



## **COUMARIN BASED MONOAZO DISPERSE DYES AND THEIR DYEING APPLICATION ON POLYESTER FIBER**

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### **ABSTRACT**

Various azo disperse dyes (D<sub>a</sub>-D<sub>o</sub>) of the type 3-{{4-(2-amino-4, 5-dihydro-1, 3-thiazol-4-yl) phenoxy} acetyl}-2H-chromen-2-one were synthesized by using 3-acetylcoumarin, thiourea and p-hydroxy acetophenone by diazotization and coupling with various substituted aminobenzene derivatives. Dyeing properties of these dyes on polyester fiber were assessed. These dyes were characterized by elemental analysis and IR spectra.

**Key words:** Coumarin, Dye, Disperse, Dyeing, Polyester fiber.

### **INTRODUCTION**

It has been known fact that coumarin and substituted coumarins have been widely used heterocyclics for different synthetic approaches. Coumarin derivatives have played an important role in textile chemistry too and subsequently they have emerged as one of the widely used chromophor used to prepare some fluorescent brighteners and synthetic heterocyclic dyes<sup>1-4</sup>. The coumarin ring system substituted by some heterocyclic residue and electron attracting substituents are characterized by their high light stability, which is the interest of our work. The main approach of our work was to synthesise the disperse dyes consisting coumarin<sup>5-12</sup> and some substituted heterocycles<sup>13</sup> with azo substituent, which has been further utilised to dye some hydrophobic fibers. The characteristic data of different molecules were studied and further applied on polyester fibers to study their light, wash and sublimation fastness.

