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Synthesis and Application of Some Bisazo Acid Dyes Based on 4-Hydroxy Quinoline Quinazoline System on Various Fabrics

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Fifteen 3-(4′-R-azo-1′-phenylazo)-4-hydroxy quinolino-[1,2-b]-4-oxoquinazolines **(IVa–o)** were prepared by coupling diazotised 3-(4′-amino-1′-phenylazo)-4-hydroxy quinolino-[1,2-b]-4-oxoquinazoline **(III)** with various coupling components **(a–o)**. The compound **(I)** was coupled with diazotised *p*-aminoacetanilide giving compound **II**, which on hydrolysis gave compound **III**. The compounds **IVa–o** were characterised by elemental and spectral analyses and their dyeing performance on silk, wool and nylon fabrics was assessed.

INTRODUCTION

Some of the dyes based on 4-oxoquinazoline ring system have been reported to be useful for natural and man-made fibres[1–4]. Syntheses of azo acid dyes based on quinolinoquinazoline ring system and their dyeing performance on various fabrics have been very recently reported[5]. Hence, it was thought interesting to undertake the synthesis and study of dyeing properties of the bisazo acid dyes **(IVa–o)**).

EXPERIMENTAL

4-Hydroxyquinolino-[1,2-b]-4-oxoquinazoline (I)

It was prepared by the method already reported[5].

3-[4′-Acetylamino-1′-phenylazo]-4-hydroxyquinolino-[1,2-b]-4-oxoquinazoline (II)

A clear solution of **I** (2.62 g, 0.01 mole) in sodium hydroxide (30 mL, 10%) and acetone (60 mL) was cooled below 5°C and then the solution of diazotised 4-aminoacetanilide (1.5 g, 0.01 mole) was slowly added to it with stirring at 0–5°C during 1 h maintaining the pH between 7.5 to 8.0. The mixture was further stirred for 2 h, at 0–5°C. The mixture was diluted with water and the pH was adjusted between 6.5 and 7.0 with acetic acid. The separated compound was filtered, washed with water and crystallised from alcohol to give **II**; yield 70%, m.p. 215°C. [Found: N, 16.42%; $C_{24}H_{17}N_5O_3$ requires N, 16.54%]. IR (KBr): 3500–3100 (—OH stretching), 1580 (C=O stretching), 1450 (N=N stretching),

1250 cm^{-1} (C—N stretching). NMR spectra (DMSO-d_6 solvent) : δ 2.47 (3H, —$COCH_3$), 2.05 (1H, —NH), 7.46 (1H, —OH).

3-[4′-Amino-1′-phenylazo]-4-hydroxyquinolino-[1,2-b]-4-oxoquinazoline (III)

A mixture of **II** (10 g), concentrated hydrochloric acid (10 mL) and distilled water (25 mL) was first heated on water-bath for 30 min and then directly on wire gauze for 1 h. The reaction mixture was cooled and neutralised with sodium bicarbonate. The separated compound was filtered, washed with water and crystallised from alcohol to give **III**, yield 65%, m.p. 230–32°C. [Found: N, 18.26%; $C_{22}H_{15}N_5O_2$ requires N, 18.37%]. IR (KBr): 3500–3000 (—OH stretching), 1630 (N—H bending), 1560 (C=O stretching), 1450 (N=N stretching), 1250 cm^{-1} (C—N stretching). NMR spectra (DMSO-d_6 solvent): δ 7.50 (1H, —OH), 3.40 (2H, —NH_2).

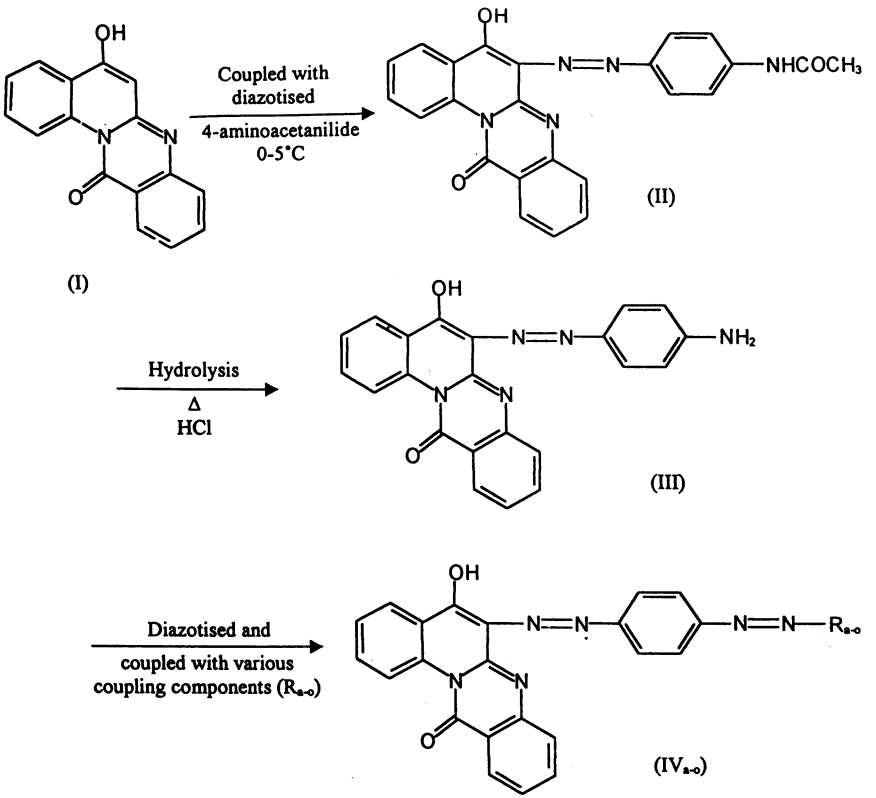
3-[4′-R-azo-1′-phenylazo]-4-hydroxyquinolino-[1,2-b]-4-oxoquinazoline (IVa–o)

