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SYNTHESIS AND APPLICATION OF 3-[4'-(3-HYDROXY-4-METHYL-PHENYLAZO)-3, 3'-DIMETHYL-BIPHENYL-4-YL) -2-METHYL-3H-QUINAZOLIN-4-ONE AND THEIR DERIVATIVES

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ABSTRACT

A series of 3-[4-(3-hydroxy-4-methyl-phenylazo)-3, 3'-dimethyl-biphenyl-4-yl]-2-phenyl]-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 specifications and several ranges, which continue to appear in the market[1-3]. The use of the dyestuff makes possible the highest degree of fastness to severe washing, abrasion, etc. At the same time, the shade ranges that can be achieved on cotton with fast dyestuff has considerably been extended[4]. Patel et al.[5] have synthesiszed fiber reactive dyes for silk, wool and rayon.

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.

The reaction of benzoyl chloride with anthranilic acid in pyridine at 8ºC gave 2-

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methyl-3, 1-benzoxazine-4 (4H)-one **(1)**. The compound **(1)** on condensation with 4, 4', -diamino-3, 3' - dimethyldiphenyl **(2)**. Compound **(2)** diazotized and coupled with different couplers **(a-h)** gives different types of dyes **(3)**. All the compounds synthesized were adequately characterized by their elemental analysis and spectral data.

EXPERIMENTAL

Melting points were taken in open capillaries and are uncorrected. The IR spectra of dyes D_I to D_P were recorded on Bio-Red FTS-40 spectrophotometer using KBr pellets. The purity of all dyes has been checked by thin-layer chromatography[6]. 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 (1)

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 get compound **(1)**. Yield - 85 %, m. p. 80^{O}C. 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 %.

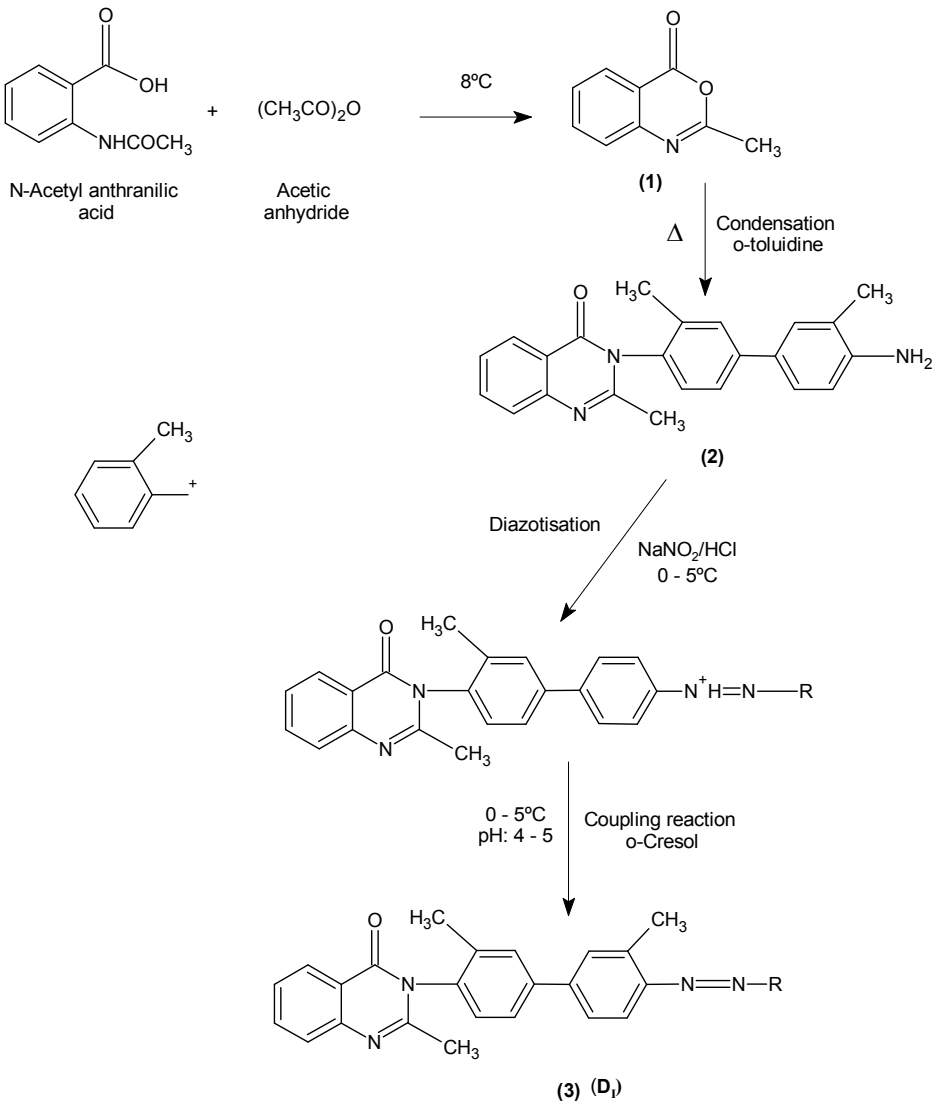
4-(2-Methyl-4-oxo-3-quinazolinyl)-4'-dimethyldipheny (2)

Equimolar ratio of compound **(1)** (161.0 g; 1M) and 1, 4-diamino-3, 3'-dimethyldiphenyl (212.0 g; 1M) (o-Tolidine) 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 rode yielded a greenish crystalline solid. It was filtered, washed with cold ethanol and recrystalised from ethanol (95%) to get compound **(2)**. Yield - 59%, m. p. 168ºC. Anal. Calcd. for $C_{23}H_{21}ON_3$: C, 77.74; H, 05.91; N, 11.83%. Found C, 77.70; H, 05.80; N, 11.99%.

