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STUDIES ON SOME NEW DYES DERIVED FORM 2-PHENYL-3, 1-BENZOXAZINE-4-(4H)-ONE

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ABSTRACT

A series of 3 - [4' - (4 - aryalazo) - 3, 3'- dimethoxy - biphenyl – 4 - yl] – 2 – phenyl - 3H – quinazolin – 4 - one derivatives **(3)** have been obtained by a reaction of a various coupling agent **(a-o)** with diazonium salt containing 4-oxo-quinazolin moiety **(2)**. The diazonium salt **(2)** is obtained by the reaction of 4-(2-phenyl-4-oxo-3-quinazolinyl)-4'-amino-3, 3'-dimethoxydiphenyl with $NaNO_2$ and HCl. The proposed constitutions of newly synthesized molecules have been supported by elemental and spectral analysis. The products exhibit promising dyeing capabilities.

Key words : 4-Oxo-quinazolin, Diazotization, Printing.

INTRODUCTION

The 4-oxo-quinazolin nucleus is found to be present in many new dyes. The importance of this moiety is further emphasized in a large number of patents and research publictions[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]. Improvements in the structure of reactive dye chromogens and in the structure selection and number of reactive group have led to an increased use of reactive dyes[5-8]. Patel et al.[9] have synthesized 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-phenyl-3, 1-benzoxazine-4(4H)-one.

The reaction of benzoyl chloride with anthranilic acid in pyridine at 8°C gave 2 – phenyl - 3, 1 – benzoxazine – 4 (4H) - one **(1)**. The compound **(1)** on condensation with 4,

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4', - diamino - 3, 3' - dimethoxydiphenyl yielded 4 - (2 – phenyl – 4 – oxo – 3 - quinazolinyl) – 4'- amino- 3, 3'- dimethoxydiphenyl **(2)**. Compound **(2)** diazotized and coupled with different coupler **(a-o)** gives different types of dyes **(3)**. All the compound synthesized were adequately characterized by their elemental analysis and spectral data.

EXPERIMENTAL

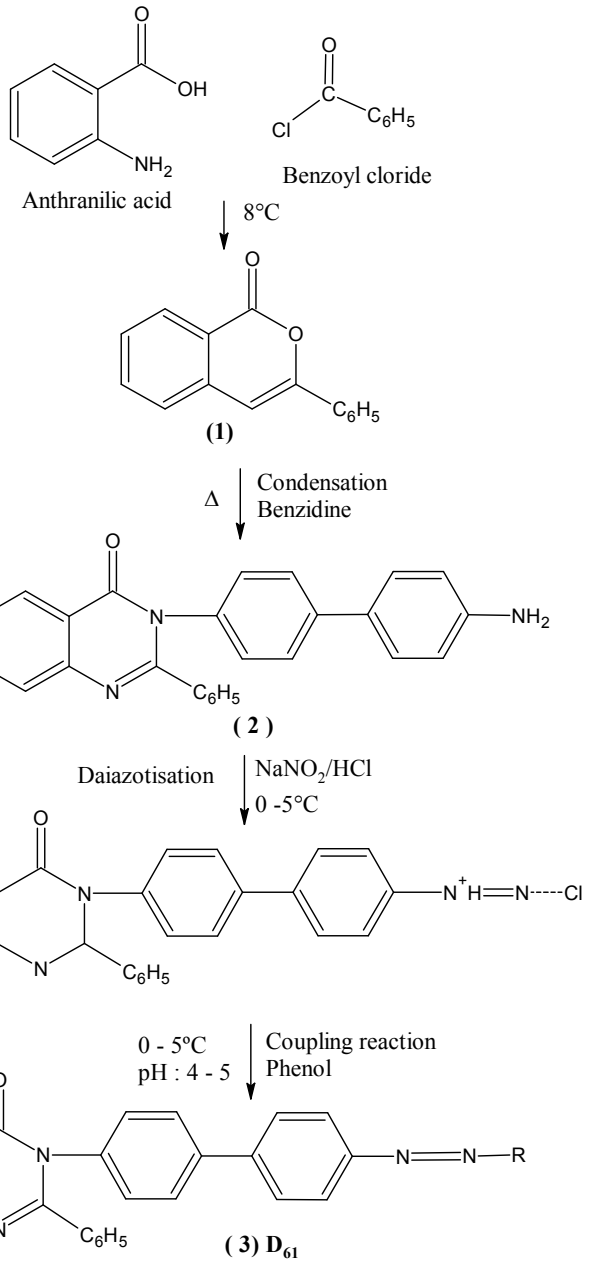
Melting points were taken in open capillaries and are uncorrected. The IR spectra of dyes D_{61} to D_{75} were recorded on Bio-Red FTS-40 spectrophotometer using KBr pellets. The purity of all dyes has been checked by thin-layer chromatography[10]. The absorption spectra of all the dyes were recorded 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-Phenyl-3, 1-benzoxazine 4(4H)-one (1)

