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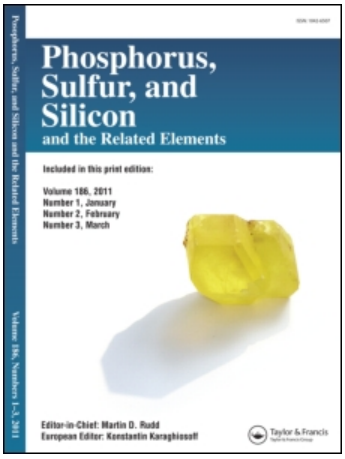

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SYNTHESIS AND APPLICATION OF 2-ARYLAZO-3-CYANO THIENO [2,3-b]NAPHTHOQUINONES

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The paper describes the synthesis of 2-amino-3-cyanothieno[2,3-b]naphthoquinone and its utilisation to prepare range of azo disperse dyes. These novel arylazo dyes were studied with respect to their color and constitution relationship. Application of these dyes on polyester fibres and their fastness properties were stated. These dyes were characterised by PMR, IR and visible absorption spectra.

Keywords: 2-Arylazo-3-cyanothieno[2,3-b]naphthoquinones; synthesis; application; disperse dyes; polyester fibres

INTRODUCTION

Thiophene derivatives have been incorporated in the synthesis of disperse dyes and fluorescent brighteners because of their intrinsic conjugation and rigidity of structures. The thiophene bearing azo disperse dyes possess small molecular structures leading to better dyeability. Thiophene azo disperse dyes also possess good sublimation fastness and dischargeability as compared to their conventional carbocyclic counterparts. The versatility of thiophenes in dyes [1–4] has encouraged us to synthesise novel naphtho[b] thiophene azo disperse dyes. Several current reports [5–11] describe the synthesis and technical importance of thiophene dyes.

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RESULTS AND DISCUSSION

In this communication, we wish to report the facile synthesis of a novel naphthoquionone based thiophene derivative with a diazotizable amino group and new azo disperse dyes derived from it for their application to polyester fibres.

It was envisaged to synthesise a novel 2-amino thiophene derivative possessing thiophene moiety fused to naphthoquinone ring and with 3-position occupied by the electron withdrawing group. For this purpose, 2,3-dichloronaphthoquinone **(1)** was selected as the starting material which was condensed with malononitrile to yield 2-chloro-3-biscyanomethyl- 1,4-naphthoquinone **(2).** The compound **(2)** was cyclized by sodium sulfide to yield 2-amino-3-cyanothieno[2,3-b]naphthoquinone **(3).** 2-Amino thiophene derivative **(3)** prepared in this manner 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 the Table I and II.

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

Compd	*Yield %*	*M.P. °C Solvent*	*Molecular Formula*	*Elemental Analysis % (calcd./found)*			
				C	*H*	*N*	*S*
2	61	190–191	$C_{13}H_5N_2O2$	70.58	2.26	12.67	----
		EtOH		70.42	2.31	12.58	----
3	68	135–138	$C_{13}H_6N_2O_2S$	61.14	2.36	11.02	12.60
		DMF		61.22	2.31	11.28	12.51
4a	52	160	$C_{23}H_{17}N_4O_2S$	66.83	4.12	13.6	7.74
		DMF		66.88	4.01	13.2	7.62
4b	55	171	$C_{25}H_{20}N_5O_3S$	63.83	4.25	14.96	6.80
		DMF		63.88	4.34	14.64	6.72
4c	49	166	$C_{27}H_{26}N_5O_4S$	63.03	5.06	13.56	6.20
		DMF		62.92	4.98	13.42	6.12
4d	53	174	$C_{26}H_{21}N_5O_4S$	62.52	4.21	14.03	6.41
		DMF		62.66	4.12	13.93	6.26
4e	56	201	$C_{25}H_{22}N_4O_5S$	61.22	4.49	11.43	6.53
		DMF		61.32	4.56	11.31	6.38
4f	50	186	$C_{27}H_{23}N_4O_5S$	61.25	4.35	13.23	6.05
		DMF		61.33	4.28	13.12	5.96.

TABLE II Spectral data of **3, 4a, 4b** and **4c**

Compound	*IR (KBr) cm^{-1} Selected bands*	*^{1}H-NMR (δ ppm) $CDCl_3$*
3	3197, 3323 (NH_2),	7.8 (m, 4H, aromatic), 8.2 (m, 2H, NH_2,
	2200 (CN).	D_2O exchangeable).
4a	1610 (N=N),	1.3 (t, 6H, 2CH3), 3.5 (q, 2H, aromatic),
	2220 (CN).	6.8 (d, 2H, aromatic), 7.8 (d, 2H, aromatic),
		8.3 (m, 2H, aromatic).
4b	1623 (N=N),	1.5 (t, 6H, 2CH3), 2.3 (S, 3H, CH3),
	2200 (CN),	3.8 (q, 4H, 2CH2), 6.8 (d, 2H, aromatic),
	3382 (NH).	7.3 (s,1H, NH), 7.9 (d, 2H, aromatic),
		8.2 – 8.3 (m, 4H, aromatic).
4c	1642(N=N),	1.2(t, 6H, 2CH3), 2.2(S, 3H, CH3),
	2212(CN),	4.2(q, 4H, 2CH2), 3.8(S, 3H, OCH3),
	3372(NH).	6.9(d, 2H, aromatic), 7.4(S, 1H, NH),
		7.9(d, 2H, aromatic), 8.1 (m, 4H, aromatic).

