

Studies on synthesis of 2-methyl-3,1-benzoxazine-4(4H)-one dyes and their application on nylon and polyester fibres

H. D. Navadiya^a, N. K. Undavia^{a*} and B. S. Patwa^b

^aDepartment of Chemistry, ^bDepartment of Industrial Chemistry, Sir P. P. Institute of Science, Bhavnagar University, Bhavnagar-364 002, Gujarat, India

E-mail : dr.navadiya@yahoo.com

Manuscript received 15 December 2008, accepted 3 July 2009

Abstract : A series of 3-{4-[4-(4-aryloxy)-benzenesulfonyl]phenyl}-2-methyl-3H-quinazolin-4-one derivatives (3) have been obtained by a reaction of a various coupling agent (a-g) 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)-4'-aminodiphenylsulfone with NaNO₂ and HCl. The product is characterized by spectral and analytical data. Most of the tested compounds show promising dyeing properties.

Keywords : 4-Oxo-quinazolin, diazotization, dyeing.

Introduction

The wide variety of 4-oxo-quinazolin derivatives are a major group of dyes and have attained a commercial status¹. The use of the dyestuff makes possible the highest degree of fastness to washing, abrasion, etc. Improvements in the structure of reactive dye chromogens and in the structure selection and number of reactive groups have led to an increased use of reactive dyes².

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 *N*-acetyl anthranilic acid with acetic anhydride gave 2-methyl-3,1-benzoxazine-4(4H)-one (1). The compound 1 on condensation with 4,4'-diaminodiphenylsulfone yielded 4-(2-methyl-4-oxo-3-quinazolinyl)-4'-aminodiphenylsulfone (2). Compound 2 diazotized and coupled with different coupling agents to (a-g) give 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 D₁₆ to D₂₃ were recorded on Bio-Red FTS-40 spectrophotometer using KBr pellets. The purity of all dyes has been checked by thin-layer chromatography³. The absorption spectra of all the dyes were recorded on Beckmann DB-GT Grafting spec-

trophotometer. 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 min and the white solid separated on cooling was filtered and washed thoroughly with dry petroleum ether to get compound 1. Yield 84%, m.p. 118 °C (Found : C, 67.10; H, 4.32; N, 8.10. Calcd. for C₉H₇O₂N : C, 67.10; H, 4.35; N, 8.10%).

4-(2-Methyl-4-oxo-3-quinazolinyl)-4'-aminodiphenylsulfone (2) : Equimolar ratio of compound 1 (161.0 g; 1 M) and 4,4'-diaminodiphenylsulfone (248.0 g; 1 M) (dapsone) 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 yellowish-white crystalline solid. It was filtered, washed with cold ethanol and recrystallised from ethanol (95%) to get compound 2. Yield 69%, m.p. 110 °C (Found : C, 64.42; S, 8.14; N, 10.72. Calcd. for C₂₁H₁₇O₃N₃S : C, 64.45; S, 8.15; N, 10.74%).

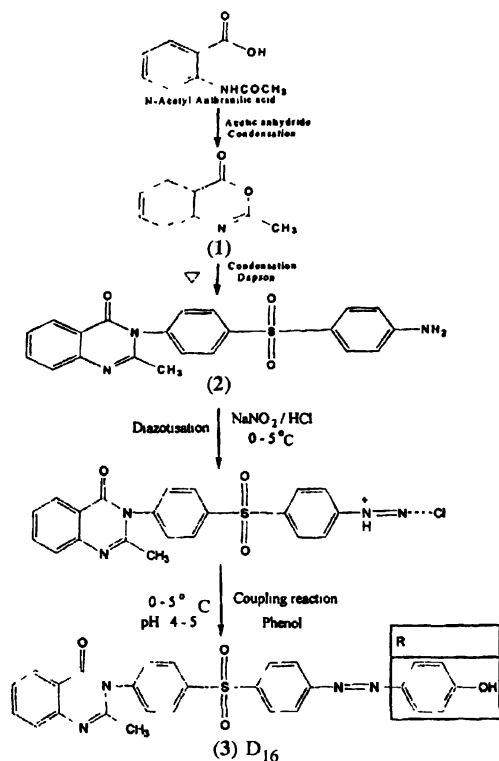
3-{4-[4-(4-Hydroxy-phenylazo)benzenesulfonyl]-phenyl}-2-methyl-3H-quinazolin-4-one (D₁₆ to D₂₃) (3) : Compound 2 (0.248 g; 0.05 M) was suspended in water

