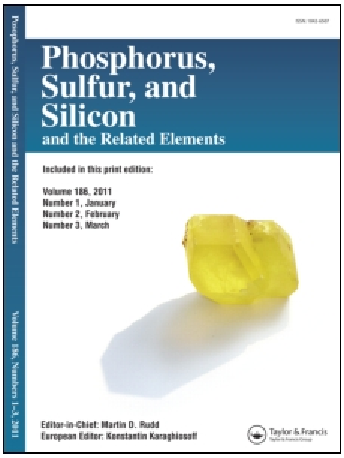

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SYNTHESIS AND APPLICATION OF 2-(ARYLAZO)-8-NITRONAPHTHO[1,2-d] THIAZOLE DISPERSE DYES

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The paper describes the synthesis of 2-amino-8-nitronaphtho[1,2-d]thiazole and its utilization to prepare a range of heterocyclic azo disperse dyes. These arylazo dyes were studied with respect to their color and constitution relationship. These dyes were applied on polyester fibre and their fastness properties were evaluated.

Keywords: 2-(Arylazo)-8-nitronaphtho[1,2-d]thiazoles; synthesis; application; disperse dyes; polyester fibres

INTRODUCTION

Recent advances in azo disperse dye chemistry mostly deals with the use of heterocyclic ring systems as diazonium components, which induce a profound bathochromic shift, brilliancy and increased fastness properties as compared to their carbocyclic analogs. In this connection, new structures of hetaryl azo disperse dyes derived from 2-aminothiazole and 2-aminobenzothiazole ring systems are interesting. The use of electronegative substitutents like arylsulphonyl[1], N-substituted sulfamide[2], nitro[3], cyano[4], thiocyanato[5] at 6-position of 2-aminobenzothiazole nucleus improve color and fastness properties. These dyes have encouraged us to synthesize novel naphtho[1,2-d]thiazole disperse dyes. Various reports[6–10] describe the syntheses and technical importance of thiazole dyes.

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RESULTS AND DISCUSSION

In this communication, we wish to report the facile syntheses of novel naphtho[1,2-d]thiazole derivative with a diazotizable amino group having electron withdrawing group at 8-position and azo dyes derived from it for their application to polyester fibre and to study their fastness properties.

TABLE I Physical and analytical data of **2**, **3** and (**4a**-**4f**)

Compd.	*Yield*[a] *%*	*M.P. °C (solvent)*	*Molecular Formula*	*Elemental Analysis % (calcd./found)*	
				N%	*S%*
2	46	190–191	$C_{13}H_5N_2O_2$	12.67	–
		(EtOH)		12.48	–
3	68	135–138	$C_{13}H_6N_2O_2S$	11.02	12.61
		(DMF)		11.10	12.70
4a	65	211–212	$C_{21}H_{19}N_5O_2S$	17.30	7.92
		(EtOH)		17.37	7.79
4b	60	190–191	$C_{23}H_{20}N_6O_2S$	18.91	7.20
		(EtOH)		19.12	7.14
4c	69	184–185	$C_{23}H_{22}N_6O_3S$	18.81	6.93
		(EtOH)		18.74	6.69
4d	65	159–161	$C_{25}H_{26}N_6O_4S$	16.68	6.32
		(EtOH)		16.80	6.18
4e	55	>280	$C_{25}H_{23}N_7O_5S$	18.38	6.08
		(EtOH)		18.20	6.20
4f	52	218–220	$C_{27}H_{26}N_6O_7S$	14.53	5.53
		(EtOH)		14.46	5.60

a. Isolated yields.

It was envisaged to synthesize a novel 2-aminothiazole derivative possessing thiazole moiety fused to naphthalene ring and with 8-position occupied by electron withdrawing group. For this purpose, 1-nitronaphthalene (**1**) was selected as a starting material, which was reacted with hydroxylamine hydrochloride and potassium hydroxide to yield 4-nitro-1-naphthylamine (**2**). Compound (**2**) was treated with ammonium thiocyanate and bromine to yield 2-amino-8-nitronaphtho[1,2-d]thiazole

(**3**). 2-Aminothiazole derivative (**3**) which then was diazotized and coupled with a variety of substituted N,N-dialkylated anilines to yield titled novel azo dyes (**4a-4f**). The physical and spectral data of dyes (**4a-4f**) are given in **Tables I and II**.

