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Synthesis and Application of 2-Arylazo-10-(oxo)-perinaphtho [1,2-d]thiazole

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2-Amino-10-(oxo)-perinaphtho[1,2-d]thiazole was synthesized and utilized to prepare a range of azo disperse dyes (**1a–f**). These novel aryl azo dyes were studied with respect to their colour and constitutional relationship. Application properties of these dyes on polyester fabric and their fastness properties were evaluated. These dyes were characterized by IR, PMR and visible absorption spectra.

Key Words: Synthesis, Application, Disperse dyes, Polyester fabric, 2-Arylazo-10-(oxo)-perinaphtho[1,2-d]thiazole.

INTRODUCTION

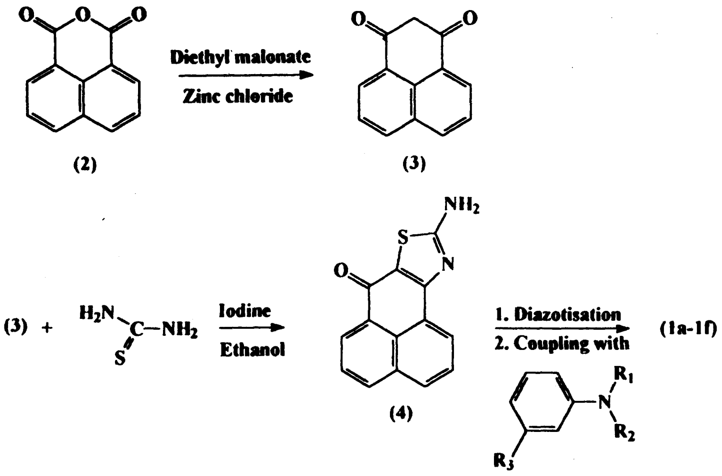
The synthesis of new heterocyclic compounds has been a subject of great interest due to their wide applicability and in the past few decades there has been a significant development in the contribution of heterocyclic compounds to dyestuff chemistry[1–3]. Many hetaryl azo disperse dyes have increasingly been explored in non-textile applications, for example, in reprographic technology, non-linear optical systems, photodynamic therapy and in lasers[4–6]. Thiazole and fused thiazole derivatives have attracted special interest in the field of dyestuff and fluorescent brighteners[7–10]. Donor-accepted or substituted conjugated thiazole compounds offer great promise by producing pronounced bathochromic shifts of the resultant dye molecules. The present investigation reports the utility of new unexploited 2-amino-10-(oxo)-perinaphtho[1,2-d]thiazole in the preparation of monoazo disperse dyes (**1a–f**) in which the keto group is in conjugation with the azo group, which leads to an enhanced effect in the shades obtained on application to polyester fabrics with very good to excellent dyeing properties.

RESULTS AND DISCUSSION

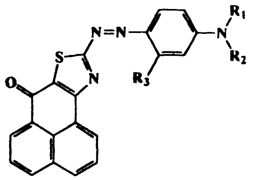
In the present paper, the facile synthesis of perinaphtho thiazole derivative with a diazotizable amino group and mono-azo disperse dyes (**1a–f**) derived form it for their application on polyester fabric has been reported. The azo disperse dyes were synthesized from the key intermediate 2-amino-10-(oxo)-perinaphtho[1,2-d]thiazole (**5**), which was prepared using naphthalic anhydride as the starting material following a series of reactions. Condensation of the anhydride

(2) with diethylmalonate in presence of zinc chloride afforded 3-hydroxy-1-oxophenalen (3). This was converted to 2-amino-10-(oxo)-perinaphtho[1,2-d]thiazole (4) by reaction with thiourea and bromine in ethanol following Hanzsh thiazole synthesis. The IR spectra showed absorption band of the amino group at 3310 cm^{-1} and an absorption band of carbonyl group at 1690 cm^{-1}. The ^1H NMR spectra of the intermediate showed a 2H singlet of amino group at δ 6.3, which was D_2O exchangeable. All data confirmed the expected structure of the intermediate (**4**).

The key intermediate (**4**) was diazotized using nitrosyl sulphuric acid and coupled with various N,N-dialkylated aniline derivatives to effect monoazo disperse dyes **(1a–f)** **(Scheme-1)**.



