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SYNTHESIS OF 3-[4-(3-HYDROXY-4-METHYL-PHENYLAZO)-PHENYL]-2-METHYL-3H-QUINAZOLIN-4-ONE DERIVATIVIES AND THEIR APPLICATION ON NYLON AND POLYESTER FIBRES

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ABSTRACT

A series of 3-[4-(3-hydroxy-4-methyl-phenylazo)-phenyl]-2-methyl-3H-quinazolin-4-one derivatives **(3)** have been obtained by a reaction of a various coupling agent **(a-h)** with diazonium salt containing 4-oxo-quinazolin moiety **(2)**. The diazonium salt **(2)** is obtained by the reaction of 4-(2-methyl-4-oxo-3-quinazolinyl)-aniline with $NaNO_2$ and HCl. The product is characterized by spectral and analytical data. Most of the tested compounds show promising dyeing properties.

Key words : Nylon, Polyester, Dyeing.

INTRODUCTION

The wide variety of 4-oxo-quinazolin derivatives are now a major group of dyes and have soon attained a commercial status. There is no slackening of activity in this field as seen from the large number of patent specification and several ranges, which continue to appear in the market[1,2]. We report here the synthesis and study of the dyeing properties of the 4-oxo-quinazolin dyes based on 2-methyl-3, 1-benzoxazine-4(4H)-one.

A mixture of N-acetyl anthranilic acid (17.9 g, 0.1 mol) and acetic anhydride (3.6 mL) was refluxed for 40 minutes and the white solid separated on cooling was filtered and washed thoroughly with dry petroleum ether to give 2-methyl-3, 1-benzoxazine-4 (4H)-one **(1)**. The compound **(1)** on condensation with 1, 4, -diaminobenzene yielded 4-(2-methyl-4-oxo-3-quinazolinyl)-aniline **(2)**. Compound **(2)** was diazotized and coupled with different phenols. The synthesized compounds **(3)** were adequately characterized by their elemental analysis and spectral data.

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EXPERIMENTAL

Melting points were taken in open capillaries and are uncorrected. The IR spectra of dyes D_A to D_H were recorded on Bio-Red FTS-40 spectrophotometer using KBr pellets. The purity of all dyes has been checked by thin-layer chromatography[3]. The absorption spectra of all the dyes were recorded on Beckmann DB-GT Grafting Spectrophotometer. Fastness to light was assessed in accordance with Bs : 1006-1978.The rubbing fastness was carried out with a crock meter (Atlas) in accordance with AATCC (1961) and the wash fastness test in accordance with IS : 765-1979.

2-Methyl-3, 1-benzoxazine 4(4H)-one[4] (1)

