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Synthesis and Dyeing Action of Novel Thioindigoid Reactive Dyes

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Some thioindigoid dyes synthesized by condensation of thiazolidinones with isatin are evaluated for their dyeing action in terms of dye exhaustion and fixation on cotton, polyester, silk and wool fibrics. Structures of products have been elucidated from molecular weight, elemental analysis, infrared and NMR spectroscopy.

Key Words: Indigoid thiazolidinones, Reactive dyes, Exhaustion, Fixation, Dyeing mechanism.

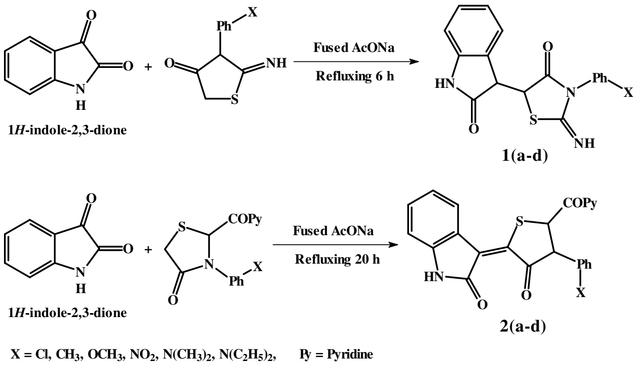
INTRODUCTION

Literature has witnessed many reports on dyeing properties of variety of coloured molecules with diverse chromophores and auxochromes working on reactive, disperse or other mechanisms. Although azo[1-3] and heterocyclic diazo compounds have been extensively used as disperse dyes but reactive dyes[4-6] which form homopolar bond with textile substrate, claim the greatest interest at the present time. The brilliance of reactive dyeings due to uncomplicated simple structure of the dye molecules and good wet fastness due to stable linkage between dye and textile fibre in both alkaline and acid media have led to their preponderance over dyes of other classes. Distinguished dyeing features of reactive dyes in particular and diverse important usages of dyes in general, such as in photosenstization of porous TiO_2 electode[7-12], electrophotographic and electroluminescent devices[13,14], photogalvanic cells[15-18], *etc.* infused considerable interest in reactive dyes. Hence, it was thought worthwhile to synthesize reactive dyes from isatin using various substituted thiazolidinone derivatives as coupling compounds and evaluate their dyeing action on silk, cotton, wool and polyester fibres which have been paid negligible attention so far.

EXPERIMENTAL

In the synthesis work Sigma, SRL, BDH/Qualigens Laboratory reagents were used as supplied. Solvents were distilled and/or dried before use.

The purity of all the dyes was checked by TLC conducted on starch bound silica gel layers using several pure and mixture solvents. Any contamination of reactant thiazolidinone was washed out by EtOH, iso-PrOH or C_6H_6. Molecular weight of the pure products were determined by Rast's method with camphor. Melting points determined by open capillary method were uncorrected. Elemental analysis was carried out on Vario-el III, elemental-R. Infrared spectra were recorded in KBr on Thermo-Nicolet FT-IR spectrometer whereas ^1H NMR spectra were recorded in DMSO-d_6 on Brucker 400 MHz spectrometer. All new products are synthesized by **Scheme-I**.



Scheme-I: Synthesis of thioindigoid dyes

Synthesis of 5-(2-oxo-3-indolidinyl)-2-imino-3-(substituted phenyl)-1-thiazolidin-4-ones (1a-d): Isatin (1.47 g, 0.01 mol) and 2-imino-3-(substituted phenyl)-1-thiazolidin-4-ones (0.01 mol) prepared by reported method[19] were mixed together in dry MeOH and fused NaOAc (5.0 g) was added to reaction mixture followed by refluxing for *ca.* 6 h. Solid separated or obtained as residues on evaporation of solvent were washed with water, dried in oven and crystallized from EtOH.