Scheme 1: Synthesis of monoazo dyes (1a–f)



(1a-1f)

Dye	R_1	R_2	R_3
1a	CH_3	CH_3	H
1b	C_2H_5	C_2H_5	H
1c	C_2H_4OH	C_2H_4OH	H
1d	C_2H_4OH	C_2H_4OH	$NHCOCH_3$
1e	C_2H_4OH	C_2H_4OH	CH_3
1f	C_2H_4OH	C_2H_4OH	Cl

The λ_{max} values for the resultant dyes in dimethyl formamide **(1a–f)** are given in Table-1. The absorption maxima for the dyes were in the range of 510–541 nm, with a broad shoulder near 517–523 nm. IR spectra of the dyes showed absorption bands at 1555–1640 cm^{-1} (—N=N— group), 1620–1715 cm^{-1} (>C=O group) and absence of amino groups, showing no peaks at 3310–3490 cm^{-1}.

TABLE-1

VISIBLE ABSORPTION SPECTRAL DATA FOR DYES **(1a–1f)**

Dye	Absorption maxima (DMF) λ_{max} (nm)	log ε
1a	510	4.01
1b	517	4.08
1c	522	4.11
1d	541	4.13
1e	523	4.09
1f	518	4.04

The dyes were applied to polyester fabric at 2% shade. Data on dye fastness properties are given in Table-2. Except for dye **1e,** lightfastness was very good for all dyes on polyester fabric. Washing, rubbing and sublimation fastness properties were found to be excellent for all dyes.

TABLE-2

FASTNESS PROPERTIES OF THE DYES[a] **(1a–1f)**

Dye	Light fastness	Wash fastness	Rubbing fastness		Sublimation fastness
			Dry	Wet	
1a	5	5	5	5	5
1b	5	5	5	5	5
1c	5	5	5	5	5
1d	5	5	5	5	5
1e	5–6	5	5	5	5
1f	5	5	5	5	5

a = light fastness, 1-8 scale; wash fastness, rubbing fastness and sublimation fastness, 1–5 scale.

The colour values of the dyes on polyester fabric are shown in Table-3. All the dyes found to be brighter as from the L* values, redder as from a* values and bluer except for dyes **(1a–c)** as from b* values.

TABLE-3
COLOUR VALUES OF THE DYES (**1a–1f**)

(light source d65/10° observer)

Dye	L*	a*	b*
1a	58.01	8.71	7.93
1b	70.22	10.25	2.32
1c	49.74	6.75	10.92
1d	53.53	17.89	–6.90
1e	47.52	12.21	–4.79
1f	53.80	10.89	–6.16

EXPERIMENTAL

The materials used were of technical grade. 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 dimethyl formamide solution were recorded on a Genysis-2 spectrophotometer. The dyeing on polyester fabric was done using high temperature high pressure dyeing method. The dyed fabrics were analyzed colorimetrically using a CE-7000A, Gretag- Macbeth computer colour matching system and its accessories. The light fastness testing was conducted according to test method BS 1006, wash fastness testing according to AATCC test method 61-1996 and rub fastness testing was performed using AATCC test method 8-1995.

Naphthalic acid and naphthalic anhydride were synthesized by the method reported in the literature[11]

3-Hydroxy-1-oxophenalen (3)

A mixture of naphthalic anhydride (19.80 g, 0.1 mol) (**2**), diethylmalonate (19.29 g, 0.12 mol) and zinc chloride (30.0 g, 0.2 mol) was heated to 145°C in 1 h and maintained for 5 h. The temperature was then raised to 175°C and kept for 2 h. The reaction mixture was cooled to room temperature and diluted with 500 mL water. The precipitated solid was filtered and washed free of chloride ions with water. The crude product was dissolved in 8% sodium hydroxide solution and filtered. The filtrate was acidified with acetic acid and the solid obtained was filtered and dried to get pure 3-hydroxy-1-oxophenalen (**3**) (15.10 g, 77%), m.p. 254 (255°C).