H-acid (3.19 g, 0.01 mole) was suspended in water (20 mL) and dissolved to neutral pH with sodium carbonate solution (10% w/v) to obtain a clear solution. It was cooled below 5°C and then solution of diazotised compound **III** (3.81 g, 0.01 mole) was slowly added to it with stirring at 0–5°C. The pH was maintained between 7.5 and 8.0 by simultaneous addition of 10% sodium carbonate solution. The stirring was continued for 1 h. To this reaction mixture, sodium chloride was added until the coupling material was precipitated. After stirring for 1 h, the liquor was filtered and the product was washed with a small amount of sodium chloride solution (5% w/v). The product was dried at 80–90°C and extracted with DMF and precipitated by diluting the DMF extract with excess of acetone. The same procedure was used to prepare $\mathbf{IV_{b-o}}$ using various coupling components ($\mathbf{R_{b-o}}$) (Scheme I). The characterisation data of compounds **IVa–o** are given in Table-1.

The structures of **IVa–o** were confirmed by their elemental analysis, IR and NMR spectra. The IR spectrum of compound **IVa** shows characteristic bands at 3400–3000 (—OH stretching), 1650 cm^{-1} (N—H bending) 1560 (C=O stretching), 1440 (N=N stretching), 1060 and 1140 cm^{-1} (S=O stretching). The NMR spectrum of compound **IVa** shows characteristic signals at δ 7.89 (1H, —OH), 6.20 (1H, —OH naphthol ring), 3.60 (2H, —NH_2) and 7.80 (1H, —SO_3H).

RESULTS AND DISCUSSION

These compounds, when applied on silk, wool and nylon fabrics as 2% shade, gave orange brown yellow, red, blue, violet and gray shades with poor to fairly good light fastness, fair to excellent wash fastness and poor to excellent exhaustion. Among these dyes the coupling components R_b, R_c, R_f, R_g and R_j give deeper shades while the whole group of dyes impart shine on wool. The



For compounds **IVa–o**

Ra	H-acid	**f**	1-(2,5-dichloro-4-sulfophenyl)-3-methyl-5-pyrazolone	**k**	Schaffer's acid
b	N-Phenyl H-acid	**g**	1-(4-sulfophenyl)-3-methyl-5-pyrazolone	**l**	Chicago acid
c	J-acid	**h**	R-acid	**m**	Oxy-Tobias acid
d	N-methyl J-acid	**i**	G-acid	**n**	K-acid
e	N-phenyl J-acid	**j**	γ-acid	**o**	Bon acid

Scheme I: Synthesis of 3-(4′-R-azo-1′-phenylazo)-4-hydroxyquinolino-[1,2-b]-4-oxoquinazolines **IVa–o**.

brilliancy and beauty of the shades and the excellent wash fastness reveal that some of the acid dyes would prove to be useful dyes for dyeing wool, silk and nylon fabrics.

TABLE-1
CHARACTERISATION DATA OF COMPOUNDS (IVa–o)

Compound	Colour	Yield (%)	m.p. > (°C)	Nitrogen (%)	
				Found	Calcd.
IVa	Violet	60	300	12.76	12.98
b	Violet	79	300	11.49	11.65
c	Red	67	300	14.74	15.00
d	Brown	72	300	14.42	14.69
e	Brown	73	300	13.28	13.44
f	Yellow	84	300	14.97	15.19
g	Yellow	56	300	16.63	16.76
h	Red	64	300	11.20	11.35
i	Brown	63	300	11.24	11.35
j	Violet	82	300	14.82	15.00
k	Red	69	300	14.98	13.16
l	Brown	76	300	12.71	12.98
m	Brown	52	300	14.89	15.05
n	Brown	65	300	12.77	12.98
o	Pink	68	300	13.74	13.95

TABLE-2
λ_{max}, EXHAUSTION AND FASTNESS PROPERTIES OF (IVa–o)

Compound	λ_{max} nm	Exhaustion (%)			Fastness properties					
					Silk		Wool		Nylon	
		Silk	Wool	Nylon	Light	Wash	Light	Wash	Light	Wash
IVa	319	69	74	63	3–4	4	3	4–5	2–3	4–5
b	318	71	70	60	2–3	3	3	4	3–4	4–5
c	325	66	70	66	2–3	3–4	2–3	3–4	2–3	3–4
d	320	63	70	64	2	3–4	2	3	2–3	3–4
e	326	72	79	67	3–4	2–3	3	4–5	2	4–5
f	338	76	84	76	2–3	4	2–3	2–3	2	4–5
g	328	57	66	59	3–4	4	2–3	2–3	2–3	4
h	335	53	63	53	2–3	2–3	4–5	3	3–4	4
i	336	79	84	74	2–3	4–5	3–4	3–4	3	4–5
j	306	62	73	68	2–3	4–5	2–3	4–5	3	3–4
k	331	70	74	62	3	2–3	2–3	4	3–4	4
l	326	69	71	67	3–4	3–4	3–4	3	2–3	3–4
m	319	72	76	67	3	3–4	2–3	2–3	2	4–5
n	337	69	72	64	3	4	2–3	3–4	2–3	4–5
o	339	69	68	66	2–3	4–5	2–3	4	3–4	4–5

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