3-[4'-(3-Hydroxy-4-methyl-phenylazo)-3, 3'-dimethyl-biphenyl-4-yl] -2-phenyl-3H-quinazolin -4-one (D_1 to D_P) : (3)

Equimolar ratio of compound **(2)** (0.1775 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 the positive test for nitrous acid on starch-iodide paper (i. e., blue color on SI paper) was obtained. The excess nitrous acid with neutralized with urea (1.0 g) and the mixture filtered to get a clear diazonium salt solution, which was used for the subsequent coupling reaction.



3-[4'-(3-Hydroxy-4-methyl-phenylazo)-3,3'-dimethyl-biphenyl]-4-yl]-2-methyl -3H-quinazolin-4-one

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

Reaction Scheme

Table 1 : Characterization

Dye No.	Shade on dyed fibres	R	Mol. formula	Yield %	M.P. (°C)	Found (%) (Calcd.)	
						C	N
$\mathbf{D_I}$	Yellow	(a) o-Cresol	$C_{29}H_{26}O_2N_4$	56	293	75.32 (75.20)	12.12 (12.22)
$\mathbf{D_J}$	Yellow	(b) m-Cresol	$C_{29}H_{26}O_2N_4$	66	135	75.20 (75.20)	12.12 (12.22)
$\mathbf{D_K}$	Brown	(c) p-Cresol	$C_{29}H_{26}O_2N_4$	71	185	75.32 (75.20)	12.12 (12.22)
$\mathbf{D_L}$	Green	(d) m-Cl-Phenol	$C_{29}H_{23}O_2N_4Cl$	76	>300	70.37 (70.30)	11.32 (11.30)
$\mathbf{D_M}$	Green	(e) m-Cl-Phenol	$C_{29}H_{23}O_2N_4Cl$	70	>300	70.37 (70.30)	11.32 (11.30)
$\mathbf{D_N}$	Greenish	(f) p-Cl-Phenol	$C_{29}H_{23}O_2N_4Cl$	73	200	70.37 (70.30)	11.32 (11.30)
$\mathbf{D_O}$	Yellow	(g) 1-Naphthol	$C_{33}H_{23}O_2N_4$	74	>300	77.64 (77.60)	10.98 (11.00)
$\mathbf{D_P}$	Coffee	(h) Phenol	$C_{29}H_{24}O_2N_4$	64	112	75.65 (75.59)	12.17 (12.22)

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 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 coffee crystals of compound **(D_I).** Yield 56%, m. p. 293ºC. Anal. Calcd. for $C_{29}H_{24}O_2N_4$: C, 75.32; H, 05.19; N, 12.12%.Found C, 75.20; H, 05.28; N, 12.22 %. IR : 1650 cm^{-1} due to >C = O and at 1620 cm^{-1} due to >N = N -; the absorption at 3430 cm^{-1} due to N-H and at 3257 cm^{-1} due to O-H; absorption at 701 and 765 cm^{-1} is due to mono substituted and 835 cm^{-1} due to 1, 4-disubstituted benzene ring were observed in IR spectra. The aromatic and aliphatic C – H also appear at 3035 are 2968 cm^{-1}, respectively. The absorption at 3350 cm^{-1} is due to –OH (polymeric association).

Other compounds **(D_J-D_P)** were synthesized similarly to **(D_I)**. Characterization data are presented in Table 1.

RESULTS AND DISCUSSION

All the dyes **(D_I)** to **(D_P)** were applied on nylon and polyester fibers using the reported printing procedure[7-10]. All the dyes were coffee, brown, violet, yellow to green and 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 given in Table 2.

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

Dye code	λmax (nm)	log ε	% Exhaustion		λ*max (nm)	% Fixation**	
			N	P		P	N
D_I	433	4.21	57	62	408	70	59
D_J	430	4.23	58	63	408	70	60
D_K	388	4.43	38	43	390	74	63
D_L	428	4.22	52	57	420	67	56

Cont…

Dye code	λmax (nm)	log ε	% Exhaustion		λ*max (nm)	% Fixation**	
			N	P		P	N
D_M	710	4.99	52	56	701	67	55
D_N	650	4.81	58	63	645	66	56
D_O	690	492	49	53	600	64	50
D_P	434	4.22	60	66	428	70	56

These 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 fibres 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 Code.	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_I	3-4	3-4	5	4-5	5	3	3	5	4	4	3	5	4-5	5
D_J	3-4	3	5	5	5	4	4	3	5	4	3	5	4-5	5
D_K	3	3-4	5	5	5	4	3	5	5	4	3	5	5	5
D_L	3	3	5	5	5	4	5	5	4	5	3	5	5	5
D_M	4-5	4	5	4-5	5	3	3	3	5	5	5	4	5	4-5
D_N	4	4-5	5	5	4	3	4	4	4	5	4	4	5	5
D_O	4	4-5	5	4-5	5	3	3	3	4	5	5	4	5	4-5
D_P	3	4	5	5	5	4	5	5	4	4	5	4	5	5

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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