

Synthesis and Spectral Studies of Some Novel Coumarin Based Disperse Azo Dyes

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Abstract. Synthesis of some novel coumarin based azo dyes was carried out by diazotization of heterocyclic amines using nitrosyl sulphuric acid and then coupling them with 7-hydroxy-4-methyl Coumarin. The synthesized dyes when applied on polyester fibers showed moderate to good light fastness and very good to excellent fastness to washing, rubbing, perspiration and sublimation.

Keywords: disperse azo dyes, coumarin-based-azo dyes, heterocyclic amines

Introduction

Azo dyes are the most widely used class of the dyes due to their versatile application in various fields such as the dyeing of textile fibers, coloring of plastics and advanced applications in the organic synthesis. Many patents and papers describing the synthesis and dyeing properties of azo compounds have been previously presented (Huang, 2008; Zhi-Gang *et al.*, 2009; Ramazan *et al.*, 2007; Alaa *et al.*, 2006; Filkret *et al.*, 2006; Saeed *et al.*, 1988).

Coumarin (2H-1-benzopyran-2-one) and its derivatives occur widely in nature. Many natural and synthetic derivatives of coumarin have been used in various applications in chemistry, biology, medicine and physics (Mach *et al.*, 1972), including additives in food and cosmetics, optical brightening agents as well as dispersed fluorescent and laser dyes (Christie, 1993; Christie and Lui 1999; Christie and Lui 2000; Siegrist *et al.*, 1991; Harold *et al.*, 1994; Ayyangar *et al.*, 1991; Griffiths and Miller, 1995; Dai and Wu, 1999). Coumarin compounds have attracted great interest in recent years in the field of optoelectronic materials (Avramenbo *et al.*, 1996; El-Ansary *et al.*, 1998; Vijayan, 1998). Due to the lactone skeleton, coumarins produce stronger fluorescence than open chain analogs (Davendra *et al.*, 2008; Fan, 2001). Their strong fluorescence is also closely associated with charge transfer configuration arising from electron transfer from the styryl to the carbonyloxy group (Hinohara *et al.*, 1981). Hue and fluorescence properties of coumarins can be affected strongly by substituting different groups at the 3- or 7-position (Wheelock, 1959). Initially these dyes were developed for

colouring synthetic fibers such as polyester; subsequently, its use extended to include daylight fluorescent pigments and functional applications such as dye lasers, solar collector systems, organic light emitting diodes (LED) and numerous biological applications. A few comparable investigations have been made using coumarin based dyes.

In the present work, synthesis of ten heteroaryl azo coumarin dyes **Da-Dj** has been reported through diazotization of heterocyclic amines using nitrosyl sulphuric acid and then coupling them with 7-hydroxy-4-methyl coumarin. Synthesized dyes were characterized using different elemental techniques and were assessed for their fastness properties using polyester fiber. The dye structures are shown in Scheme 1.

Materials and Methods

All the chemicals used in the synthesis were obtained from Sigma-Aldrich and Acros Organics and were used without further purification. Melting points were taken on a Gallenkemp melting point apparatus and are uncorrected. Elemental analysis was performed on Perkin Elmer CHNS Analyser. IR spectra were recorded on Shimadzu FTIR 8400, mass spectra on Jeol D-3000 Spectrometer and UV absorption spectra on Cecil 2000 UV-VIS spectrometer. ¹H-NMR spectra were recorded on Bruker AC-300MHz and chemical shifts were reported in ppm relative to Me₄Si as internal standard.

Synthesis of 7-hydroxy-4-methyl coumarin. Sixteen gram of poly- phosphoric acid was added to a solution of 1.1g (0.1mol) of resorcinol in 13g (0.1 mol) of ethyl acetoacetate. The mixture was stirred and heated at 75-80 °C for about

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20 min and then poured into ice-water. The pale yellow solid was collected by suction filtration, washed with cold water and dried at 60 °C. The yield of 7-hydroxy-4-methyl coumarin was 1.8 g (89%). The compound was recrystallised using ethanol. Its m.p. was found to be 185 °C.

Synthesis of nitrosyl sulphuric acid. Nitrosyl sulphuric acid was prepared by mixing sodium nitrite (1g), conc. sulphuric acid (7 ml) at 70 °C for 6-7 h. It was further stirred for an additional 1 h at 0 °C.

