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STUDIES ON SYNHESIS OF SULFONE DYES AND THEIR APPLICATION ON VARIOUS FIBRES

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ABSTRACT

A series of 3-{4-[4-(4-aryalazo)-benzenesulfonyl]-phenyl}-2-phenyl-3H-quinazolin-4-one derivatives **(3)** have been obtained by a reaction of a various coupling agents 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'-aminodiphenylsulfone 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 : 4-Oxo-quinazolin, Diazotization, Dyeing, Sulphone dyes.

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[1-3.]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[5-7.]Patel et al.[8] 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.

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The reaction of benzoyl chloride with anthranilic acid in pyridine at 8^{o}C gave 2 – phenyl - 3, 1 – benzoxazine – 4 (4H) - one **(1)**. The compound **(1)** on condensation with 4, 4’ - diaminodiphenylsulfone yielded 4 - (2 – phenyl – 4 – oxo – 3 - quinazolinyl) - 4’ - aminodiphenylsulfone **(2)**. Compound **(2)** diazotized and coupled with different coupler **(a-o)** gives different types of dyes **(3)**. The entire compounds synthesized were adequately characterized by their elemental analysis and spectral data.

EXPERIMENTAL

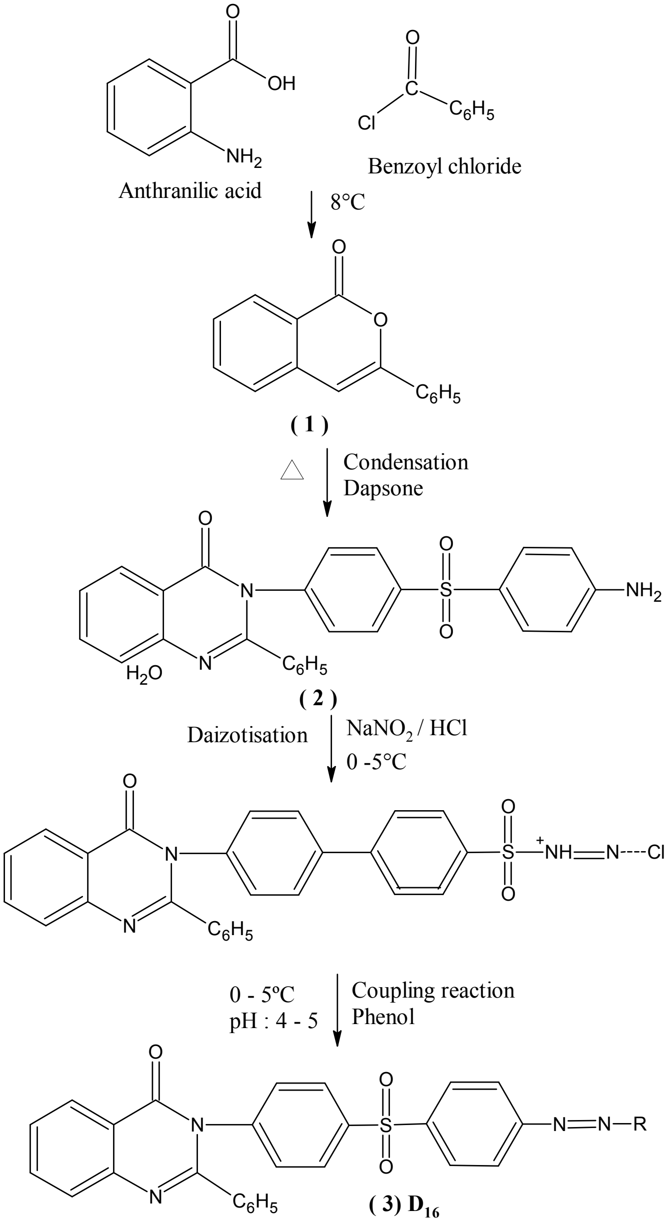
Melting points were taken in open capillaries and are uncorrected. The IR spectra of dyes D_{16} to D_{30} were recorded on Bio-Red FTS-40 spectrophotometer using KBr pellets. The purity of all dyes has been checked by thin-layer chromatography[9]. The absorption spectra of all the dyes were recorded 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; 1M) 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 was almost solidified. The solid mass was poured into cold water, filtered, washed successively with aqueous sodium bicarbonate solution (10% to remove unreacted anthranilic acid) and water, 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’ – aminodiphenylsulfone (2)

