4,-Di-Azophenyl-(1/-phenyl-3/-Aryl-4/-Substituted phenyl)-pyrazoles (4a –m).*

Comp	**R**	**Mol Formula**	**M.P. (°C).**	**Yield (%)**	**Analysis formula (calcd)% (obs)**		
					C	H	N
4a	- H	$C_{38}H_{28}O_2N_6$	153	65	76.0 (76.3)	4.6 (4.6)	14.0 (14.1)
4b	2-OH	$C_{38}H_{28}O_3N_6$	168	92	74.02 (74.74)	4.5 (4.0)	13.6 (13.3)
4c	3-OH	$C_{38}H_{28}O_3N_6$	159	64	74.02	4.5	13.6

					(74.74)	(4.0)	(13.3)
4d	4-OH	$C_{38}H_{28}O_3N_6$	172	58	74.02 (74.74)	4.5 (4.0)	13.6 (13.3)
4e	2-NO_2	$C_{38}H_{27}O_4N_7$	137	78	71.4 (71.6)	4.0 (4.2)	14.2 (14.0)
4f	3-NO_2	$C_{38}H_{27}O_4N_7$	149	66	71.4 (71.6)	4.0 (4.2)	14.2 (14.0)
4g	4-NO_2	$C_{38}H_{27}O_4N_7$	198	65	71.4 (71.6)	4.0 (4.2)	14.2 (14.0)
4h	2-CI	$C_{38}H_{27}O_2N_6Cl$	156	60	71.92 (71.6)	04.2 (4.1)	13.2 (13.7)
4i	4-CI	$C_{38}H_{27}O_2N_6Cl$	163	63	71.92 (71.6)	04.2 (4.1)	13.2 (13.7)
4j	2-OCH_3	$C_{39}H_{30}O_3N_6$	129	62	74.2 (77.4)	4.76 (4.0)	13.3 (13.6)
4k	4-OCH_3	$C_{39}H_{30}O_3N_6$	149	78	74.2 (77.4)	4.76 (4.0)	13.3 (13.6)
4l	3, 4, 5-$(OCH_3)_3$	$C_{41}H_{34}O_5N_6$	198	68	72.3 (72.6)	5.0 (5.2)	12.3 (12.2)
4m	-$N(CH_3)_2$	$C_{49}H_{31}O_2N_7$	133	54	78.5 (78.6)	4.1 (4.1)	13.0 (13.7)

4. Synthesis of 1, 4-Diamino phenyl (2)

The 4-nitro aniline (1) (0.1mol) in 250 ml round bottom flask in presence of Sn/HCl, the mixture was heated for five hours in water bath, the solid separated out, filtered dried and crystallized from suitable sovent.

Synthesis of 1-phenyl-3-(2/-hydroxy phenyl)-4-substituted phenyl-pyrazoles (3a-m)

A mixture of substituted chalcones and $NH_2NH_2.H_2O$ (0.01mol) in ethanol (30 ml) was refluxed for six hours. The reaction mixture was poured on ice cold water and acidified with dil. HCl. A pale brown solid **(3a-m)** slowly separated out. It was filtered, washed with water, and dried.

Synthesis of 1, 4,-Di-Azophenyl-(1/-phenyl-3/-Aryl-4/-Substituted phenyl)-pyrazoles (4a-m)

A mixture of 1, 4-Diamino phenyl **(2)** (0.1mol) was dissolved in (20ml) 4% HCl and the solution was cooled to 0-5°C. To this saturated sodium nitrite solution was added drop wise followed by addition of 1-phenyl-3-(2/-hydroxy phenyl)-4-substituted phenyl-pyrazoles **(3a-m)** (0.1mol) in 20ml of 7% NaOH for a period of 10min till the coloured solution is obtained. The solution was stirred for 30min and then neutralized to pH 7 by adding 10% HCl, the solid separated out, filtered dried and crystallized from suitable sovent.

4a: 1, 4,-Di-Azophenyl-(1/-phenyl-3/-Aryl-4/-phenyl)-pyrazoles.

Yield 65%, M.Pt. 153°C; IR (KBr);3319cm^{-1} (-OH), 3337cm^{-1} (NH-pyrazole), 1660cm^{-1} (C = 0), 1545cm^{-1} (C-N), 3143cm^{-1} (CH of pyrazole) 1632cm^{-1} (N=N), 752cm^{-1}; ^{1}HNMR (DMSO-d_6) 9.7 (1H, s, NH-pyrazole), 5.3 (s, 1H, OH), 6.3-7.1 (Ar- H).