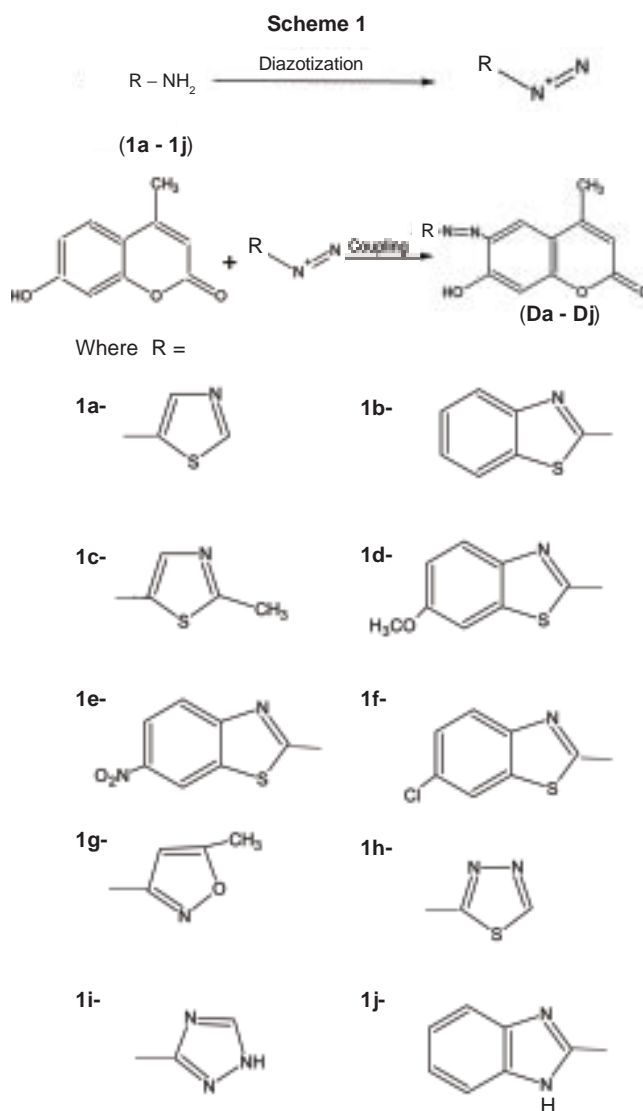
Diazotization of heterocyclic amine (2-amino thiazole). Diazotization of heterocyclic amine (2-amino thiazole) was carried out with nitrosyl sulphuric acid. The procedure for diazotization of 2-amino thiazole (**1a**) was given as follows:

2-amino thiazole (2m mol) was dissolved in hot glacial acetic acid (2.5 ml) and then shifted to an ice bath temperature maintained between 0 to -5 °C. The liquor was then added in portions to cold solution of nitrosyl sulphuric acid in span of 30 min.

Coupling. After completion of diazotization, the azo liquor was slowly added to the vigorously stirred solution of 7-hydroxy-4-methyl coumarin (2m mol) in sodium carbonate solution made by dissolving 2m mol of Na₂CO₃ in 2 ml water. Sodium carbonate was added in portions periodically to maintain the pH of the reaction mixture at 7-8. Stirring was continued for about 1 h maintaining the temperature at 0 to 5 °C and pH at 7-8. The reaction was monitored by TLC using hexan-ethylacetate (1:1) as the solvent mixture. After completion of the reaction, the resulting dye was filtered, washed with cold water and dried in a hot air oven. Recrystallization was carried out using the same hexan-ethylacetate (1:1) mixture. Yield of the dye **Da** was 72 %.

Synthesis of dyes Db-Dj. The same procedure was repeated as described above for synthesis of **1a** but using different amines i.e. **1b-1j** to get the dyes **Db-Dj**. Physical and analytical data of the synthesized dyes are given in Table 1.

Dyeing of polyester fabrics using dyes Da-Dj. A paste of dye (35 mg), dispersing agent (Dodamol 75 mg) and 3-4 drops of the wetting agent (1% Tween-80) was prepared by mixing all the compounds in mortar and pestle. To this mixture, water (100 ml) was added while stirring till dispersion of the dye was achieved. The pH of the solution was maintained at 7-8 by adding sodium carbonate. Dyeing of polyester was carried out at 115 °C for 90 min. The dyed fabric was then treated with a solution of detergent (0.2 g) and Na₂CO₃ (0.1g) in 200 ml of water at 60 °C for 30 min. Later, the fabric was washed several times with water to remove any attached dye and then dried.



Fastness properties of synthesized dyes. Light fastness, wash fastness, fastness to rubbing, perspiration and sublimation of dyes on polyester fabric was determined after dyeing pieces of fabric with all the synthesized dyes (**Da-Dj**), using standard test methods as adopted by Hari *et al.* (2002). Results obtained are shown in Table 2.