Equimolar ratio of compound **(1)** (223.0 g; 1M) and 4, 4’-diaminodiphenylsulfone (248.0 g; 1M) (Dapson) 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 yellowish-white crystalline solid. It was filtered, washed with cold ethanol and recrystalised from ethanol (95%) to get compound **(2)**. Yield 69%, m. p. 110^{O}C. Anal. Calcd. for $C_{26}H_{19}O_3N_3S$: C, 68.87; S, 7.06; N, 9.43.Found C, 68.84; S, 7.01; N, 9.44%.



Where R = Phenol, o-Cresol, m-Cresol, p-Cresol, o-Cl-Phenol, m-Cl-Phenol, I-Naphthol, 2-Naphthol, Salicyclic acid, Resorcinol, H-acid, J-acid, R-acid and Gama acid for D_{16} to D_{30}, respectively

Scheme

3 – { 4 - [4 - (4 – Hydrocxy - phenylazo) – benzenesulfonyl] – phenyl } – 2 – phenyl - 3H – quinazolin – 4 - one (D_{16} to D_{30}) (3)

Equimolar ratio of compound **(2)** (0.2265 g; 0.05 M) was suspended in water (10.0 mL), conc. hydrochloric acid (5.0 mL; 0.025 M) was added dropwise to the well stirred suspension and the solution was cooled to 0-5ºC in an ice bath. A solution of sodium nitrite (5.0ml; 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; 0.05 M) was dissolved in sodium hydroxide solution (15.0 mL; 5% W/V) and the solution was cooled to 0–5^{0}C, in an ice-bath. To this well-stirred solution, the above mentioned diazo solution was then gradually added in 1 hr. at 0–5^{0}C 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 0-5^{0}C 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 **($3D_{16}$)**. Yield 75%, m. p. 219^{O}C. Anal. Calcd. for $C_{32}H_{22}O_4N_4S$: C, 68.82; S, 5.73; N, 10.04.Found C, 68.80; S, 5.70; N, 10.00%. IR : 1648 cm^{-1} due to >C = O and at 1586 cm^{-1} due to –N = N –. The absorption at 704 and 758 cm^{-1} is due to mono substituted and at 846 cm^{-1} is due to 1, 4-disubstituted benzene ring. The aromatic and aliphatic C-H appear at 3034 cm^{-1} and 2924 cm^{-1} respectively. The absorption at 1144 cm^{-1} is due to S=O of sulfone. The absorption at 3380 cm^{-1} is due to – OH (polymeric association).

Other compounds **($3D_{17}$-D_{30})** were synthesized similarly from **(3)**, respectively. Characterization data are presented in Table 1.