(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 0–5 °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 was 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 °C, in an ice-bath. To this well-stirred solution, the above mentioned diazo solution was then gradually added in 1 h at 0–5 °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 h at 0–5 °C until all the diazo salt was consumed (spot test with alkaline phenol solution). After being stirred for further 2 h 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 (3D₁₆). Yield 75%, m.p. 219 °C (Found : C, 53.20; S, 6.40; N, 11.25. Calcd. for C₂₇H₂₀O₄N₄S : C, 53.22; S, 6.45; N, 11.29%); 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 (3D₁₇-D₂₃) were synthesized similarly from 3, respectively. Characterization data are presented in Table 1.



where, R = phenol, *o*-cresol, *m*-cresol, *p*-cresol, *o*-Cl-phenol, *m*-Cl-phenol, *p*-Cl-phenol, 1-naphthol

Table 1. Characterization

Dye no.	Shade on dyed fibres	R	Molecular formula	Yield (%)	M.p. (°C)	Analysis (%) : Found (Calcd.)		
						C	N	S
D ₁₆	Orange	(a) Phenol	C ₂₇ H ₂₀ O ₄ N ₄ S	75	219	53.22 (53.20)	11.29 (11.25)	6.45 (6.40)
D ₁₇	Creamson red	(b) <i>o</i> -Cresol	C ₂₈ H ₂₂ O ₄ N ₄ S	73	191	67.46 (67.45)	11.24 (11.23)	6.42 (6.40)
D ₁₈	Orange	(c) <i>m</i> -Cresol	C ₂₈ H ₂₂ O ₄ N ₄ S	77	109	67.46 (67.45)	11.24 (11.23)	6.42 (6.40)
D ₁₉	Pale yellow	(d) <i>p</i> -Cresol	C ₂₈ H ₂₂ O ₄ N ₄ S	78	179	67.46 (67.45)	11.24 (11.23)	6.42 (6.40)
D ₂₀	Green	(e) <i>o</i> -Cl-Phenol	C ₂₇ H ₁₉ O ₄ N ₄ SCl	75	> 300	61.07 (61.05)	10.55 (10.51)	6.03 (6.00)
D ₂₁	Green	(f) <i>m</i> -Cl-Phenol	C ₂₇ H ₁₉ O ₄ N ₄ SCl	77	> 300	61.07 (61.05)	10.55 (10.51)	6.03 (6.00)
D ₂₂	Green	(g) <i>p</i> -Cl-Phenol	C ₂₇ H ₁₉ O ₄ N ₄ SCl	74	> 300	61.07 (61.05)	10.55 (10.51)	6.03 (6.00)
D ₂₃	Coffee	(h) 1-Naphthol	C ₃₁ H ₂₂ O ₄ N ₄ S	81	127	68.13 (68.10)	10.25 (10.20)	5.86 (5.85)

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

Dye no.	λ_{\max} (nm)	log Σ	Exhaustion (%)		λ_{\max}^* (nm)	Fixation (%)**	
			N	P		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

Table 3. Evaluation of fastness properties 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	3-5	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

Results and discussion

All the dyes D₁₆ to D₂₃ were applied on nylon and polyester fibres using the reported procedure⁴. 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. The data reveals 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.

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.

Acknowledgement

The authors are grateful to Dr. D. R. Korat, Principal, Sir P. P. Institute of Science, Bhavnagar University, Bhavnagar for providing necessary research facilities. Authors are also thankful to Professor Dr. S. B. Mehta, Head, Department of Chemistry, Bhavnagar University, Bhavnagar and Color Tax - Dyeing and Printing Industry, Surat to help and encouragement during the study.

References

1. ICI, Eur. Pat. Appl. EP. 225, 1987, 730; G. Jones, "The Quinolines", Wiley Interscience, London, 1977, 318; CIBA, Eur. Pat. Appl. ER. 775, 1997, 730.
2. A. H. M. Renfew and J. A. Taylor, *Rev. Prog. Col.*, 1990, 20, 1; M. H. Hahnke, *Textilveredlung*, 1986, 21, 285; S. Abeta, T. Yoshida and A. Imada, *Am. Dyestuff Rept.*, 1984, 73, 26.
3. Fried Bernard and Sherma Joseph, "Thin Layer Chromatography Technique and Applications", Marcel Dekker, Inc, New York and Basel, 1982.
4. C. K. Whittaker and C. C. Wilcock, "Dyeing with Coal Tar for Dyestuffs", London, 1952; F. Sadovkorchagin and A. Maketsky, "Chemical Technology of Fibrous Material", Mir Publication, Moscow, 1973; V. A. Sheni, "Chemistry of Dyes and Principles of Dyeing", Sevak Publication, Mumbai, 1973; E. R. Trotman, "Dyeing and Chemical Technology of Textile Fabrics", London, 1970, pp. 333-334, 590.