

Synthesis and dyeing characteristics of 3-arylaazo-8-nitro-2,4-disubstituted-pyrimido[1,2-*a*]benzimidazoles

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Nine monoazo disperse dyes, 3-arylaazo-8-nitro-2,4-dioxo- and 2,4-bis(morpholino/piperidino)-pyrimido[1,2-*a*]benzimidazoles, and three monoazo disperse reactive dyes, 3-arylaazo-2,4-dichloro-8-nitropyrimido[1,2-*a*]benzimidazoles were prepared and their dyeing performance on polyester and polyamide was assessed. The dyeings on polyester had yellow shades with low pick-up, moderate light fastness and good sublimation fastness and the dyeings on polyamide had orange shades with low pick-up and moderate light fastness.

Keywords: Azo disperse dyes, Azo disperse reactive dyes, Dyeing, Polyamide, Polyester, Pyrimido[1,2-*a*]benzimidazoles

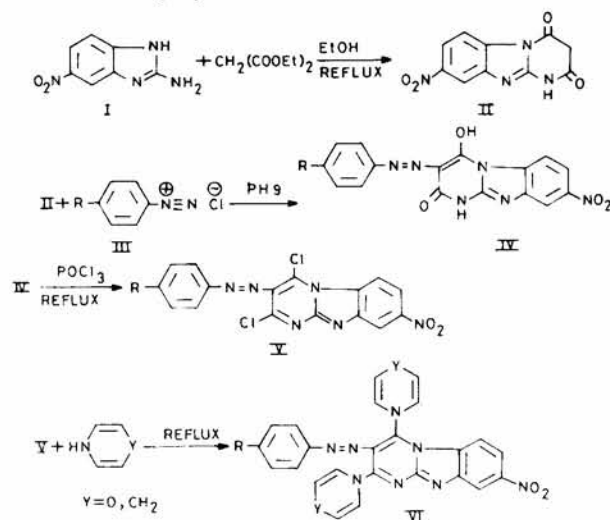
1 Introduction

In recent years, many fused heterocyclic systems have been used in the synthesis of azo dyes. The compact structure and extension of conjugation present in fused heterocyclic systems are valuable for the dyes in their application to synthetic fibres. We have recently reported the incorporation of novel fused heterocycles, such as fused quinoxalines¹⁻⁴, pyrazolotriazoles⁵ and pyrimido[1,2-*a*] benzimidazoles⁶⁻⁹, in the synthesis of disperse dyes and fluorescent brighteners and their application to polyester. The synthesis and application of azo disperse dyes, derived from pyridine¹⁰, naphthalimide¹¹, quinoxaline¹², coumarin¹³ and benzo [*b*] thiophene¹⁴, and of azo disperse reactive dyes derived from pyridine¹⁵ and pyrimidine¹⁶ have been reported earlier. In the present study, monoazo disperse dyes and disperse reactive dyes have been synthesized using pyrimido[1,2-*a*] benzimidazole and their spectral properties and dyeing performance on polyester and polyamide have been examined.

2 Materials and Methods

2-Amino-5-nitrobenzimidazole (**I**), prepared by the reported method¹⁷, was condensed with diethylmalonate in refluxing ethanol to get 8-nitro-2,4-dioxypyrimido[1,2-*a*] benzimidazole (**II**) in excellent yield (92%). The coupling component **II** was coupled with aryldiazonium salts (**III**) derived from *p*-toluidine, *p*-anisidine and *p*-nitroaniline in

weakly alkaline conditions to get 3-arylaazo-8-nitro-2,4-dioxypyrimido[1,2-*a*] benzimidazoles (**IV**). These 3-arylaazo-2,4-dioxo dyes (**IV**) were refluxed with excess phosphorus oxychloride to get 3-arylaazo-2,4-dichloro-8-nitropyrimido[1,2-*a*] benzimidazoles (**V**). The 3-arylaazo-2,4-dichloro dyes (**V**) were reacted with refluxing morpholine/piperidine to get 3-arylaazo-2,4-bis(morpholino/piperidino)-8-nitropyrimido[1,2-*a*] benzimidazoles (**VI**).