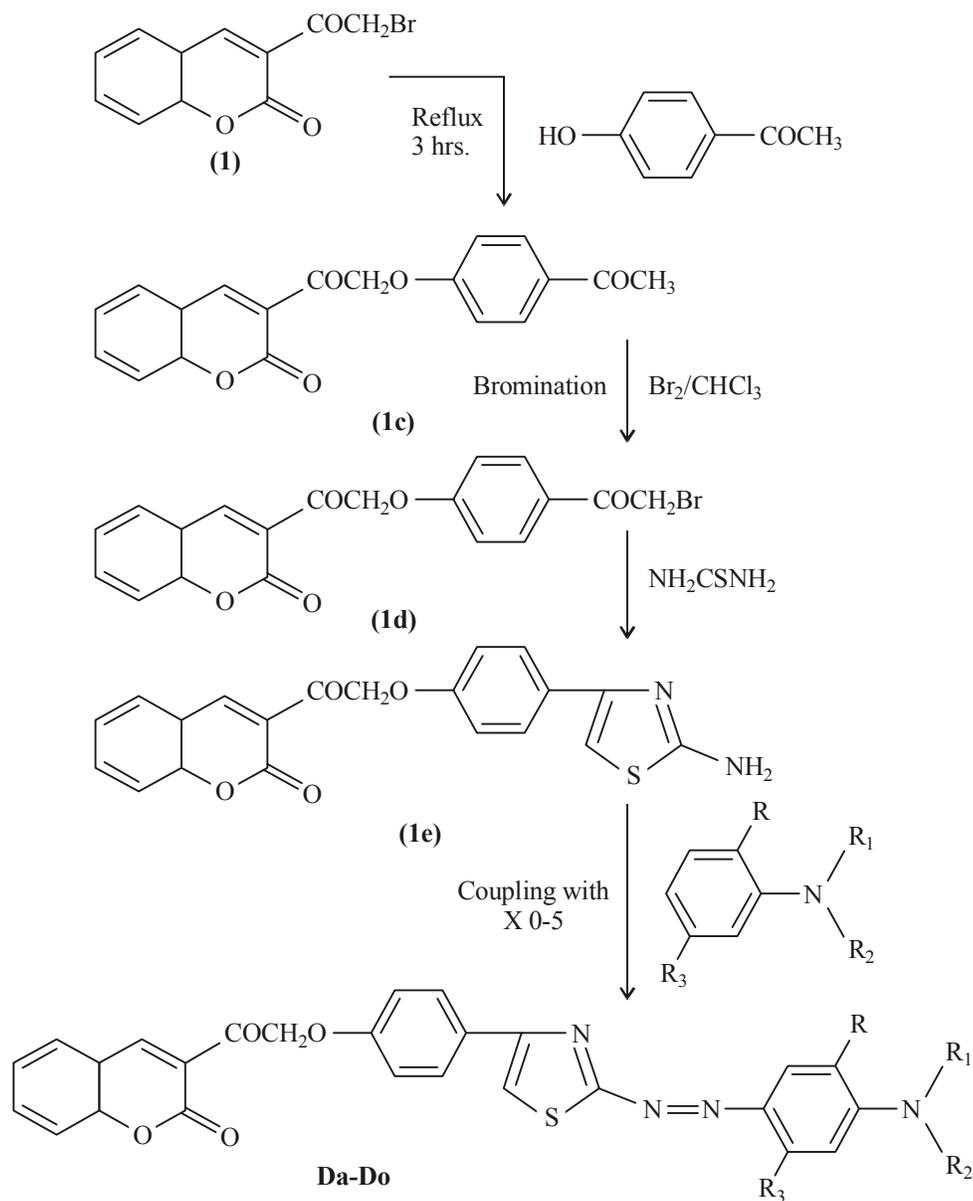
### **EXPERIMENTAL**

3-Bromoacetylcoumarin (**1**) was synthesized by the literature methods<sup>14</sup>.

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## Scheme



**Preparation of 3-[(4-acetylphenoxy) acetyl]-2H-chromen-2-one (1c)**

In a 250 mL round bottom flask, 3-bromoacetyl coumarin (2.67 g, 0.01 mole) in methanol (30 mL) was treated with p-hydroxyacetophenone (1.36 g, 0.01 moles) and this mixture was heated for 4 hours at 80°C temp. in water bath. Reaction mixture was then poured into ice water. The solid was filtered, dried and recrystallised from methanol. Yield: 65% M.P.: 128°C.

**Preparation of 3-[[4-(bromoacetyl) phenoxy] acetyl]-2H-chromen-2-one (1d)**

In a 250 mL round bottom flask, 3-[(4-acetylphenoxy) acetyl]-2H-chromen-2-one (3.22 g, 0.01 mole) in CHCl<sub>3</sub> (15 mL) and bromine (1.7 g) in CHCl<sub>3</sub>, (6 mL) was added dropwise with shaking below 5°C. The mixture was heated for 15 minutes on a water-bath to remove most of the HBr. It was then poured into ice water. The solid was filtered, dried and recrystallised from acetic acid. Yield: 60%, M.P.: 162°C.

**Preparation of 3-[[4-(2-amino-1, 3-thiazol-4-yl) phenoxy] acetyl]-2H-chromen-2-one (1e)**

In a 250 mL round bottom flask, 3-[[4-(bromoacetyl) phenoxy] acetyl]-2H-chromen-2-one (4.01g, 0.01 mole) in ethanol (30 mL) was treated with thiourea (0.76 g 0.01mole). A clear solution was obtained, which soon gave some crystals. After that, sodium acetate in water was added and refluxed for 4 hours. Reaction mixture was then poured into ice water. The solid was filtered, dried and recrystallised from ethanol. Yield: 62%, M.P.: 202°C.

**Dyeing procedure**

The dyeing of the polyester fabric samples was carried out by HTHP dyeing method<sup>15</sup>.

**RESULTS AND DISCUSSION**

Structures of the new synthetic azo disperse dyes were characterized by means of elemental analysis and IR spectra. For example Dye **D<sub>i</sub>** shows —C=N stretching vibration near 1495—1485 cm<sup>-1</sup>, C—O—C stretching at 1005 cm<sup>-1</sup>, =C—S stretching at 715 cm<sup>-1</sup>, —N=N—stretching at 1640 cm<sup>-1</sup>; C—Cl stretching vibration at 770 cm<sup>-1</sup>, —C=O stretching at 1683 cm<sup>-1</sup> and O—H stretching at 3640—3300 cm<sup>-1</sup>. All the dyes have good substantivity for polyester fibre. Table 2 shows moderate to fairly good light fastness. However, compounds **D<sub>c</sub>**, **D<sub>g</sub>** and **D<sub>h</sub>** show some what better light fastness. This may be due to the

presence of an additional acceptor substituent such as cyano group, which results into increasing electron mobility in these compounds and thus into good light-fastness.

The wash-fastness of all the compounds, as may be anticipated on the basis of their increased molecular weight and polarity to less substituted analogues, was also of an acceptably very good order. Introducing  $\beta$ -hydroxyethyl group at the terminal amino group for better dispersibility does not give any notable change in the percentage exhaustion. Overall, the prepared dyes gave generally satisfactory dyeing on polyester fibres.