Synthesis of 5-(2-oxo-3-indolidinyl)-2-(2-ketopyridinyl)-3-(substituted phenyl)-1-thiazolidin-4-ones (2a-d): To prepare **2a-c**, 2-ketopyridinyl-3-(substituted phenyl)-1-

thiazolidin-4-ones (0.016 mol) synthesized by reported method[20], isatin (0.016 mol) and fused NaOAc (0.08mol) mixed in dry MeOH were refluxed for 20 h. For synthesis of **2d** reactants were mixed in 1:2:9 molar ratio. Solids obtained on dilution of concentrated reaction mixtures with water were filtered out, washed with water, dried in oven and crystallized from EtOH.

Dyeing and post dyeing treatments: Two of the four pre-washed white cloth pieces (6 cm × 6 cm) of silk, wool, polyester and cotton were dipped in 10 mL dye solution (1000 ppm; in MeOH-H_2O, 1:3 v/v) in each test tube at room temperature *ca.* 31 and 95 ºC containing necessary H_2SO_4 concentration for producing maximum colour intensity of each dye (Table-1), determined spectrophotometrically by plotting optical density *vs.* varying concentrations of H_2SO_4 in equiconcentrate solutions of each dye, left for 35-50 min, squeezed and were dried in sunlight.

From concentration of extracts obtained from squeezed cloths (one piece) determined from calibration curves of corresponding dyes, prepared under similar conditions of temperature and solvent, dyes exhaustions were calculated. For determination of fixation of each dye on different fibres each dyed dry cloth was dipped in 5 mL water and left for 25-30 min, squeezed and concentration of extracts was determined from respective calibration curves. From concentration of these extracts fixation of dyes on diverse fibres was calculated.

RESULTS AND DISCUSSION

Theortically proposed molecular formulae of dyes are in conformity of experimental data of molecular weight and elemental analysis (Table-2).

The common characteristic groups of **1a-d** and **2a-d** series of dyes, cyclic C=O, C-N, C-S-C, N-H, aromatic C=C & C-H and *para* & *meta* substituted ring, display stretching vibrations in their infrared spectra at 1743-1700, 1355-1216, 755-611, 3476-3226, 1594-1401 & 3065-3019 and 840-811 & 785 cm^{-1}, respectively whereas an additional group C=NH of **1a-d** dyes and C=O of **2a-d** dyes exhibit stretching band at 1659-1614 and 1618-1607 cm^{-1} respectively. Strong band observed at 1890-1700 cm^{-1} due to stretching vibrations of C=C of two fused rings owing to condensation of C=O group of isatin with CH_2 group of thiazolidinone ring and absence of any peak of CH_2 of pentacyclic ring support the proposed structure of thioindigoid dyes. For further verification ^1H NMR spectra of two compounds, 5-(2-oxo-3-indolidinyl)-2-imino-3-(*m*-methyl phenyl)-1-thiazolididin-4-one and 5-(2-oxo-3-indolidinyl)-2-imino-3-(*p*-methoxy phenyl)-1-thiazolididin-4-one, have been examined. Bands at δ 6.438, 10.415, 2.470 and 3.315 in NMR spectra, characteristic of chemical shifts of benzenoid, enolic, methyl and methoxy hydrogens respectively and absence of any peak corresponding to CH_2 of thaizolidinone ring involved in condensation with C=O group of isatin confirm infrared inferences.