2-Amino-10-(oxo)-perinaphtho[1,2-d]thiazole (4)

3-Hydroxy-1-oxophenalen (**3**) (19.60 g, 0.10 mol) was taken in ethanol (100 mL) and the reaction mixture was cooled to 5°C. Bromine (20 g, 0.12 mol) in 60 mL ethanol was slowly added in 30–40 min, so that the temperature does not exceed 5°C. The reaction mixture was further stirred for 30 min and thiourea (15.20 g, 0.2 mol) was added portionwise to the solution. It was stirred for 15 min at this temperature and slowly heated to reflux and maintained for 7 h. When the reaction completed, 50 mL ethanol was distilled off and the reaction mixture was cooled to 5°C. The precipitated product was filtered off, washed with sodium thiosulphate followed by cold ethanol. The product was recrystallized from ethanol to yield **(4)** (14.86 g, 63%), m.p. 210–212°C. Elemental analysis: Calculated (%) for $C_{14}H_8N_2S$: C, 70.51; H, 3.36; N, 5.58; Found (%): C, 70.57; H, 3.30; N, 5.96. IR (KBr, cm^{-1}): 3310 ν(—NH_2), 1690 ν(>C=O). ^1H NMR (DMSO): δ 6.3 (s, 2H, NH_2) (D_2O exchangeable), δ 7.8 (m, 6H, aromatic).

General method for the preparation of monoazo dyes (1a–f)

2-Amino-10-(oxo)-perinaphtho[1,2-d]thiazole **(4)** (0.01 mol) was dissolved in acetic acid 20 mL at 10°C and stirred for 15 min. After complete dissolution, nitrosyl sulphuric acid (4.6 mL) equivalent to sodium nitrite (0.01 mol) was slowly added at 5°C with constant stirring for 1 h. The excess nitrous acid was destroyed using sulphamic acid.

The coupler (0.01 mol) was dissolved in acetic acid (10 mL) and cooled to 10°C with external cooling. The clear diazo solution was slowly run into the above solution at 10–15°C with vigorous stirring over a period of 30 min. The pH of the reaction was maintained at 4.5–5.5 by the addition of solid sodium acetate in portions, throughout the coupling period. When the reaction was completed, it was poured into ice and water followed by addition of sodium carbonate solution (20%) until neutral. The separated dye was filtered, washed with water, dried and recrystallized from dimethyl formamide.

2-(4-N,N-dimethylaminophenyl)azo-10-(oxo)-perinaphtho[1,2-d]thiazole (1a)

Dye **(1a)** was obtained as a pink powder (yield 58%, m.p. 223°C). Elemental analysis: Calculated (%) for $C_{22}H_{16}N_4OS$: C, 69.29; H, 4.19; N, 14.69. Found (%): C, 69.12; H 4.26; N, 14.50. IR (KBr, cm^{-1}): 1556 ν(—N=N—); 1635 ν(>C=O); absence of (—NH_2). ^1H NMR ($CDCl_3$): δ 2.3 (s, 6H, CH_3), δ 7–9 (m, 10H, aromatic).

(2-(4-N,N-diethylaminophenyl)azo-10-(oxo)-perinaphtho[1,2-d]thiazole (1b)

Dye **(1b)** was obtained as a pink powder (yield 61%, m.p. 210°C). Elemental analysis: Calculated (%) for $C_{24}H_{20}N_4O_3S$: C, 69.90; H, 4.85; N, 13.59. Found (%): C, 69.71; H, 4.70; N, 13.68. IR (KBr, cm^{-1}): 1610 ν(—N=N—); 1640 ν(>C=O); absence of (—NH_2); ^1H NMR ($CDCl_3$): δ 1.3 (t, 6H, CH_3), δ 2.5 (q, 4H, CH_2), δ 7–9 (m, 10H, aromatic).

(2-(4-N,N-diethyl-β-hydroxyphenylamino)azo-10-(oxo)-perinaphtho[1,2-d] thiazole (1c)

Dye **(1c)** was obtained as a pink powder (yield 73%, m.p. 240°C). Elemental analysis: Calculated (%) for $C_{24}H_{20}N_4O_3S$: C, 64.86; H, 4.50; N, 12.61. Found (%): C, 64.69; H, 4.38; N, 12.79. IR (KBr, cm^{-1}): 1610 ν(—N=N—); 1645 ν(>C=O); absence of (—NH_2). ^1H NMR ($CDCl_3$): δ 2.4–2.7 (m, 8H, CH_2), δ 7–9 (m, 10H, aromatic), δ 9.2 (s, 2H, OH) (D_2O exchangeable).