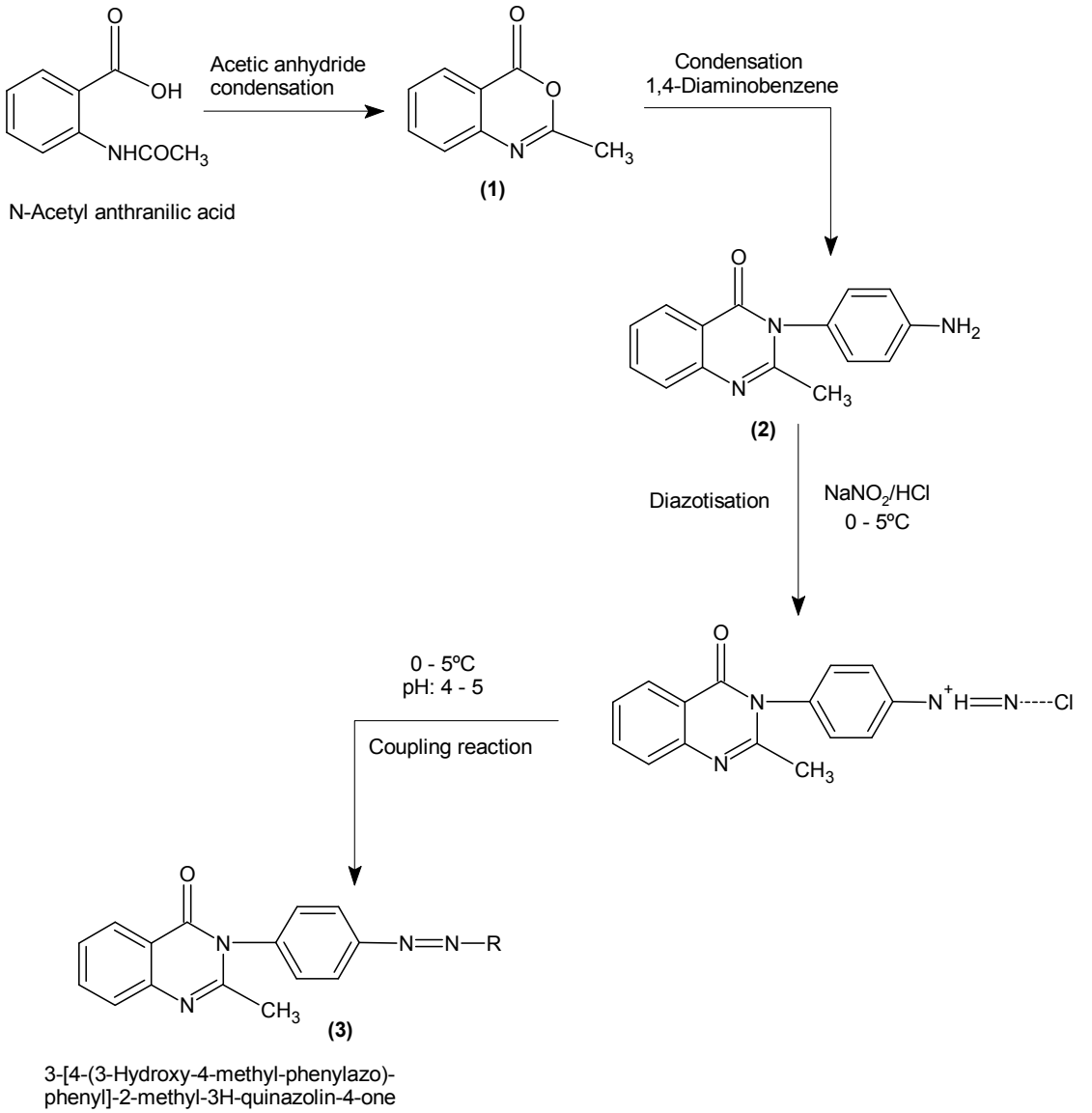
A mixture of N-acetyl anthranilic acid (17.9 g, 0.1 mol) and acetic anhydride (3.6 mL) was refluxed for 40 minute. The white solid separated on cooling was filtered and washed thoroughly with dry petroleum ether to get compound **(1)**. Yield 85 %, m. p. 80ºC. Anal. Calcd. for $C_9H_7O_2N$: C, 67.10; H, 4.35; N, 8.10%. Found C, 67.10; H, 4.32; N, 8.10%.

4-(2-Methyl-4-oxo-3-quinazolinyl)-aniline (2)

Equimolar ratio of compound **(1)** (161.0 g; 1M) and 1, 4-diaminobenzene (108.0 g; 1M) were intimately mixed and heated on a free flame for five minutes with vigorous shaking. To the hot reaction mixture, ethanol (750.0 mL) was added and the contents of the flask were allowed to cool. Scratching the side with a glass rod yielded a black crystalline solid. It was filtered, washed with cold ethanol and recrystallized from ethanol (95%) to get compound **(2)**. Yield 70%, m. p. 190ºC. Anal. Calcd. for $C_{15}H_{13}ON_3$: C, 71.42; H, 05.15; N, 16.66.Found C, 71.45; H, 05.10; N, 16.70%.