Benzoyl chloride (140.5 g; 1M) was added dropwise to anthranilic acid (137.0 g; 1 M) dissolved in pyridine (60 mL) with constant stirring at 8^{o}C over the period of 1 hour. After the addition of benzoyl chloride, reaction mixture was stirred for half an hour at room temperature. At the end of the reaction, reaction mixture almost solidified. The solid mass was poured into cold water, filtered and washed successively with aqueous sodium bicarbonate solution (10% to remove unreacted anthranilic acid) and water. Then it is dried and recrystalised from ethanol (95%) to get compound **(1)**. Yield 84%, m. p. 118^{O}C. Anal. Calcd. for $C_{14}H_9O_2N$: C, 75.33; H, 4.03; N, 6.27. Found C, 75.35; H, 4.00; N, 6.25%.

4 - (2 – Phenyl – 4 – oxo – 3 - quinazolinyl) - 4'- amino -3, 3'- dimethoxydiphenyl. (2)

Equimolar ratio of compound **(1)** (223.0 g; 1M) and 4, 4' – diamino – 3, 3'-dimethoxydiphenyl (244.0 g; 1M) (o-Di-anisidine) 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 gray crystalline solid. It was filtered, washed with cold ethanol and recrystalised from ethanol (95%) to get compound **(2)**. Yield 71%, m. p. 90^{O}C. Anal. Calcd. for $C_{28}H_{23}O_3N_3$: C, 74.83; H, 5.12; N, 09.35. Found C, 74.85; H, 5.15; N, 09.25%.



Where R = Phenol, o-Cresol, m-Cresol, p-Cresol, o-Cl-Phenol, m-Cl-Phenol, l-Naphthol, 2-Naphthol, Salicyclic acid, Resorcinol, H-acid, J-acid, R-acid and Gama acid for D_1 to D_{15}, respectively

Scheme

3 – [4' - (4 – Hydroxy - phenylazo) – 3, 3' – dimethoxy – biphenyl -4 - yl] – 2 – phenyl - 3H – quinazolin – 4 - one (D_{61} to D_{75}) : (3)

Equimolar ratio of compound **(2)** (0.2245 g; 0.05M) was suspended in water (10.0 mL), conc. hydrochloric acid (5.0 mL; 0.025M) was added dropwise to the well stirred suspension and the solution was cooled to 0-5^{o}C 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). The excess nitrous acid was 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.

Phenol (0.188 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 orange crystals of compound **($3D_{61}$)**. Yield 79%, m. p. 87^{O}C. Anal. Calcd. for $C_{34}H_{26}O_4N_4$: C, 73.65; H, 4.69; N, 10.11.Found C, 73.63; H, 4.66; N, 10.11%. IR : 1661 cm^{-1} due to >C = O and at 1596 cm^{-1} due to – N = N –. The absorption at 3401 and 3521 cm^{-1} is due to – OH and at 705 and 760 cm^{-1} is due to mono-substituted benzene ring. The aromatic and aliphatic C–H stretching appear at 3060 cm^{-1} and 2974 cm^{-1}, respectively. The absorption at 1132 cm^{-1} is due to C – O (ether).

Other compounds **($3D_{62}$-D_{75})** were synthesized similarly from **(3)**, respectively. Characterization data are presented in Table 1.

RESULTS AND DISCUSSION

All the dyes D_{61} to D_{75} were applied on nylon and polyester fibers using the reported printing procedure[11-16]. All the dyes were coffee, brown, blue, yellow, orange 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 furnished in Table 2.