Results and Discussion

Dyes **Da-Dj** were synthesized by coupling 7-hydroxy-4-methylcoumarin with diazotized heterocyclic amines (**1a-1j**) in nitrosyl sulphuric acid. Characteristics of the resultant dyes **Da-Dj** are given in Table 1. The dyes were applied to the polyester fiber at a 2% shade. All the dyes gave good coloration of polyester from bright yellow to deep brown hues (Table 2). All the dyes tested showed good to very good light fastness properties except **Da, Db and Dj**. Washing and

Table 1. Physical and analytical data of the synthesized dyes

Dye	Molecular formula	Mol.Wt	Yield (%)	M.P(°C)	Absorption maximum (λ_{\max} /nm)	Exhaustion (%)
Da	C ₁₃ H ₁₁ N ₃ O ₃ S	289.301	72	142	421	77
Db	C ₁₇ H ₁₃ N ₃ O ₃ S	339.368	71	125-126	426	70
Dc	C ₁₄ H ₁₃ N ₃ O ₃ S	303.336	67	234-235	359	77
Dd	C ₁₈ H ₁₅ N ₃ O ₄ S	369.394	73	138	470	73
De	C ₁₇ H ₁₂ N ₄ O ₅ S	384.365	71	153-154	481	81
Df	C ₁₇ H ₁₂ ClN ₃ O ₃ S	373.813	76	211	462	67
Dg	C ₁₄ H ₁₃ N ₃ O ₄	287.270	74	167	413	71
Dh	C ₁₂ H ₁₀ N ₄ O ₃ S	290.297	69	171	419	80
Di	C ₁₂ H ₁₁ N ₅ O ₃	273.243	77	232-233	353	78
Dj	C ₁₇ H ₁₄ N ₄ O ₃	322.318	74	128	355	85

Table 2. Fastness characteristics (score) of the synthesized dyes

Dye	Colour of the dyed fabric	Light fastness	Wash fastness	Rubbing fastness	Perspiration fastness	Sublimation fastness
Da	Orange	4-5	4	4	4	3-4
Db	Orange	4-5	4	4	4	4-5
Dc	Bright yellow	3-4	4	4	4	4
Dd	Reddish brown	4-5	4	3-4	4	3
De	Reddish brown	3	4	4-5	4	4-5
Df	Bright yellow	4	4	5	4	3-4
Dg	Yellowish orange	4-5	4	4-5	4	3
Dh	Yellowish orange	4	4	4-5	4	4-5
Di	Yellow	3-4	3	4	4	3-4
Dj	Yellow	3	4	4	4	4

Table 3. Elemental composition of the synthesized dyes

Dye	C		H		N		O		S	
	Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)
Da	53.98	53.86	3.83	3.81	14.52	14.48	16.58	16.51	11.10	11.03
Db	60.16	60.09	3.86	3.78	12.39	12.32	14.15	14.09	9.44	9.38
Dc	55.42	55.41	4.34	4.31	13.84	13.82	15.86	15.78	10.51	10.47
Dd	58.52	58.48	4.09	4.06	11.38	11.29	17.33	17.28	8.68	8.61
De	53.12	53.09	3.15	3.11	14.57	14.52	20.80	20.79	8.34	8.28
Df	54.62	54.55	3.24	3.18	11.24	11.18	12.84	12.77	8.58	8.49
Dg	58.52	58.50	4.55	4.47	14.62	14.59	22.28	22.21	-	-
Dh	49.65	49.61	3.47	3.44	19.31	19.28	16.52	16.48	11.05	10.98
Di	52.75	52.66	4.06	4.01	25.63	25.60	17.57	17.51	-	-
Dj	63.35	63.22	4.38	4.33	17.38	17.29	14.89	14.77	-	-