4b: 1, 4,-Di-Azophenyl-(1/-phenyl-3/-Aryl-4/-(2-hydroxy phenyl))-pyrazoles.

Yield 92%, M.Pt. 168°C:IR (KBr) ; 3439cm^{-1} (-OH) 3335, (NH-pyrazole), 1683 (C = 0), 1585cm^{-1} (C-N), 3044cm^{-1} (CH of pyrazole) 1635cm^{-1} (N=N) 755cm^{-1}; ^{1}HNMR (DMSO-d6) 8.7 (1H, s, NH-pyrazole), 6.3 (s, 1H, OH), 7.1 (Ar- H).

4c: 1, 4,-Di-Azophenyl-(1/-phenyl-3/-Aryl-4/- (3-hydroxy phenyl))-pyrazoles.

Yield 64% , M.P. 159° C; IR (KBr) ; 3419cm^{-1} (-OH), 3334 (NH-pyrazole) , 1653 (C = 0), 1547cm^{-1} (C-N), 3044cm^{-1} (CH of pyrazole) 1635cm^{-1} (N=N) 742cm^{-1}; ^{1}HNMR (DMSO-d6) 9.2 (1H, s, NH-pyrazole), 5.7 (s, 1H, OH), 6.8 (Ar- H).

4d: 1, 4,-Di-Azophenyl-(1/-phenyl-3/-Aryl-4/- (4-hydroxy phenyl))-pyrazoles.

Yield 58% , M.P. 172° C; IR (KBr) ; 3422cm^{-1} (-OH), 3315 (NH-pyrazole) , 1613 (C = 0), 1527cm^{-1} (C-N), 3024cm^{-1} (CH of pyrazole) 1605cm^{-1} (N=N), 742cm^{-1}; ^{1}HNMR (DMSO-d6) 8.2 (1H, s, NH-pyrazole), 6.3 (s, 1H, OH), 6.9 (Ar- H).

4e: 1, 4,-Di-Azophenyl-(1'-phenyl-3'-Aryl-4'-(2-nitro phenyl)-pyrazoles.

Yield 78% , M.P. 137° C; IR (KBr) ; 3422cm^{-1} (-OH), 3315 (NH-pyrazole) , 1683 (C = 0), 1559cm^{-1} (C-N), 3044cm^{-1} (CH of pyrazole) 1635cm^{-1} (N=N) 746cm^{-1}(C-NO_2); ^{1}HNMR (DMSO-d6) 8.7 (1H, s, NH-pyrazole), 6.8 (s, 1H, OH), 7.6 (Ar- H).

4f: 1, 4,-Di-Azophenyl-(1'-phenyl-3'-Aryl-4'-(3-nitro phenyl))-pyrazoles.

Yield 66% , M.P. 149° C; IR (KBr) ; 3429cm^{-1} (-OH), 3335 (NH-pyrazole) , 1683 (C = 0), 1587cm^{-1} (C-N), 3044cm^{-1} (CH of pyrazole) 1635cm^{-1} (N=N) 744cm^{-1}(C-NO_2); ^{1}HNMR (DMSO-d6) 9.7 (1H, s, NH-pyrazole), 5.3 (s, 1H, OH), 6.3-7.1 (Ar- H).

4g: 1, 4,-Di-Azophenyl-(1'-phenyl-3'-Aryl-4'-(4-nitro phenyl))-pyrazoles.

Yield 65% , M.P. 198° C; IR (KBr) ; 3421cm^{-1} (-OH), 3335 (NH-pyrazole) , 1683 (C = 0), 1548cm^{-1} (C-N), 3044cm^{-1} (CH of pyrazole) 1635cm^{-1} (N=N); ^{1}HNMR (DMSO-d6) 9.5 (1H, s, NH-pyrazole), 6.6 (s, 1H, OH), 6.3 (Ar- H).

4h: 1, 4,-Di-Azophenyl-(1'-phenyl-3'-Aryl-4'-(2-chloro phenyl))-pyrazoles.

