



## STUDIES ON SYNTHESIS AND APPLICATION OF STILBENE DYES

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### ABSTRACT

A series of 4-(2-phenyl-4-oxo-3-quinazoliny)-[4'-(4-aryalazo)-phenyl]-stilbene-2, 2'-disulfonic acid derivatives (**3**) have been obtained by reaction of various coupling agents (**a-o**) with diazonium salt containing 4-oxo-quinazolin moiety (**2**). The diazonium salt (**2**) is obtained by the reaction of 4-(2-phenyl-4-oxo-3-quinazoliny)-4'-aminostilbene-2, 2'-disulfonic acid with NaNO<sub>2</sub> and HCl. The newly synthesized molecules have been characterized by spectral and analytical techniques. The synthesized molecule exhibit good dyeing characteristics.

**Key words** : Stilbene dyes, Diazotization, Dyeing.

### INTRODUCTION

In the list of new dyes reported, 4-oxo-quinazolin nucleus finds its position frequently. There is no slackening of activity in this field as seen from the large number of patent specification and several ranges, which continue to appear in the market<sup>1-3</sup>. The use of the dyestuff makes possible the highest degree of fastness to severe washing, abrasion, etc. At the same time, the shade ranges that can be achieved on cotton with fast dyestuff has considerably been extended<sup>4</sup>. Improvements in the structure of reactive dye chromogens and in the structure selection and number of reactive group have led to an increased use of reactive dyes<sup>5-7</sup>. Patel et al.<sup>8</sup> have synthesized fiber reactive dyes for silk, wool and rayon.

We report here the synthesis and study of the dyeing properties of the 4-oxo-quinazolin dyes based on 2-phenyl-3, 1-benzoxazine-4(4H)-one.

The reaction of benzoyl chloride with anthranilic acid in pyridine at 8°C gave 2 –

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phenyl - 3, 1 – benzoxazine – 4 (4H) - one (**1**). The compound (**1**) on condensation with 4, 4'-diaminostilbene - 2, 2' - disulfonic acid yielded 4 - (2 – phenyl – 4 – oxo – 3 - quinazoliny) - 4' – aminostilbene - 2, 2' - disulfonic acid (**2**). Compound (**2**) diazotized and coupled with different couplers (**a-o**) gives different types of dyes (**3**). All the compound synthesized were adequately characterized by their elemental analysis and spectral data.