TABLE-1
FIBRE COLOUR, EXHAUSTION AND FIXATION DATA OF DYES

Dye	Dyeing method	Dye colour				Exhaustion (%)				Fixation (%)				Necessary H_2SO_4 conc. (ppm)
		Silk	Cotton	Wool	Polyester	Silk	Cotton	Wool	Polyester	Silk	Cotton	Wool	Polyester	
1a	Cold	Pink gray	Brown gray	Ruby brown	Ruby gray	19.0	20.8	17.2	17.8	84.2	71.6	70.3	84.8	1019
	Hot	Yellow gray	Brown gray	Ruby brown	Ruby gray	22.0	22.6	19.0	19.0	85.0	75.2	73.1	89.5	1019
1b	Cold	Brown	Brown	Brown	Violet	38.2	43.0	43.6	41.2	99.5	98.4	96.6	100.0	6116
	Hot	Brown	Brown	Brown	Violet	9.4	2.8	14.8	7.6	100.0	96.4	85.13	100.0	6116
1c	Cold	Brown gray	Brown	Brown	Violet	42.4	43.0	41.2	37.6	100.0	99.8	98.5	100.0	1835
	Hot	Brown gray	Brown	Brown	Violet	26.2	24.4	26.8	12.4	100.0	100.0	93.8	100.0	1835
1d	Cold	Brown gray	Pink gray	Brown gray	Violet	22.6	22.0	17.8	17.2	82.3	78.2	16.8	22.1	3670
	Hot	Brown gray	Pink gray	Brown gray	Violet	4.9	15.4	7.4	12.4	87.1	61.7	14.3	21.0	3670
2a	Cold	Grape yellow	Light yellow	Off white	Off white	83.4	82.9	84.2	84.3	97.4	88.5	94.8	87.7	1633
	Hot	Grape yellow	Light yellow	Off white	Off white	71.7	78.9	79.0	79.3	97.2	87.0	98.2	87.7	1633
2b	Cold	Violet brown	Brilliant brown gray	Brown violet	Gray brown	91.80	91.3	91.5	16.0	98.3	95.0	70.6	98.7	4288
	Hot	Brown gray	Brown gray	Brown gray	Gray brown	91.00	90.4	92.1	0.5	98.8	97.1	4.6	98.3	4288
2c	Cold	Gray brown	Muddy brown	Violet gray	Muddy brown	91.7	90.6	87.4	13.0	100.0	97.5	100.0	96.1	3266
	Hot	Gray brown	Muddy brown	Muddy brown	Muddy brown	90.6	87.4	89.0	90.1	98.8	97.1	25.0	98.6	3266
2d	Cold	Yellow	Dirty yellow	Dirty yellow	Yellow	62.0	61.8	70.6	63.0	74.0	75.8	91.4	77.7	2450
	Hot	Yellow	Dirty yellow	Dirty yellow	Yellow	47.4	57.6	67.0	61.6	95.8	78.7	92.0	76.7	2450

TABLE-2
PHYSICO-CHEMICAL PROPERTIES OF DYES

Dye	m.f.	Substituents	Yield (%)	m.p. (ºC)	m.w., calcd. (found)	Elemental analysis (%): Calcd. (Found)				λ_{max} (nm)
						C	H	N	S	
1a	$C_{17}H_{10}N_3O_2SCl$	4-Cl	56	77	355.5 (357.0)	57.38 (57.14)	2.81 (3.11)	11.81 (11.41)	9.00 (8.73)	360
1b	$C_{18}H_{13}N_3O_2S$	3-CH_3	52	140	335.0 (336.0)	64.47 (64.75)	3.88 (3.86)	12.53 (12.74)	9.55 (9.50)	390
1c	$C_{18}H_{13}N_3O_3S$	4-OCH_3	76	130	351.0 (350.0)	61.53 (61.05)	3.70 (4.09)	11.96 (11.82)	9.11 (8.77)	370
1d	$C_{19}H_{16}N_4O_2S$	4-$N(CH_3)_2$	81	162	379.0 (380.0)	60.15 (59.90)	4.22 (4.41)	14.77 (14.57)	8.44 (8.23)	380
2a	$C_{23}H_{14}N_4O_5S$	4-NO_2	72	120	458.0 (459.7)	60.26 (60.18)	3.06 (3.38)	12.23 (12.69)	7.00 (7.09)	390
2b	$C_{25}H_{20}N_4O_3S$	4-$N(CH_3)_2$	78	>260	456.0 (–)	65.79 (65.39)	4.39 (4.35)	12.28 (12.67)	7.03 (7.07)	350
2c	$C_{27}H_{24}N_4O_3S$	4-$N(C_2H_5)_2$	88	88	484.0 (485.6)	66.94 (67.32)	4.96 (4.69)	11.57 (11.78)	6.63 (6.98)	360
2d	$C_{41}H_{23}N_7O_{16}S_2$	4-NO_2	68	162	837.0 (834.5)	58.78 (58.85)	2.75 (2.61)	11.71 (11.39)	7.66 (7.60)	390