Yield 60%, M.Pt. 156°C; IR (KBr);3421cm^{-1} (-OH), 3337cm^{-1} (NH-), 1666cm^{-1} (C = 0), 1545cm^{-1} (C-N), 3143cm^{-1} (CH) 1632cm^{-1} (N=N), 752cm^{-1} (C-Cl); ^{1}HNMR (DMSO-d_6) 9.7 (1H, s, NH), 5.3 (s, 1H, OH), 6.3-7.1 (Ar- H).

4i: 1, 4,-Di-Azophenyl-(1'-phenyl-3'-Aryl-4'-(4-chloro phenyl))-pyrazoles.

Yield 63%, M.Pt. 163°C; IR (KBr);3423cm^{-1} (-OH), 3327cm^{-1} (NH-pyrazole), 1660cm^{-1} (C = 0), 1545cm^{-1} (C-N), 3143cm^{-1} (CH of pyrazole) 1632cm^{-1} (N=N), 732cm^{-1} (C-Cl); ^{1}HNMR (DMSO-d_6) 9.7 (1H, s, NH-pyrazole), 5.3 (s, 1H, OH), 6.3-7.1 (Ar- H).

4j: 1, 4,-Di-Azophenyl-(1'-phenyl-3'-Aryl-4'-(2-methoxy phenyl))-pyrazoles.

Yield 62%, M.Pt. 129°C; IR (KBr);3426cm^{-1} (-OH), 3337cm^{-1} (NH-pyrazole), 1664cm^{-1} (C = 0), 1545cm^{-1} (C-N), 3143cm^{-1} (CH of pyrazole) 1632cm^{-1} (N=N), 712cm^{-1}; ^{1}HNMR (DMSO-d_6) 9.7 (1H, s, NH-pyrazole), 5.3 (s, 1H, OH), 6.3-7.1 (Ar- H).

4k: 1, 4,-Di-Azophenyl-(1'-phenyl-3'-Aryl-4'-(4-methoxy phenyl))-pyrazoles.

Yield 78%, M.Pt. 149°C; IR (KBr);34229cm^{-1} (-OH), 3337cm^{-1} (NH-pyrazole), 1660cm^{-1} (C = 0), 1545cm^{-1} (C-N), 3143cm^{-1} (CH of pyrazole) 1632cm^{-1} (N=N), 744cm^{-1}; ^{1}HNMR (DMSO-d_6) 9.7 (1H, s, NH-pyrazole), 5.3 (s, 1H, OH), 6.3-7.1 (Ar- H).

4l: 1, 4,-Di-Azophenyl-(1'-phenyl-3'-Aryl-4'-(3, 4, 5-tri methoxy phenyl))-pyrazoles.

Yield 68%, M.Pt. 198°C; IR (KBr);3419cm^{-1} (-OH), 3337cm^{-1} (NH-pyrazole), 1664cm^{-1} (C = 0), 1545cm^{-1} (C-N), 3143cm^{-1} (CH of pyrazole) 1632cm^{-1} (N=N), 752cm^{-1}; ^{1}HNMR (DMSO-d_6) 9.7 (1H, s, NH-pyrazole), 5.3 (s, 1H, OH), 6.3-7.1 (Ar- H).

4m: 1, 4,-Di-Azophenyl-(1'-phenyl-3'-Aryl-4'-(N, N-Dimethyl phenyl))-pyrazoles.

Yield 54%, M.Pt. 133°C; IR (KBr);3420cm^{-1} (-OH), 3337cm^{-1} (NH-pyrazole), 1664cm^{-1} (C = 0), 1545cm^{-1} (C-N), 3143cm^{-1} (CH of pyrazole) 1632cm^{-1} (N=N), 710cm^{-1}; ^{1}HNMR (DMSO-d_6) 9.7 (1H, s, NH-pyrazole), 5.3 (s, 1H, OH), 6.3-7.1 (Ar- H).

5. Conclusion

A series of 1, 4,-Di-Azophenyl-(1'-phenyl-3'-Aryl-4'-Substituted phenyl)-pyrazoles **(4a-m)**, were 1-phenyl-3-(2'-hydroxy phenyl)-4-substituted phenyl-pyrazoles **(3a-m)** and 1, 4-Diamino phenyl **(2)**. These compounds were screened for their antibacterial activity against S. aureus and E. coli as well as for their antifungal activity against C. albicans and A. niger Showing good result.

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