TABLE II Spectral data of 3 and **4a**

Compound	*IR (KBr) cm^{-1} Selected bonds*	*^{1}H-NMR (δ ppm) $CDCl_3$, $DMSO\text{-}d_6$*
3	3310, 3374 (NH_2)	7.8 (m, 4H, aromatic), 8.6 (s, 1H, aromatic), 9.8 (m, 2H, NH_2, D_2O exchangeable).
4a	1598 (N=N)	2.3 (t, 6H, $2CH_3$), 3.5 (q, 4H, $2CH_2$), 6.8 (d, 2H, aromatic), 7.6–8.3 (m, 6H, aromatic), 8.7 (s, 1H, aromatic)

These dyes (**4a-4f**) were brown to green solids which gave intense colored solutions in DMF and methanol (1:99). These dyes when applied to polyester fibre as disperse dyes gave violet to greenish blue shades. Volume (100 mL) of dispersion corresponding to 1% shade on azo dyes (1g) was based on the weight of the fabric (2g). The wavelength of the absorption for the compound (**4a-4f**) ranged from 547–586 nm. The pick-up was good for the dyes **4b, 4e** and **4f**, whereas it was excellent for the dyes **4a, 4c** and **4d**. The light fastness was fairly good for **4c, 4d** and **4f**, whereas it was good for dyes **4a** and **4b**. The sublimation fastness of the dyes (**4a-4f**) on polyester fibres was found to be excellent.

EXPERIMENTAL

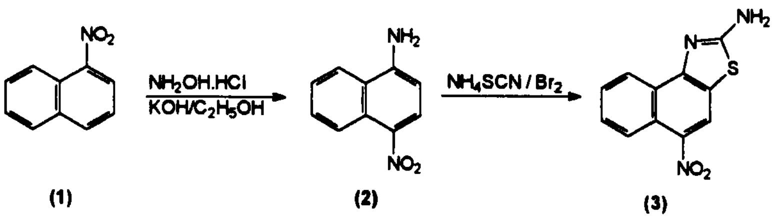
All melting points are uncorrected. IR spectra were recorded in KBr pellet on a Bomem Hartmann and Braun FTIR spectrophotometer. ^{1}H-NMR spectra were recorded on a 60 MHz Hitachi R-1200 RS-NMR spectrophotometer using TMS as internal standard and the chemical shifts are given in δ ppm. Absorption spectra in methanol solution were recorded on a Beckmann Model 25 spectrophotometer.

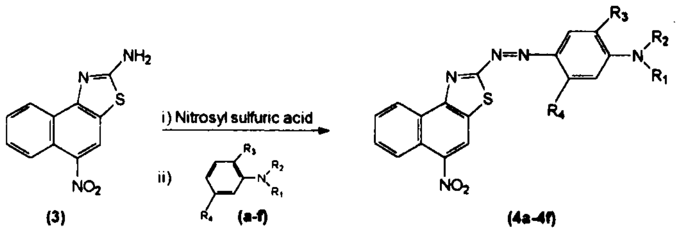
4-Nitro-1-naphthylamine (2)

4-Nitro-1-naphthylamine (2) was prepared[11] by reacting 1-nitronaphthalene (1)with hydroxylamine hydrochloride and potassium hydroxide in ethanol at 50–60°C.

2-Amino-8-nitronaphtho[1,2-d]thiazole (3)

4 -Nitro-1-naphthylamine (2) (0.1 mole) was treated with ammonium thiocyanate (0.2 mole) and bromine (0.12 mole) in glacial acetic acid at room temperature. The reaction mixture was filtered and the filtrate treated with ammonia solution (25%) to adjust pH 8. The resulting solid was isolated by filtration, washed with cold water and dried at 60°C. The results are given in **Table I**.