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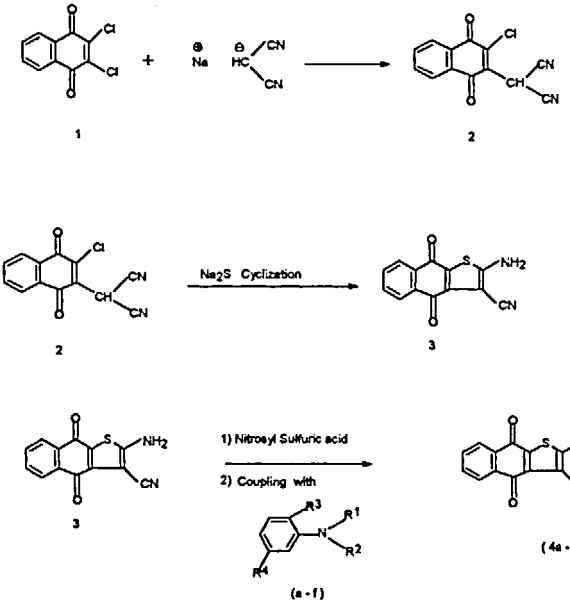
These dyes **(4a-4f)** were brown to grey solids which gave intense colored solutions in methanol and DMF. These dyes when applied on polyester fibres as disperse dyes gave brown to grey shades. Volume (100 ml) of dispersion corresponding to 1% shade of an azo dye (1 g) was based on the weight of the fabric (2 g). The wavelength of absorption for the compound **(4a-4f)** ranged from 515–546 nm. The pick-up was moderate **(2)** for the dye **4f,** whereas it was excellent **(4)** for the dyes **4b** and **4e.** The lightfastness was poor in the case of dye 4e, moderate in the case of dyes **(4a-4d)** and good for the dye **4f.** The sublimation fastness of the dyes **(4a-4f)** on polyester fabric 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.

2-Chloro-3-biscyanomethyl-1,4-naphthoquinone(2)

A mixture of sodium salt of malononitrile (0.01 mole) and 2,3-dichloro-1,4-naphthoquinone **(1)** (0.01 mole) was taken in ethanol and was refluxed for 2 h. The reaction mixture was cooled to room temperature when the product separated. It was filtered and dried. The results are given in Table I.



Dye No	R^1	R^2	R^3	R^4
4a	C_2H_5	C_2H_5	H	H
4b	C_2H_5	C_2H_5	H	$NHCOCH_3$
4c	C_2H_5	C_2H_5	OCH_3	$NHCOCH_3$
4d	CH_2CH_2CN	CH_2CH_2OH	H	$NHCOCH_3$
4e	CH_2CH_2OH	CH_2CH_2OH	H	$NHCOCH_3$
4f	CH_2CH_2CN	CH_2CH_2OH	OCH_3	$NHCOCH_3$

2-Amino-3-cyanothieno [2,3-b]naphthoquinone(3)

Previously cooled solution of sodium sulfide (0.01 mole) was taken in water. To this solution 2-chloro-3-biscyanomethyl-1,4-naphthoquinone **(2)** (0.01 mole) dissolved in acetone was added and mixed rapidly. The precipitate thus formed

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was filtered, washed with water and recrystallised from DMF. The results are given in Table I and II.

General method for the preparation of 2-(substituted N,N-dialkylaminoaryl)azo-3-cyanothieno [2,3-b]naphthoquinone (4a –4f)

2-Amino-3-cyanothieno[2,3-b]naphthoquinone (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 1 h. The excess nitrous acid was destroyed using urea.

N,N-Dialkylaniline (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 and water followed by addition of sodium carbonate solution until neutral. The separated dye was filtered, washed with water and dried. The results are given in Table I and II.

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TABLE III Visible absorption spectra and dyeing data of 4a-4f

Dye	*Color on polyester*	*Absorption λ max(nm)*	*Log ε*	*Pick-up*	*Light Fastness*	*Sublimation Fastness*
4a	Reddish orange	525	3.98	3	2–3	4–5
4b	Reddish grey	535	4.00	4	2–3	4–5
4c	Reddish grey	540	4.20	3	2–3	4–5
4d	Bluish pink	515	4.10	3	2–3	4–5
4e	Greenish grey	538	4.15	4	2	4–5
4f	Bluish violet	546	4.20	2	3	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.

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 dyeings, 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 gradings are given in ascending order from 1 to 8. The standard called grey cards are strips of wool dyed fabrics already exposed to natural sunlight and graded for comparison.

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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 rating are given in ascending order from 1 to 5.

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