## EXPERIMENTAL

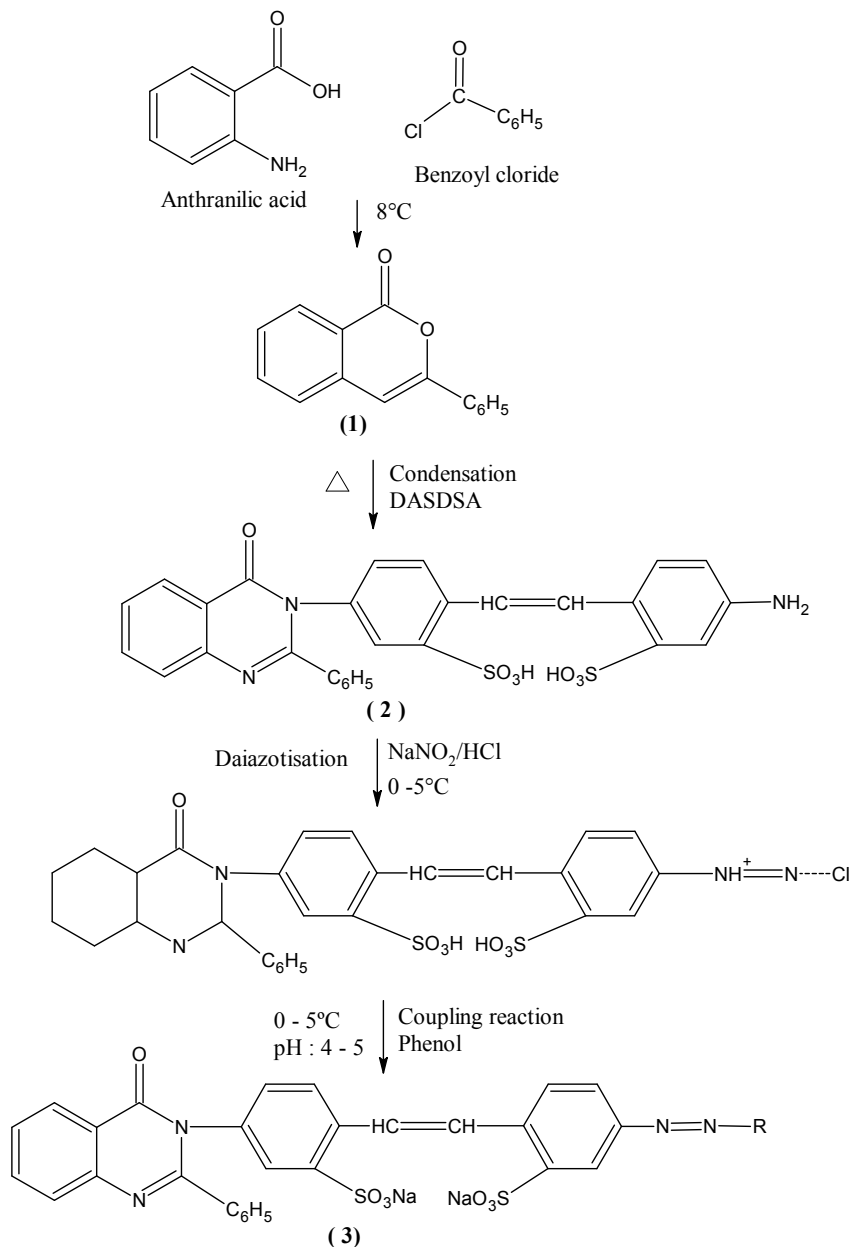
Melting points were taken in open capillaries and are uncorrected. The IR spectra of dyes D<sub>91</sub> to D<sub>105</sub> were recorded on Bio-Red FTS-40 spectrophotometer using KBr pellets. The purity of all dyes has been checked by thin-layer chromatography<sup>9</sup>. The absorption spectra of all the dyes were recorded on Beckmann DB-GT Grafting Spectrophotometer. 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-Phenyl-3, 1-benzoxazine 4(4H)-one (**1**)

Benzoyl chloride (140.5 g; 1M) was added dropwise to anthranilic acid (137.0 g; 1M) dissolved in pyridine (60 mL) with constant stirring at 8°C over the period of 1 hour. After the addition of benzoyl chloride, reaction mixture was stirred for half an hour at room temperature. At the end of the reaction, reaction mixture almost solidified. The solid mass was poured in to cold water, filtered, washed successively with aqueous sodium bicarbonate solution (10% to remove unreacted anthranilic acid) and water, dried and recrystallised from ethanol (95%) to get compound (**1**). Yield 84%, m. p. 118°C. Anal. Calcd. for C<sub>14</sub>H<sub>9</sub>O<sub>2</sub>N : C, 75.33; H, 4.03; N, 6.27. Found C, 75.35; H, 4.00; N, 6.25%.

### 4-(2-Phenyl-4-oxo-3-quinazoliny)-4'-aminostilbene-2, 2'-disulfonic acid (**2**)

Equimolar ratio of compound (**1**) (223.0 g; 1M) and 4, 4'-diaminostilbene-2, 2'-disulfonic acid (370.0 g; 1M) (DASDSA) 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 orange crystalline solid. It was filtered, washed with cold ethanol and recrystallised from ethanol (95%) to get compound (**2**). Yield 80%, m. p. 279°C. Anal. Calcd. for C<sub>28</sub>H<sub>21</sub>O<sub>7</sub>N<sub>3</sub>S<sub>2</sub> : C, 58.43; S, 11.13; N, 7.30. Found C, 58.40; S, 11.10; N, 7.31%.



