

Synthesis of Monoazo Reactive Dyes Based on 2-(3'-Chlorostyryl)-6-Amino-4-Oxoquinazoline System and Their Application

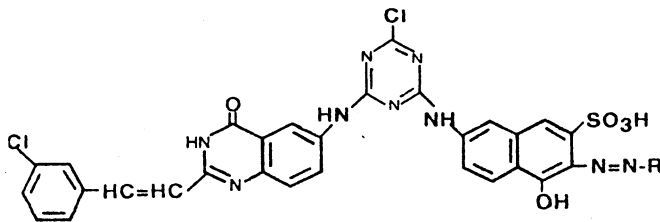
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2-(1'-Hydroxy naphthyl-3'-monosulphonic acid-6'-yl-amino)-4-(2''-meta-chloro-styryl-4''-oxoquinazoline-6''-yl-amino)-6-chloro-S-triazine used as coupling component was synthesised by treatment of 2-(1'-hydroxy naphthyl-3'-monosulphonic acid-6'-yl-amino)-4,6-dichloro-S-triazine with 2-(3'-chloro-styryl)-6-amino-4-oxoquinazoline was coupled with diazo solutions of various amines to give 2-(1'-hydroxy-2'-azo-naphthyl-3' monosulphonic acid-6'-yl-amino)-4-(2''-meta-chloro-styryl-4''-oxoquinazoline-6''-yl-amino)-6-chloro-S-triazine. Coupling component was prepared by dissolving a mixture of J-acid and cyanuric chloride. Dyeing properties of these dyes on cotton, wool and silk were assessed. A study of the fastness of dyed patterns showed that dyes had good light fastness, good to excellent fastness to washing and rubbing and very good to excellent exhaustion.

INTRODUCTION

The utility of quinazoline derivatives^{1,2} for the production of some commercial dyes and pigments useful both to natural and manmade fibres has been known. The synthesis of styryl quinazoline dyes has previously been described³. In view of the encouraging results we report here the synthesis and dyeing properties of monoazo reactive dyes based on 2-(3'-chloro-styryl)-6-amino-4-oxoquinazoline system which has the following general structure.



Where, *R* = Various Coupling Components.

EXPERIMENTAL

2-(1'-Hydroxy naphthyl-3'-monosulphonic acid-6'-yl-amino)-4,6-dichloro-S-triazine

Cyanuric chloride (1.84 g, 0.01 mol) and J-acid (2.39 g, 0.01 mol) in acetone (30 mL) was stirred around 0–5°C for 2 h, at neutral pH. The solution was obtained used for subsequent coupling reaction.

2-(1'-Hydroxy-naphthyl-3'-monosulphonic acid-6'-yl-amino)-4-(2''-meta-chloro-styryl-4''-oxoquinazoline-6''-yl-amino)-6-chloro-S-triazine

2-(3'-Chloro-styryl)-6-amino-4-oxoquinazoline (2.97 g, 0.01 mol) dissolved in acetone (30 mL) was stirred for 2 h. After this time a suspension solution of 2-(1'-hydroxy-naphthyl-3'-monosulphonic acid-6'-yl-amino)-4-6-dichloro-S-triazine was added at 25°C. The temperature was then gradually raised to 45°C and the mixture was stirred for 12 h maintaining the pH 7–8. The reaction mixture was poured on crushed ice, filtered, washed with water, dried and crystallised. Yield 85%.

TABLE-1
ANALYTICAL AND PHYSICAL DATA

Dye No.	Diazo Component (R)	Yield (%)	m.p (°C)	Nitrogen %	
				Found	Required
D ₁	Aniline	84	285	16.73	16.76
D ₂	<i>o</i> -Toluidine	82	296(d)	16.41	16.44
D ₃	<i>m</i> -Toluidine	85	>300(d)	16.42	16.44
D ₄	<i>p</i> -Toluidine	86	298(d)	16.41	16.44
D ₅	<i>m</i> -Chloroaniline	88	280	16.00	16.02
D ₆	<i>p</i> -Chloroaniline	89	285	16.01	16.02
D ₇	<i>o</i> -Nitroaniline	83	>300(d)	17.55	17.57
D ₈	<i>m</i> -Nitroaniline	81	>300(d)	17.54	17.57
D ₉	<i>p</i> -Nitroaniline	80	>300(d)	17.55	17.57
D ₁₀	<i>o</i> -Dianisidine	83	>300(d)	15.47	15.50
D ₁₁	<i>o</i> -chloro- <i>p</i> -nitroaniline	85	295	16.82	16.84
D ₁₂	<i>p</i> -Nitro- <i>o</i> -toluidine	79	292	17.24	17.26
D ₁₃	2,5-Dichloroaniline	80	282	15.32	15.35

Diazotisation of aniline: Aniline (0.093 g, 0.01 mol) was diazotised in the usual manner to get diazo solution⁴.