2.1 Preparation of 8-nitro-2,4-dioxypyrimido[1,2-*a*] benzimidazole (**II**)

Diethylmalonate (16.0 g, 0.1 mol) was added to 2-amino-5-nitrobenzimidazole (**I**, 17.8 g, 0.1 mol)

dissolved in ethanol (50 ml) and the mixture was refluxed until the reaction was complete (2h, monitored by TLC). The reaction mixture was cooled to room temperature and the separated solid was filtered, washed with ethanol, dried and recrystallized from formic acid-water to give **II** as pale yellow crystals (22.6 g, 92%) m.p. $> 300^{\circ}\text{C}$ (Found: C, 48.3; H, 2.3; N, 22.7%. $\text{C}_{10}\text{H}_6\text{N}_4\text{O}_4$ requires C, 48.8; H, 2.4; and N, 22.8%).

2.2 Preparation of 3-arylazo-8-nitro-2, 4-dioxypyrimido [1, 2-*a*] benzimidazoles (IV)

A mixture of arylamine (0.02 mol), conc. hydrochloric acid (12 ml, 30% solution) and water (8 ml) was heated on a water-bath to obtain a clear solution. To this solution, cooled at $0-5^{\circ}\text{C}$, sodium nitrite (1.45 g, 0.021 mol) dissolved in water (10 ml) was added in 30 min with stirring. The mixture was stirred for 1 h and the excess nitrous acid was removed by the addition of urea (0.2 g) and the mixture was filtered to get a clear diazo solution. This aryldiazonium salt solution was gradually added to a fine suspension of **II** (4.92 g, 0.02 mol) in sodium carbonate solution (300 ml, 30%) at $0-5^{\circ}\text{C}$ in 30 min, maintaining the pH at 9 during coupling. The stirring was continued until the aryldiazonium salt solution was consumed (4-5 h, spot test with alkaline

H-acid solution). The mixture was neutralized with dil. hydrochloric acid (10% solution) and the separated dye was filtered, washed with water, dried and recrystallized from ethanol (Table 1).

2.3 Preparation of 3-arylazo-2, 4-dichloro-8-nitropyrimido [1, 2-*a*] benzimidazoles (V)

A mixture of dye **IV** (0.02 mol) and phosphorus oxychloride (40 ml, 0.43 mol) was gently refluxed until the reaction was complete (8 h, monitored by TLC). Most of the excess phosphorus oxychloride was vacuum distilled and the remaining mixture (about 10 ml) was added to crushed ice (about 300 g) with vigorous stirring. The separated dye was filtered, washed with water, dried and recrystallized from benzene (Table 1).

2.4 Preparation of 3-arylazo-2, 4-bis(morpholino/piperidino)-8-nitropyrimido [1, 2-*a*] benzimidazoles (VI)

A mixture of dye **V** (0.01 mol) and morpholine (10 ml) or piperidine (10 ml) was refluxed until the reaction was complete (3 h, monitored by TLC). The mixture was cooled to room temperature and added to crushed ice (about 50 g). The separated dye was filtered, washed with water, dried and recrystallized from ethanol (Table 1).

Table 1 – Physical data of 3-arylazo-8-nitro-2,4-disubstituted pyrimido[1,2-*a*]benzimidazoles (IV-VI)

Compd ^a	R	Y	Colour	Yield %	m.p. ^b °C	λ_{max} nm	log ϵ	Molecular formula
IVa	CH ₃	—	Yellow	83	> 300	416	3.97	C ₁₇ H ₁₂ N ₆ O ₄
IVb	OCH ₃	—	Yellow	86	> 300	418	4.01	C ₁₇ H ₁₂ N ₆ O ₅
IVc	NO ₂	—	Yellow	88	> 300	420	4.17	C ₁₆ H ₉ N ₇ O ₆
Va	CH ₃	—	Red	72	181	450	3.94	C ₁₇ H ₁₀ N ₆ O ₂ Cl ₂
Vb	OCH ₃	—	Red	76	145	448	3.99	C ₁₇ H ₁₀ N ₆ O ₃ Cl ₂
Vc	NO ₂	—	Red	81	192	458	3.98	C ₁₆ H ₇ N ₇ O ₄ Cl ₂
VIa	CH ₃	O	Yellow	74	141	404	4.09	C ₂₅ H ₂₆ N ₈ O ₄
VIb	CH ₃	CH ₂	Yellow	62	149	408	4.10	C ₂₇ H ₂₀ N ₈ O ₂
VIc	OCH ₃	O	Brownish yellow	69	171	412	4.12	C ₂₅ H ₂₆ N ₈ O ₅
VIId	OCH ₃	CH ₂	Brownish yellow	63	164	408	4.10	C ₂₇ H ₃₀ N ₈ O ₃
VIe	NO ₂	O	Brownish yellow	72	139	408	4.14	C ₂₄ H ₂₃ N ₉ O ₆
VIIf	NO ₂	CH ₂	Brownish yellow	66	128	412	4.12	C ₂₆ H ₂₇ N ₉ O ₄

^a All compounds gave satisfactory elemental analyses.