Table 4. Structural characterization of the synthesized dyes

Dye	Spectral data
Da	IR (cm ⁻¹ KBr) 1591 (C=C), 1698 (C=O) ¹ H NMR (DMSO-d ⁶) 6.32 (s, 1H, -OH), 3.39-3.83 (m, 2H, Ar-H), 4.31-4.52 (m, 2H, Ar-H), 1.96 (s, 3H, -CH ₃) Molecular ion peak (m/z) = 289.012
Db	IR (cm ⁻¹ KBr) 11665 (C=C), 1688 (C=O) ¹ H NMR (DMSO-d ⁶) 5.14 (s, 1H, -OH), 7.50-7.67 (m, 2H, Ar-H), 7.83-8.19 (m, 2H, Ar-H), 2.03 (s, 3H, -CH ₃) Molecular ion peak (m/z) = 337.918
Dc	IR (cm ⁻¹ KBr) 1599 (C=C), 1699 (C=O) ¹ H NMR (DMSO-d ⁶) 6.34 (s, 1H, -OH), 7.53-8.47 (m, 2H, Ar-H), 7.79-8.10 (m, 2H, Ar-H), 2.51 (s, 3H, -CH ₃) Molecular ion peak (m/z) = 301.325
Dd	IR (cm ⁻¹ KBr) 1601 (C=C), 1698 (C=O) ¹ H NMR (DMSO-d ⁶) 6.12 (s, 1H, -OH), 7.06-7.47 (m, 2H, Ar-H), 7.88-8.14 (m, 2H, Ar-H), 3.75 (s, 3H, -CH ₃) Molecular ion peak (m/z) = 367.881
De	IR (cm ⁻¹ KBr) 1593 (C=C), 1698 (C=O) ¹ H NMR (DMSO-d ⁶) 6.12 (s, 1H, -OH), 7.36-7.87 (m, 2H, Ar-H), 8.08-8.34 (m, 2H, Ar-H), 2.47 (s, 3H, -CH ₃) Molecular ion peak (m/z) = 383.301
Df	IR (cm ⁻¹ KBr) 1691 (C=C), 1699 (C=O) ¹ H NMR (DMSO-d ⁶) 7.12 (s, 1H, -OH), 7.14-7.38 (m, 2H, Ar-H), 7.46-8.14 (m, 2H, Ar-H), 2.19 (s, 3H, -CH ₃) Molecular ion peak (m/z) = 371.015
Dg	IR (cm ⁻¹ KBr) 1599 (C=C), 1698 (C=O) ¹ H NMR (DMSO-d ⁶) 6.92 (s, 1H, -OH), 7.48-7.68 (m, 2H, Ar-H), 7.86-8.04 (m, 2H, Ar-H), 1.96 (s, 3H, -CH ₃) Molecular ion peak (m/z) = 285.124
Dh	IR (cm ⁻¹ KBr) 1585 (C=C), 1698 (C=O) ¹ H NMR (DMSO-d ⁶) 6.22 (s, 1H, -OH), 7.45-7.68 (m, 2H, Ar-H), 7.96-8.04 (m, 2H, Ar-H), 2.49 (s, 3H, -CH ₃) Molecular ion peak (m/z) = 289.195
Di	IR (cm ⁻¹ KBr) 1695 (C=C), 1698 (C=O), 3567 (N-H) ¹ H NMR (DMSO-d ⁶) 6.81 (s, 1H, -OH), 7.65-7.82 (m, 2H, Ar-H), 7.96-8.04 (m, 2H, Ar-H), 3.99 (s, 3H, -CH ₃) Molecular ion peak (m/z) = 273.011
Dj	IR (cm ⁻¹ KBr) 3146 (NH), 1699 (C=O) ¹ H NMR (DMSO-d ⁶) 6.81 (s, 1H, -OH), 3.82-4.30 (m, 2H, Ar-H), 4.52-5.67 (m, 2H, Ar-H), 2.17 (s, 3H, -CH ₃) Molecular ion peak (m/z) = 321.129

rubbing fastness properties were good to excellent and perspiration and sublimation fastness properties were excellent.

Spectrophotometric properties of the prepared monoazo disperse dye stuffs were determined and the absorption maxima of these dyes and their intensities were obtained (Table 1).

The structure and the purity of the prepared dyes (**Da-Dj**) were confirmed by elemental analysis, UV-VIS. absorption spectra, FT-IR, ¹H-NMR, and MS. The structural analysis of the dyes is presented in Table 3&4. IR spectra showed typical aromatic absorption. IR spectra of the dyes showed absorption band at 1550-1575 cm⁻¹ (-N=N- group), 1700 cm⁻¹ (-C=O group). The ¹H-NMR chemical shift data and M⁺ values were in consistent with the structure of dye.

Conclusion

The present investigation explores the suitability of coumarin based monoazo dispersed dyes for dyeing polyester. The optical and dyeing properties, light fastness, wash fastness and sublimation fastness of synthesized dye stuffs were proved to be reasonable good.

Thus, it may be concluded that the hydroxy coumarin related compounds could be used as reasonably good monoazo disperse dyes with all round dyeing properties for polyester fabrics.

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