Coupling of diazo solution with 2-(1'-hydroxy-naphthyl-3'-monosulphonic acid-6'-yl-amino)-4-(2''-meta-chloro-styryl-4''-oxoquinazoline-6''-yl-amino)-6-chloro-S-triazine.

2-(1'-Hydroxy-naphthyl-3'-monosulphonic acid-6'-yl-amino)-4-(2''-meta-chloro-styryl-4''-oxoquinazoline-6''-yl-amino)-6-chloro-S-triazine (6.16 g, 0.01 mol) was suspended in acetone (30 mL). The solution was cooled to 0–5°C in an ice-bath and

stirred for 1 h. To this well stirred solution, the above mentioned diazo solution was added gradually in 1 h at 0–5°C, maintaining pH at 7.0. The mixture was stirred for 5 h. The reaction mixture was poured on crushed ice. The dye was isolated, dried and purified by dissolving in a minimum amount of DMF. Yield 84%.

Application

2% Shade on Cotton, Wool and Silk: Materials and conditions of the experiment are given in Table-2

TABLE-2

S.No	Material/condition	
1	Fabric	2 g
2	Dye solution under study (mL, 0.1% w/v)	40
3	pH	3
4	MLR	1 : 40
5	Dyeing time (min)	60 min
6	Dyeing temperature (°C)	80–85°C
7	Total volume of dye bath (mL)	80 mL

The dye-bath (40 mL; 0.1% w/v) with MLR 1 : 40 was adjusted to pH 3 by dilute acetic acid. The sample of fabric was introduced in a dye-bath at room temperature and the temperature was slowly raised to 80–85°C in 20 min. The fabric was worked up in dye-bath for 1 h. The dyeing was terminated by removing the fabric from dye-bath and stirring it in water (50 mL). The fabric was then removed, squeezed and rinsed with water (100 mL) and resqueezed.

Determination of λ_{\max} : Absorption maxima of the dyes were determined in water at 28°C using Bausch and Lomb spectronic-20-spectrophotometer. The results are shown in Table-3.

TABLE-3

Dye No.	Colour	λ_{\max}	R_f Value	% Exhaustion		
				Cotton	Wool	Silk
D ₁	Light khakhi	465	0.62	78	72	70
D ₂	Red orange	505	0.68	76	70	72
D ₃	Red orange	515	0.71	72	68	75
D ₄	Red orange	509	0.74	75	76	68
D ₅	Light orange	385	0.69	68	70	73
D ₆	Light orange	390	0.67	62	65	69
D ₇	Dark red	407	0.72	71	70	74
D ₈	Dark red	414	0.77	67	73	76
D ₉	Dark red	420	0.66	70	67	78
D ₁₀	Dark violet	565	0.79	64	69	71
D ₁₁	Light brown	480	0.73	66	71	79
D ₁₂	Light orange	495	0.75	75	78	68
D ₁₃	Orange	530	0.71	73	75	72

Exhaustion study: The percentage exhaustion study of dyes was performed using the standard procedure. The results are given in Table-3.

The IR spectra (cm^{-1}) (KBr) of the dyes contained characteristic bands at 3450–3380 ν (free —OH), 1610–1605 ν (—N=N—), 855 ν (C_3N_3), 3310–3300 ν (2° amine), 3015 ν (—CH=CH—), 1620 ν (C=N), 1780 ν (C=O), 755 ν (C—Cl), 2980 ν (NH).

NMR spectra of dye D₉ recorded in DMSO- d_6 on FT NMR Hitachi R-600 using TMS as internal standard (chemical shifts in δ ppm) showed signals at δ 5.85 (—NH), 10.4 (—CONH), 5.70 (—OH), 5.3 (—CH=CH—), 6.8 (—Ph—NO₂), 8.0–6.5 (Ar-protons), 8.5 (quinazoline heterocyclic).

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