RESULTS AND DISCUSSION

All the dyes D_{16} to D_{30} were applied on nylon and polyester fibers using the reported procedure[10-13.]All the dyes were orange-yellow-red-green-violet to coffee 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. (ºC)	Found (%) (Calcd.)		
						C	N	S
D_{16}	Orange	(a) Phenol	$C_{32}H_{22}O_4N_4S$	75	219	68.8 (68.82)	10 (10.04)	5.7 (5.73)
D_{17}	Crimson red	(b) o-Cresol	$C_{33}H_{24}O_4N_4S$	73	191	68.59 (68.57)	9.99 (10.00)	5.65 (5.71)
D_{18}	Orange	(c) m-Cresol	$C_{33}H_{24}O_4N_4S$	77	109	68.51 (68.57)	9.98 (10.00)	5.66 (5.71)
D_{19}	Pale Yellow	(d) p-Cresol	$C_{33}H_{24}O_4N_4S$	78	179	68.51 (68.57)	10.03 (10.00)	5.61 (5.71)
D_{20}	Green	(e) o-Cl-Phenol	$C_{32}H_{21}O_4N_4SCl$	75	>300	64.76 (64.81)	9.41 (9.45)	5.31 (5.40)
D_{21}	Green	(f) m-Cl-Phenol	$C_{32}H_{21}O_4N_4SCl$	77	>300	64.77 (64.81)	9.37 (9.45)	5.31 (5.40)
D_{22}	Green	(g)p-Cl-Phenol	$C_{32}H_{21}O_4N_4SCl$	74	>300	64.75 (64.81)	9.4 (9.45)	5.33 (5.40)
D_{23}	Coffee	(h)1-Naphthol	$C_{36}H_{24}O_4N_4S$	81	127	71.01 (71.05)	9.16 (9.21)	5.18 (5.26)
D_{24}	Orange	(i) 2-Napthol	$C_{36}H_{24}O_4N_4S$	84	133	71.07 (71.05)	9.17 (9.21)	5.19 (5.26)
D_{25}	Yellow	(j) Salicylic acid	$C_{33}H_{22}O_6N_4S$	74	194	65.72 (65.72)	9.21 (9.30)	5.32 (5.31)
D_{26}	Light Orange	(k) Resorcinol	$C_{32}H_{22}O_5N_4S$	85	>300	66.81 (66.90)	9.71 (9.76)	5.5 (5.57)
D_{27}	Radish	(l) H-Acid	$C_{36}H_{23}O_{10}N_5S_3Na_2$	81	>300	52.18 (52.24)	8.44 (8.46)	11.65 (11.60)
D_{28}	Light Violet	(m) J-Acid	$C_{36}H_{24}O_7N_5S_2Na$	84	>300	59.52 (59.59)	9.59 (9.66)	8.8 (8.83)
D_{29}	Light Violet	(n) R-Acid	$C_{36}H_{23}O_9N_5S_3Na_2$	87	>300	53.19 (53.27)	8.65 (8.63)	11.8 (11.84)
D_{30}	Radish	(o) Gama-Acid	$C_{36}H_{24}O_7N_5S_2Na$	83	>300	59.53 (59.59)	9.6 (9.66)	8.82 (8.83)

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

Dye No.	λ_{max}	Log Σ	% Exhaustion		λ_{max}	% Fixation	
	(nm)		N	P	(nm)	P	N
D_{16}	471	4.15	55	51	457	71	69
D_{17}	535	4.24	60	57	540	79	75
D_{18}	498	4.50	68	65	500	75	71
D_{19}	483	4.27	62	55	485	84	79
D_{20}	555	4.55	68	60	560	72	70
D_{21}	570	4.60	69	62	575	70	69
D_{22}	600	4.73	70	66	602	74	71
D_{23}	463	4.46	68	65	468	72	65
D_{24}	492	4.13	68	62	496	78	70
D_{25}	499	4.27	64	61	504	65	62
D_{26}	483	4.58	60	55	488	75	70
D_{27}	482	4.27	51	48	486	73	69
D_{28}	540	4.70	70	66	552	75	66
D_{29}	543	4.49	60	64	549	65	62
D_{30}	535	4.24	60	57	540	79	75

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	
	N	P	N	P	Dry		Wet		Acidic		Alkaline		N	P
					N	P	N	P	N	P	N	P		
D_{16}	3	3-4	4	5	5	5	5	5	5	5	4	5	5	5
D_{17}	4-5	4-5	5	5	4	5	4	5	5	5	4	5	5	5
D_{18}	3-4	3-4	5	4	5	5	5	5	5	4	5	5	4	5
D_{19}	3	3	5	5	4	5	4	4	5	5	5	5	4	4
D_{20}	4	4-5	5	4	5	5	5	5	4	5	5	5	5	5
D_{21}	4	3-4	4	5	4	5	4	4	5	4	4	5	4	5
D_{22}	3	3-4	5	5	4	5	4	5	4	5	4	5	5	5
D_{23}	4-5	4-5	4	5	5	5	5	5	5	5	4	5	5	5
D_{24}	4-5	4-5	5	5	5	5	5	5	4	5	5	5	5	5
D_{25}	4	4-5	4	5	5	5	4	5	5	5	5	5	4	5
D_{26}	3	3-4	5	4	4	5	4	5	4	5	5	5	5	5
D_{27}	3	3	5	5	4	5	5	5	5	5	5	5	5	5
D_{28}	3-4	3-4	4	5	5	5	4	4	5	5	5	5	4	4
D_{29}	3	3	5	4	5	5	5	5	5	5	5	4	5	5
D_{30}	3-4	3-4	4	5	5	5	4	4	5	5	5	5	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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