3-[4-(3-Hydroxy-4-methyl-phenylazo)-phenyl]-2-methyl-3H-quinazolin -4-one (D_A to D_H) : (3)

Equimolar ratio of compound **(2)** (0.126 g; 0.05M) was suspended in water (10.0 mL). Conc. hydrochloric acid (5.0 mL; 0.025 M) was added drop-wise to the well stirred suspension and the solution was cooled to 0-5ºC in an ice bath. A solution of sodium nitrite (5.0 mL; 10% w/v) was then added and the reaction mixture was stirred until positive test for nitrous acid on starch-iodide paper was there (i. e., blue color on starch-iodide paper). The excess nitrous acid was neutralized with urea (1.0 g) and the mixture was filtered to get a clear diazonium salt solution, which was used for the subsequent coupling reaction.



N-Acetyl anthranilic acid

3-[4-(3-Hydroxy-4-methyl-phenylazo)-phenyl]-2-methyl-3H-quinazolin-4-one

Where R = o-Cresol, m-Cresol, p-Cresol, o-Cl-phenol, p-Cl-phenol, 1-Napthol, Phenol

Reaction Scheme

Table 1 : Characterization

Dye No.	Shade on dyed fibres	R	Mol. formula	Yield %	M.P. (°C)	Found (%) (Calcd.)	
						C	N
D_A	Yellow	(a) o-Cresol	$C_{22}H_{18}O_2N_4$	79	190	71.35 (71.29)	15.13 (15.29)
D_B	Brown	(b) m-Cresol	$C_{22}H_{18}O_2N_4$	78	129	70.78 (71.29)	15.13 (15.29)
D_C	Brown	(c) p-cresol	$C_{22}H_{18}O_2N_4$	71	198	70.78 (71.29)	15.13 (15.29)
D_D	Violet	(d) m-Cl-Phenol	$C_{21}H_{15}O_2N_4Cl$	67	250	64.53 (64.50)	14.34 (1430)
D_E	Violet	(e) m-Cl-Phenol	$C_{21}H_{15}O_2N_4Cl$	75	>300	64.53 (64.50)	14.34 (1430)
D_F	Black	(f) p-Cl-Phenol	$C_{21}H_{15}O_2N_4Cl$	70	>300	64.53 (64.50)	14.34 (1430)
D_G	Brown	(g) 1-Naphthol	$C_{25}H_{18}O_2N_4$	77	>300	73.78 (73.78)	13.79 (13.70)
D_H	Black	(h) Phenol	$C_{21}H_{16}O_2N_4$	78	129	70.78 (70.75)	15.73 (15.69)

o-Cresol (0.047 g; 0.05M) was dissolved in sodium hydroxide solution (15.0 mL; 5% w/v) and the solution was cooled to 0-5ºC, in an ice-bath. To this well-stirred solution, the above mentioned diazo solution was then gradually added in 1 hr. at 0-5ºC maintaining pH 4-5 by the addition of the concentrated hydrochloric acid slowly and with vigorous stirring to the cold mixture until it is strongly acidic to litmus paper. The mixture was stirred for 3-4 hrs. at 0-5ºC until all the diazo salt was consumed (spot test with alkaline phenol solution). After being stirred for further 2 hrs. to complete the separation, the dye was isolated by filtration, washed with ice water, dried and crystallized from ethanol (95%) to get black crystals of compound (D_A). Yield 79%, m. p. 190ºC. Anal. Calcd. for $C_{22}H_{18}O_2N_4$: C, 71.35; H, 04.86; N, 15.13%. Found C, 71.29; H, 04.80; N, 15.29%. IR : 1659 cm^{-1} (>C=O), 1620 cm^{-1} (>C = N-), 3430 cm^{-1} (N-H), 3257 cm^{-1} (O-H), 701 and 765 cm^{-1} (monosubstituted), 845 cm^{-1} (1, 4-disubstituted benzene ring) and 1572 cm^{-1} (–N=N–).

Other compounds **(D_B-D_H)** were synthesized similarly from **(D_A)**, respectively. Characterization data are presented in Table 1.