Where R = Phenol, o-Cresol, m-Cresol, p-Cresol, o-Cl-Phenol, m-Cl-Phenol, l-Naphthol, 2-Naphthol, Salicylic acid, Resorcinol, H-acid, J-acid, R-acid and Gamma acid for D<sub>91</sub> to D<sub>105</sub> respectively

**Scheme**

**Disodium salt of 4 - (2 - phenyl - 4 - oxo - 3 - quinazoliny) - [4' - (4 - hydroxyl phenylazo)] - stilbene - 2, 2' - disulfonic acid (D<sub>91</sub> to D<sub>105</sub>) (3)**

Equimolar ratio of compound (2) (0.2875 g; 0.05M) was suspended in water (10.0 mL), conc. hydrochloric acid (5.0mL ; 0.025M) was added drop-wise 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 filtered to get a clear diazonium salt solution which was used for the subsequent coupling reaction.

Phenol (0.188 g; 0.05M) 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 hr. 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 hrs. at 0-5°C until all the diazo salt was consumed (spot test with alkaline phenol solution). After being stirred for further 2 hrs. to complete the separation, the dye was isolated by salting, filtration, washed with ice water, dried and crystallized from water to get orange crystals of compound (3D<sub>91</sub>). Yield 74%, m. p. >300°C. Anal. Calcd. for C<sub>34</sub>H<sub>22</sub>O<sub>8</sub>N<sub>4</sub>S<sub>2</sub>Na<sub>2</sub> : C, 56.35; S, 8.88; N, 7.73. Found C, 56.31; S, 8.81; N, 7.70%. IR : 1656 cm<sup>-1</sup> due to >C = O and at 1621 cm<sup>-1</sup> due to >C = N -. The absorption at 706 and 755 cm<sup>-1</sup> is due to mono substituted benzene ring. The absorption at 3394 cm<sup>-1</sup> is due to N - H and at 3690 cm<sup>-1</sup> is due to O - H. The absorption at 1147 and 1141 cm<sup>-1</sup> is due to S=O of sulfonic acid.

Other compounds (3D<sub>92</sub>-D<sub>105</sub>) were synthesized similarly from (3), respectively. Characterization data are presented in Table 1.

## RESULTS AND DISCUSSION

All the dyes D<sub>91</sub> to D<sub>105</sub> were applied on cotton and wool fibers using the reported dyeing procedure<sup>10-13</sup>. All the dyes were orange-yellow-green-violet-brown to pink and obtained in excellent yield. Data on λ<sub>max</sub> value (in DMF solvent) and the results of exhaustion and fixation of all the dyes on cotton and wool fabrics are furnished in Table 2.