Table 1. Characterization

Dye No.	Shade on dyed fibres	R	Molecular formula	Yield (%)	M. P. (°C)	Found (%) (Calcd.)		
						C	N	S
D_{61}	Orange	(a) Phenol	$C_{34}H_{26}O_4N_4$	76	87	73.63	10.11	-
						(73.65)	(10.11)	(-)
D_{62}	Orange	(b) o-Cresol	$C_{34}H_{28}O_4N_4$	79	107	73.32	10.08	-
						(73.38)	(10.07)	(-)
D_{63}	Orange	(c) m-Cresol	$C_{34}H_{28}O_4N_4$	76	139	73.33	10.03	-
						(73.38)	(10.07)	(-)
D_{64}	Brown	(d) p-Cresol	$C_{34}H_{28}O_4N_4$	81	239	73.3	10.04	-
						(73.38)	(10.07)	(-)
D_{65}	Green	(e) o-Cl-Phenol	$C_{34}H_{25}O_4N_4Cl$	79	>300	69.33	11.85	-
						(69.32)	(11.89)	(-)
D_{66}	Green	(f) m-Cl-Phenol	$C_{34}H_{25}O_4N_4Cl$	77	>300	69.28	11.88	-
						(69.32)	(11.89)	(-)
D_{67}	Green	(g) p-Cl-Phenol	$C_{34}H_{25}O_4N_4Cl$	76	>300	69.29	11.8	-
						(69.32)	(11.89)	(-)
D_{68}	Blue	(h)1-Naphthol	$C_{38}H_{28}O_4N_4$	83	138	75.51	9.25	-
						(75.50)	(9.27)	(-)
D_{69}	Green	(i) 2-Napthol	$C_{38}H_{28}O_4N_4$	81	141	75.55	9.29	-
						(75.50)	(9.27)	(-)
D_{70}	Yellow	(j) Salicylic acid	$C_{35}H_{26}O_6N_4$	78	151	70.2	9.3	-
						(70.23)	(9.36)	(-)
D_{71}	Blue	(k) Resorcinol	$C_{34}H_{26}O_5N_4$	88	155	71.6	9.8	-
						(71.58)	(9.82)	(-)
D_{72}	Violet-red	(l) H-Acid	$C_{38}H_{27}O_{10}N_5S_2Na_2$	84	>300	55.4	8.5	7.7
						(55.41)	(8.51)	(7.78)
D_{73}	Red	(m) J-Acid	$C_{38}H_{28}O_7N_5SNa$	81	>300	63.21	9.77	4.4
						(63.25)	(9.71)	(4.44)
D_{74}	Violet-black	(n) R-Acid	$C_{38}H_{27}O_9N_5S_2Na_2$	79	>300	56.55	8.68	7.9
						(56.51)	(8.67)	(7.93)
D_{75}	Violet	(o) Gama-Acid	$C_{38}H_{28}O_5N_5SNa$	87	>300	63.22	9.71	4.48
						(63.25)	(9.71)	(4.44)

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

Dye No.	λ_{max} (nm)	log Σ	% Exhaustion		λ^*_{max} (nm)	% Fixation**	
			N	P		P	N
D_{61}	480	4.30	72	70	482	74	70
D_{62}	492	4.35	65	60	495	80	74
D_{63}	520	4.15	70	65	525	78	76
D_{64}	500	4.10	76	72	506	80	77
D_{65}	550	4.55	68	60	560	72	70
D_{66}	570	4.60	69	62	575	70	69
D_{67}	600	4.73	70	66	602	74	71
D_{68}	395	4.36	52	50	398	80	75
D_{69}	473	4.38	65	62	475	79	72
D_{70}	392	4.38	63	60	392	69	63
D_{71}	485	4.60	55	52	489	76	71
D_{72}	525	4.36	70	65	528	80	73
D_{73}	540	4.22	50	47	542	72	68
D_{74}	548	4.30	55	50	554	74	70
D_{75}	550	4.36	57	52	560	75	70

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

Table 3. Evaluation of fastness propeties of dyed nylon and polyester patterns with dyes (N = Nylon, P = Polyester)

Dye No	Light fastness		Wash fastness		Rubbing fastness				Perspiration fastness				Sublimation fastness	
					Dry		Wet		Acidic		Alkaline			
	N	P	N	P	N	P	N	P	N	P	N	P	N	P
D_{61}	3-4	4	5	5	5	4	5	4	5	4	5	4	5	5
D_{62}	4	3	5	4	5	5	5	5	4	5	4	5	4	5
D_{63}	3	3	4	5	4	5	4	5	5	5	5	5	5	5
D_{64}	3	3	4	5	4	4	4	4	5	5	5	5	5	4
D_{65}	3	3	4	4	4	4	4	4	5	5	5	5	5	5
D_{66}	4	4	5	5	4	5	4	5	4	4	4	4	5	5
D_{67}	4	4	5	5	5	5	5	5	5	5	5	5	4	5
D_{68}	2-3	3	5	5	5	5	5	5	5	5	5	5	5	5
D_{69}	3	3	5	5	5	4	5	5	5	4	5	5	4	5
D_{70}	3	4	4	5	4	5	4	5	4	5	5	5	4	5
D_{71}	3	3	5	4	5	5	5	5	5	5	4	5	4	5
D_{72}	2-3	3	5	5	5	5	5	5	4	5	5	4	5	5
D_{73}	3	2-3	5	5	4	5	5	5	5	5	5	5	5	5
D_{74}	3	3	4	5	5	4	4	5	4	5	4	5	4	5
D_{75}	3	3	5	4	4	5	4	5	4	5	4	5	5	5

The 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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