Dyeing properties of dyes: All the thioindigoids are reactive dyes with two or three reactive chromophores, C=O; **2(a-d)** compounds have an additional C=N chromophore. Primary alcoholic groups of cotton and polyester fibres interact with carbonyl group of indigoid dyes in presence of acid to yield unstable hemiacetals or hemiketals and a nucleophilic substitution converts them to stable acetals or ketals (I) (Fig. 1).

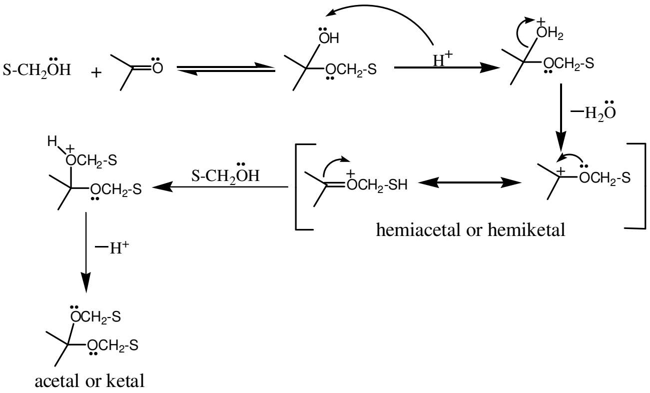


Fig. 1. Interactions of thioindigoid dyes with cotton and polyester fibres

Whereas, silk and wool, the protein fibres, possess >CONH- characteristic group which interacts with enolic group of dyes in their enolic structure (II) in presence of acid (Fig. 2).

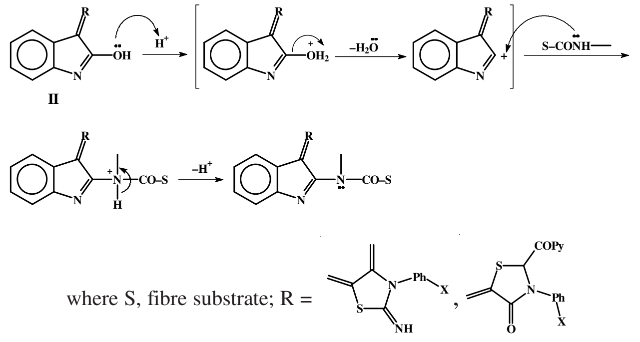


Fig. 2. Interactions of thioindigoid dyes with silk, wool and protein fibres

Better fixation of all the dyes on cotton and polyester fibers than silk and wool could be accounted for in terms of several reactive sites offered for interaction by the dyes. For cotton and wool two or three carbonyl groups of dyes are available for interaction with fiber substrate whereas for silk and wool only one enolic (OH) group of dyes could react with fibre substrate. It is interesting to note that electron donor ability of auxochromic substituents plays pivotal role in dye fixation. Dye fixation values (Table-2) for each fibre fall in opposite order to the sequence in electron donor ability of dye auxochromic substituents; **1(a-d)**, $Cl < N(CH_3)_2 < CH_3 < OCH_3$ and **2(a-d)**, $NO_2 < N(C_2H_5)_2 \leq N(CH_3)_2$. This adverse effect of electron donor ability of dye auxochromes owes to weakening of homopolar bond between textile substrate and dye by the electronic charge transfer from the dye auxochromic group.

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