Table 1. Characterization

Dye No.	Shade on dyed fibres	R	Molecular formula	Yield (%)	M. P. (°C)	Found (%) (Calcd.)		
						C	N	S
D <sub>91</sub>	Orange	(a) Phenol	C <sub>34</sub> H <sub>22</sub> O <sub>8</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub>	74.00	>300	56.31 (56.35)	7.70 (7.73)	8.81 (8.88)
D <sub>92</sub>	Brown	(b) o-Cresol	C <sub>35</sub> H <sub>24</sub> O <sub>8</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub>	78.00	>300	56.88 (56.91)	7.55 (7.59)	8.66 (8.67)
D <sub>93</sub>	Brown	(c) m-Cresol	C <sub>35</sub> H <sub>24</sub> O <sub>8</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub>	79.00	>300	56.89 (56.91)	7.57 (7.59)	8.64 (8.67)
D <sub>94</sub>	Brown	(d) p-Cresol	C <sub>35</sub> H <sub>24</sub> O <sub>8</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub>	73.00	>300	56.90 (56.91)	7.60 (7.59)	8.60 (8.67)
D <sub>95</sub>	Greenish	(e) o-Cl-Phenol	C <sub>34</sub> H <sub>21</sub> O <sub>8</sub> N <sub>4</sub> S <sub>2</sub> ClNa <sub>2</sub>	74.00	>300	53.75 (53.79)	7.39 (7.38)	8.41 (8.44)
D <sub>96</sub>	Green	(f) m-Cl-Phenol	C <sub>34</sub> H <sub>21</sub> O <sub>8</sub> N <sub>4</sub> S <sub>2</sub> ClNa <sub>2</sub>	75.00	>300	53.76 (53.79)	7.32 (7.38)	8.40 (8.44)
D <sub>97</sub>	Blaxk-Green	(g) p-Cl-Phenol	C <sub>34</sub> H <sub>21</sub> O <sub>8</sub> N <sub>4</sub> S <sub>2</sub> ClNa <sub>2</sub>	76.00	>300	53.70 (53.79)	7.30 (7.38)	8.43 (8.44)
D <sub>98</sub>	Brown	(h) 1-Naphthol	C <sub>38</sub> H <sub>24</sub> O <sub>8</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub>	86.00	>300	58.89 (58.92)	7.25 (7.24)	8.21 (8.27)
D <sub>99</sub>	Orange	(i) 2-Naphthol	C <sub>38</sub> H <sub>24</sub> O <sub>8</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub>	83.00	>300	58.90 (58.92)	7.23 (7.24)	8.25 (8.27)
D <sub>100</sub>	Yellow	(j) Salicylic acid	C <sub>35</sub> H <sub>22</sub> O <sub>10</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub>	74.00	>300	54.60 (54.69)	9.17 (9.11)	8.30 (8.33)
D <sub>101</sub>	Pink	(k) Resorcinol	C <sub>34</sub> H <sub>22</sub> O <sub>9</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub>	85.00	>300	55.10 (55.14)	7.50 (7.57)	8.61 (8.65)
D <sub>102</sub>	Violet	(l) H-Acid	C <sub>38</sub> H <sub>23</sub> O <sub>14</sub> N <sub>5</sub> S <sub>4</sub> Na <sub>4</sub>	83.00	>300	45.90 (45.92)	7.00 (7.07)	12.80 (12.89)
D <sub>103</sub>	Violet	(m) J-Acid	C <sub>38</sub> H <sub>24</sub> O <sub>11</sub> N <sub>5</sub> S <sub>3</sub> Na <sub>3</sub>	75.00	>300	51.11 (51.18)	7.85 (7.86)	10.71 (10.77)
D <sub>104</sub>	Dark-Violet	(n) R-Acid	C <sub>38</sub> H <sub>25</sub> O <sub>13</sub> N <sub>5</sub> S <sub>4</sub> Na <sub>2</sub>	81.00	>300	48.80 (48.87)	7.45 (7.50)	13.71 (13.72)
D <sub>105</sub>	Dark-Violet	(o) Gama-Acid	C <sub>38</sub> H <sub>24</sub> O <sub>11</sub> N <sub>5</sub> S <sub>3</sub> Na <sub>3</sub>	83.00	>300	51.10 (51.18)	7.80 (7.86)	10.70 (10.77)

**Table 2. Evaluation of exhaustion and fixation study of dyes on nylon and polyester fibers (C = Cotton, W = Wool).**

Dye No.	$\lambda_{\max}$ (nm)	Log $\Sigma$	% Exhaustion		$\lambda_{\max}^*$ (nm)	% Fixation**	
			C	W		C	W
D <sub>91</sub>	498	4.50	29	72	500	50	85
D <sub>92</sub>	468	4.22	24	67	471	61	82
D <sub>93</sub>	496	4.60	25	70	501	58	86
D <sub>94</sub>	530	4.70	21	65	534	50	84
D <sub>95</sub>	600	4.91	29	55	609	66	60
D <sub>96</sub>	660	4.80	28	65	665	68	66
D <sub>97</sub>	720	4.98	22	58	721	69	65
D <sub>98</sub>	510	4.20	27	64	514	57	89
D <sub>99</sub>	528	4.15	25	72	530	61	90
D <sub>100</sub>	470	4.40	30	68	475	53	86
D <sub>101</sub>	510	4.32	21	72	514	58	82
D <sub>102</sub>	516	4.27	30	60	520	60	85
D <sub>103</sub>	526	4.39	22	62	530	55	88
D <sub>104</sub>	572	4.22	26	76	583	48	79
D <sub>105</sub>	530	4.21	29	72	535	54	84