RESULTS AND DISCUSSION

All the dyes D_A to D_H were applied on nylon and polyester fibers using the reported procedure[5–8]. All the dyes were black, brown, violet, yellow to orange in colour and these were obtained in excellent yield. Data on λ_{max} value (in DMF solvent) and the results of exhaustion and fixation of all the dyes on nylon and polyester fabrics are furnished in Table 2.

Table 2 : Evaluation of exhaustion and fixation study of dyes on nylon and polyester fibres (N = Nylon, P = Polyester)

Dye No.	λmax (nm)	log ε	% Exhaustion		λ*max (nm)	% Fixation**	
			N	P		P	N
D_A	444	4.13	56	61	452	63	60
D_B	468	4.34	61	50	477	64	60
D_C	453	4.50	64	52	446	60	60
D_D	150	4.29	69	68	458	69	60

Cont…

Dye No.	λmax (nm)	log ε	% Exhaustion		λ*max (nm)	% Fixation**	
			N	P		P	N
D_E	724	4.68	60	58	719	79	66
D_F	650	4.84	66	55	663	78	67
D_G	620	4.71	54	65	607	76	64
D_H	462	4.47	63	53	473	69	70

The data reveal that the percentage exhaustion on nylon fibres is higher, which may be due to the relatively open structure of the nylon fibre. The results of fastness to light, washing, rubbing, perspiration and sublimation of nylon and polyester fibres are shown in Table 3.The light fastness of all the dyes on both the fiber is found to be fair to fairly good to good.

Table 3 : Evaluation of fastness properties of dyes on nylon and polyester patterns with dyes (N = Nylon, P = Polyester)

Dye No.	Light fastness		Wash fastness		Rubbing fastness				Perspiration fastness				Sublimation fastness	
	N	P	N	P	Dry		Wet		Acidic		Alkaline		N	P
					N	P	N	P	N	P	N	P		
D_A	3-4	3	4-5	4	5	5	4	3	4	5	4	3	5	4
D_B	3-4	3	4-5	4	5	5	4	4	4	5	4	3	5	4
D_C	4-5	4	5	4	4	5	4	3	4	5	3	3	4	4
D_D	3-4	3	4-5	4	5	5	4	4	4	5	4	4	5	4
D_E	4	5	5	4	4	5	4	3	4	5	3	5	4	4
D_F	3	4	4-5	5	5	5	4	3	4	5	4	5	4	4
D_G	4	3-4	5	5	4	5	4	3	4	5	3	3	4	4
D_H	4	4	4-5	5	5	5	4	3	4	5	4	3	5	4

The obtained results of washing fastness of the prepared dyes for both the fibres showed that they are very good to excellent. Fastness to rubbing of dyed patterns was very good to excellent for all the dyes on both the fibres. This is attributed to good penetration and affinity of present dyes to synthetic fibres. The perspiration and sublimation fastness is very good to excellent. These are attributed to thermally and chemically stable

quinazolinone ring system.

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REFERENCES

1. G. Jones, The Quinolines, Wiley Inter Science, London, (1977) pp. 191-197.
2. Ciba-Geigy, Eur. Pat. Appl. 230, 210 (1987).
3. CIBA, Eur. Pat. Appl. ER. 775, 730 (1997).
4. Bemard Fried and Joseph Sherma; Thin Layer Chromatography Technique and Applications, Marcel Dekkar, Inc., New York and Basel (1982).
5. C. K. Whittaker and C. C. Wilcock, Dyeing with Coal Tar for Dyestuffs's, London (1952).
6. F. Sadovkorchagin and A. Maketsky, Chemical Technology of Fibrous Material, Mir Publication, Moscow (1973).
7. V. A. Sheni, Chemistry of Dyes and Principles of Dyeing, Sevak Publication, Bombay (1973).
8. E. R. Trotman, Dyeing and Chemical Technology of Textile Fabrics, London (1970) pp. 333-334 and 590.

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