Dye No	R1	R2	R3	R4
4a	C_2H_5	C_2H_5	H	H
4b	C_2H_5	C_2H_4CN	H	CH_3
4c	C_2H_5	C_2H_5	H	$NHCOCH_3$
4d	C_2H_5	C_2H_5	OC_2H_5	$NHCOCH_3$
4e	C_2H_4OH	C_2H_4CN	OCH_3	$NHCOCH_3$
4f	$CH_2CH_2COOCH_3$	$CH_2CH_2COOCH_3$	H	$NHCOCH_3$

General method for the preparation of 2-(substituted aryl azo)-8-nitronaphtho[1,2-d]-thiazoles

2-Amino-8-nitronaphtho[1,2-d]thiazole (3) (0.01 mole) was dissolved in acetic acid (10 mL) at 10°C and stirred for 15 minutes. After complete dissolution, nitrosyl sulfuric acid (4.6 mL) equivalent to sodium nitrite (0.01 mole) was slowly added at 5°C with constant stirring for one hour. The excess nitrous acid was destroyed using urea.

N,N-Dialkylaniline derivative **(a-f)** (0.01 mole) was dissolved in acetic acid (20 mL) and cooled to 10°C with crushed ice (10 g). The clear diazo solution was slowly run into the above solution at 10–15°C with vigorous stirring over a period of 30 minutes. The pH of the reaction was maintained at 4.5 to 5.5 by the addition of solid sodium acetate in portions throughout the coupling period. The reaction mixture was poured into the ice-water followed by addition of sodium carbonate solution until neutral. The resulting dye was isolated by filtration, washed with water and dried at 60°C. The results are given in **Table I, II and III.**

TABLE III UV – Visible spectra and dyeing data of **4a-4f**

Dye No.	*Color on polyester*	*Absorption max. (nm)*	*Log ε*	*Pick-up*	*Light fastness*	*Sublimation fastness*
4a	Violet	558	4.18	5	5	4–5
4b	Violet	547	4.21	4	5	4–5
4c	Blue	567	4.25	5	4	4–5
4d	Blue	568	4.31	5	4	4–5
4e	Greenish blue	584	4.23	4	4	4–5
4f	Greenish blue	586	4.12	4	4	4–5

Pick-up: Values are based on standard depths. 5 = 1 Standard depth (commercial), 4 = 1/3 standard depth (commercial), 3 = 1/4 standard depth (commercial), 2 = 1/6 standard depth (commercial), 1 = 1/12 standard depth (commercial). **Light fastness**: 8 = Outstanding, 7 = excellent, 6 = very good, 5 = good, 4 = fairly good, 3 = fair, 2 = poor, 1 = very poor. **Sublimation fastness**: 5 = Excellent, 4 = good, 3 = fair, 2 = poor, 1 = very poor.

PICK-UP

For finding out the pick-up values, the depth of color of a commercial dye for each hue is selected as a standard and compared with the deepness of colors from equivalent 1% shade (1 g of dye on 100 g of fabric) of the new dye on the same fabric.

LIGHT FASTNESS

The fastness to light of dyeing, prints and dyestuffs is resistance to the effect of daylight without direct effect of weather. Light fastness is measured with a set of standards consisting of eight blue wool dyed graded strips of fabrics. The sample dyed fabric is exposed to natural sunlight or light equivalent to natural sunlight. Based on the fading of a sample dyed fabric compared with a standard in a number of hours ranging from eight to one hundred and sixty, light fastness grading are given in ascending order from 1 to 8. The standards, called Grey cards, are strips of wool dyed fabrics already exposed to natural sunlight and graded for comparison.

SUBLIMATION FASTNESS

The sublimation fastness was assessed by keeping a composite specimen of dyed polyester between two undyed polyester pieces in a precision press at 180°C for one minute. Hence when printed fabrics are subjected to the high temperature, the dye from the printed area sublimes off and stain the unprinted area. The standard ratings are given in ascending order from 1 to 5.

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