The data of exhaustion and fixation value show that the percentage exhaustion on wool is higher than that on cotton fabrics. The results of fastness to light, washing, perspiration and sublimation of cotton and wool fibers are shown in Table 3. The light fastness of all the dyes on both the fibers was found to be fair to fairly good to good.

**Table 3. Evaluation of fastness properties of dyed nylon and polyester patterns with dyes**  
(C = Cotton, W = Wool)

Dye No.	Light fastness		Wash fastness		Perspiration fastness				Sublimation fastness		
	C	W	C	W	Acidic		Alkaline		C	W	
					C	W	C	W			
D <sub>91</sub>	3	3	3	5	4	4	4	4	4	4	5
D <sub>92</sub>	3	4	3	4	5	4	5	4	5	5	5
D <sub>93</sub>	3	3	3	5	5	5	4	3	5	5	5
D <sub>94</sub>	3	3-4	3	4	4	4	4	4	4	4	4
D <sub>95</sub>	3	4	3	4	4	4	5	4	5	5	5
D <sub>96</sub>	3	4	3	5	5	4	5	4	5	5	5
D <sub>97</sub>	3	3	3	4	5	4	5	5	5	5	5
D <sub>98</sub>	3	3-4	3	4	4	5	4	5	4	5	5
D <sub>99</sub>	3	3	3	5	4	4	3	4	5	5	5
D <sub>100</sub>	3	3	3	4	5	4	5	4	5	5	5
D <sub>101</sub>	3-4	4	3	5	4	4	4	4	4	4	4
D <sub>102</sub>	3	3	3	5	5	5	4	3	5	5	5
D <sub>103</sub>	2	3	3	4	4	4	5	3	5	5	5
D <sub>104</sub>	3	4	3	4	4	4	4	4	4	4	5
D <sub>105</sub>	3	4	3	4	5	3	5	4	5	5	5

The obtained results of washing fastness of the prepared dyes for both the fibers showed that they are very good to excellent. 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.

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### **REFERENCES**

1. ICI, Eur. Pat. Appl. Ep., **225**, 730 (1987).
2. G. Jones, *The Quinolines*, Wiley Inter Science, London, (1977) p. 318.
3. Ciba, Eur. Pat. Appl. Er., **775**, 730 (1997).
4. H. M. El-Nahas, *J. Am. Dyestuff Rept.*, **86**, 9 (1997).
5. A. H. M. Renfew and J. A. Taylor, *Rev. Prog. Col.*, **20**, 1 (1990).
6. M. H. Hahnke, *Textilveredlung*, **21**, 285 (1986).
7. S. Abeta, T. Yoshida and K. Imada, *Am. Dyestuff Rept.*, **73**, 26 (1984).
8. N. B. Patel, S. K. Patel and K. C. Patel., *Acta Ciencia Indica*, **XXVC**, 79 (1990).
9. Bernard Fried and Joseph Sherma, *Thin Layer Chrometography: Technique and Applications*, Marcel Dekkar, Inc., New York and Basel (1982).
10. C. K. Whittaker and C. C. Wilcock, *Dyeing With Coal Tar for Dyestuffs*, London (1952).
11. F. Sadovkorchagin and A. Maketsky, *Chemical Technology of Fibrous Material*, Mir Publication, Moscow (1973).



12. V. A. Sheni, *Chemistry of Dyes and Principles of Dyeing*, Sevak Publication, Bombay (1973).
13. E. R. Trotman, *Dyeing and Chemical Technology of Textile Fabrics*, London (1970)  
(a) pp. 333-334, (b) p. 590.

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