**Table 1: Yield, melting points and elemental analysis of monoazo disperse dyes**

Dye No.	Coupling component (x)				Yield (%)	Nitrogen (%)	
	R	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>		Found	Calcd.
D <sub>a</sub>	H	CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>3</sub>	58	9.50	9.58
D <sub>b</sub>	OCH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	NHCOCH <sub>3</sub>	62	10.93	10.95
D <sub>c</sub>	H	CH <sub>2</sub> CH <sub>2</sub> CN	CH <sub>2</sub> CH <sub>2</sub> CN	H	70	14.20	14.28
D <sub>d</sub>	OCH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	NHCOCH <sub>3</sub>	78	11.05	11.19
D <sub>e</sub>	H	CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>2</sub> CH <sub>2</sub> OH	H	72	9.75	9.82
D <sub>f</sub>	OCH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>2</sub> CH <sub>2</sub> OH	NHCOCH <sub>3</sub>	81	10.20	10.43
D <sub>g</sub>	H	CH <sub>2</sub> CH <sub>2</sub> CN	CH <sub>2</sub> CH <sub>2</sub> CN	NHCOCH <sub>3</sub>	68	15.02	15.18
D <sub>h</sub>	H	CH <sub>2</sub> CH <sub>2</sub> CN	CH <sub>2</sub> CH <sub>2</sub> CN	CH <sub>3</sub>	64	13.88	13.94
D <sub>i</sub>	H	CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>2</sub> CH <sub>2</sub> OH	Cl	70	9.24	9.26
D <sub>j</sub>	H	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>3</sub>	63	9.81	9.85
D <sub>k</sub>	H	CH <sub>2</sub> CH <sub>2</sub> CN	CH <sub>2</sub> CH <sub>2</sub> OH	NHCOCH <sub>3</sub>	74	13.02	13.20
D <sub>l</sub>	H	CH <sub>2</sub> CH <sub>2</sub> OCOCH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> OCOCH <sub>3</sub>	NHCOCH <sub>3</sub>	72	9.79	9.84
D <sub>m</sub>	H	CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>2</sub> CH <sub>2</sub> OH	NHCOCH <sub>3</sub>	65	11.08	11.14
D <sub>n</sub>	H	CH <sub>2</sub> CH <sub>2</sub> CN	CH <sub>2</sub> CH <sub>2</sub> OCOCH <sub>3</sub>	NHCOCH <sub>3</sub>	77	12.28	12.38
D <sub>o</sub>	H	CH <sub>2</sub> CH <sub>2</sub> OCOCH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> OCOCH <sub>3</sub>	Cl	78	9.25	9.26

**Table 2: K/S, R<sub>f</sub> value,  $\lambda_{\text{max}}$ , shade and fastness properties of the disperse dyes**

Dye No.	Shade on polyester	$\lambda_{\text{max}}$ (nm)	R <sub>f</sub> (Value)	Fastness to		Sublimation		K/S Value	R Value
				Light	Washing	Staining of cotton	Staining of polyester		
D <sub>a</sub>	Corn silk	520	0.83	5	5	5	5	2.20	16.1
D <sub>b</sub>	Misty rose	548	0.75	5	5	5	5	3.01	12.5
D <sub>c</sub>	Gold orange	481	0.80	5	5	5	5	7.07	7.45
D <sub>d</sub>	Reddish brown	515	0.73	5	5	5	5	4.40	9.7
D <sub>e</sub>	Reddish orange	519	0.70	4-5	4	5	5	5.43	8.6
D <sub>f</sub>	Purple	558	0.78	5	5	5	5	3.57	10.8
D <sub>g</sub>	Dark pink	526	0.82	5	5	5	5	3.47	11.2
D <sub>h</sub>	Light orange	488	0.79	5	5	5	5	3.92	10.1
D <sub>i</sub>	Red	524	0.75	4-5	4-5	5	5	5.85	8.3
D <sub>j</sub>	Dark red	510	0.73	4-5	3-4	5	5	8.96	4.95
D <sub>k</sub>	Violet red	522	0.70	5	5	5	5	3.44	11.4
D <sub>l</sub>	Light pink	512	0.78	5	5	5	5	1.88	18.0
D <sub>m</sub>	Purple	550	0.83	5	5	5	5	1.42	23.7
D <sub>n</sub>	pink	520	0.77	5	5	5	5	2.00	17.4
D <sub>o</sub>	Dark orange	495	0.81	5	5	5	5	5.98	8.1

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