^b Melting points are uncorrected.

Table 2 – Fastness properties of 3-aryazo-8-nitro-2,4-disubstituted pyrimido[1,2-*a*]benzimidazoles (IV-VI)

Dye	Shade	Pick-up	Light fastness	Sublimation fastness
IVa	Lemon yellow (PE)	1	3	4
IVb	Lemon yellow (PE)	1	4	4
IVc	Lemon yellow (PE)	1	4	4
Va	Orange (PA)	1	3	—
Vb	Orange (PA)	2	4	—
Vc	Orange (PA)	1	3	—
VIa	Yellow (PE)	1	3	4
VIb	Yellow (PE)	1	3	4
VIc	Yellow (PE)	1	3	4
VI d	Yellow (PE)	1	4	4
VIe	Yellow (PE)	1	3	3
VI f	Yellow (PE)	1	4	4

PE – Polyester; and PA – Polyamide.

3 Results and Discussion

Table 1 shows that the yield of various 3-arylazo-8-nitro-2, 4-dioxypyrimido [1, 2-*a*] benzimidazoles (IV) was excellent (84-88%) and that these dyes were yellow in colour. The yield of 3-arylazo-2, 4-dichloro-8-nitropyrimido [1, 2-*a*] benzimidazoles (V) was very good (72-81%) and these dyes were red in colour. The yield of 3-arylazo-2, 4-bis (morpholino/piperidino)-8-nitropyrimido [1, 2-*a*] benzimidazoles (VI) was good (62-74%) and these were yellow and brownish yellow in colour.

The absorption spectral data of IV and VI, recorded in DMF, are given in Table 1. The absorption maxima of these dyes were in the range of 404-458 nm. The values of logarithm of extinction coefficient ($\log \epsilon$) varied from 3.94 to 4.14. A bathochromic shift was observed in the absorption maxima of V as compared to IV and a hypsochromic shift was observed in the absorption maxima of VI as compared to V.

The dyes IV and VI were applied on polyester as disperse dyes and dyes V were applied on po-

lyamide as disperse reactive dyes. The disperse dyes IV and VI gave lemon yellow shade and yellow shade respectively on polyester whereas the disperse reactive dyes V gave orange shade on polyamide (Table 2). The pick-up of these dyes was low (1) except for the dye Vb, which showed moderate pick-up (2). The light fastness of these dyes was moderate (3-4). The sublimation fastness of the dyes IV and VI was very good (4) except for the dye VIe which showed moderate (3) sublimation fastness.

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References

- Rangnekar D W & Phadke R C, *J Chem Technol Biotechnol*, 36 (1986) 230.
- Rangnekar D W & Tagdiwala P V, *Dyes Pigm*, 7 (1986) 445.
- Rangnekar D W & Tagdiwala P V, *Indian J Chem*, 25B (1986) 1057.
- Rangnekar D W & Phadke R C, *Dyes Pigm*, 10 (1989) 159.
- Rangnekar D W & Tagdiwala P V, *Dyes Pigm*, 7 (1986) 289.
- Rangnekar D W & Rajadhyaksha D D, *J Chem Technol Biotechnol*, 36 (1986) 300.
- Rangnekar D W & Rajadhyaksha D D, *Dyes Pigm*, 7 (1986) 365.
- Rangnekar D W & Rajadhyaksha D D, *Indian J Chem*, 26B (1987) 143.
- Rangnekar D W & Dhamnaskar S V, *Dyes Pigm*, 9 (1988) 467.
- Kanhere J M & Rangnekar D W, *Indian J Text Res*, 13 (1988) 213.
- Lokhande S B & Rangnekar D W, *Indian J Technol*, 25 (1987) 122.
- Tagdiwala P V & Rangnekar D W, *Dyes Pigm*, 8 (1987) 151.
- Lokhande S B & Rangnekar D W, *Indian J Chem*, 25B (1986) 638.
- Rangnekar D W & Sabnis R W, *Dyes Pigm*, 10 (1989) 295.
- Rangnekar D W & Parekh R R, *Dyes Pigm*, 9 (1988) 475.
- Rangnekar D W & Parekh R R, *Dyes Pigm*, 8 (1987) 475.
- Berg S S & Parnell E W, *J Chem Soc*, (1961) 5275.