2-(4-N,N-diethyl-β-hydroxy-3-acetamidophenylamino)azo-10-(oxo)-perinaphtho[1,2-d]thiazole (1d)

Dye **(1d)** was obtained as a violet powder (yield 69%, m.p. 281°C). Elemental analysis: Calculated (%) for $C_{26}H_{23}N_5O_4S$: C, 62.27; H, 4.59; N, 13.97. Found (%): C, 62.01; H, 4.40; N, 13.79. IR (KBr, cm^{-1}): 1610 ν(—N=N—); 1710 ν(>C=O); absence of (—NH_2). ^1H NMR ($CDCl_3$): δ 1.9 (s, 3H, CH_3), δ 2.2–2.6 (m, 8H, CH_2), δ 7.1 (s, 1H, NH) (D_2O exchangeable), δ 7–9 (m, 9H, aromatic), δ 9.1 (s, 2H, OH) (D_2O exchangeable).

2-(4-N,N-diethyl-β-hydroxy-3-methylphenylamino)azo-10-(oxo)perinaphtho [1,2-d]thiazole (1e)

Dye **(1e)** was obtained as a violet powder (yield 63%, m.p. 263°C). Elemental analysis: Calculated (%) for $C_{25}H_{22}H_4O_3S$: C, 65.50; H, 4.80; N, 12.22; Found (%): C, 65.41; H, 4.91; N, 12.09. IR (KBr, cm^{-1}) 1640–1610 ν(—N=N—); 1715 ν(>C=O); absence of (—NH_2). ^1H NMR ($CDCl_3$): δ 1.9 (s, 3H, CH_3), δ 2.2–2.5 (m, 8H, CH_2), δ 7–9 (m, 9H, aromatic), δ 9.2 (s, 2H, OH) (D_2O exchangeable).

2-(4-N,N-diethyl-β-hydroxy-3-chlorophenylamino)azo-10-(oxo)perinaphtho [1,2-d]thiazole (1f)

Dye **(1f)** was obtained as a pink powder (yield 68%, m.p. 227°C). Elemental analaysis: Calculated (%) for $C_{24}H_{19}ClN_4O_4S$: C, 58.24; H, 3.84; N, 11.32. Found (%): C, 57.94; H, 3.82; N, 10.92. IR (KBr, cm^{-1}): 1640–1610 ν(—N=N—); 1690 ν(>C=O); absence of (—NH_2). ^1H NMR ($CDCl_3$): δ 1.9–2.2 (m, 8H, CH_2), δ 7–9 (m, 9H, aromatic), δ 9.2 (s, 2H, OH) (D_2O exchangeable).

Conclusion

Azo disperse dyes based on 2-amino-10-(oxo)-perinaphtho[1,2-d]thiazole have been synthesized. These dyes give reddish violet to blue shades on polyester fabric that have very good fastness properties including light fastness, which is very uncommon in heterocyclic disperse dyes. The colour values on polyester fabric and spectral chracteristics in dimethyl formamide are determined.

REFERENCES

1. M.A. Weaver and L. Shuttleworth, *Dyes and Pigments*, **3**, 81 (1982).
2. A.D. Towns, *Dyes and Pigments*, **42**, 3, 28 (1999) [and references cited therein].
3. G. Hallas, in: J. Griffiths (Ed.), Developments in the Chemistry and Technology of Organic Dyes, Blackwell Scientific, London, p. 33 (1984).
4. P. Gregory, *Rev. Prog. Coloration*, **24**, 1 (1994).
5. P.F. Gordon, in: D.R. Waring and G. Hallas (Eds.), The Chemistry and Application of Dyes, Plenum, New York, Chapter 8 (1990).
6. E. Sternberg and D. Dolphin, in: M. Matsuoka (Ed.), Infrared Absorbing Dyes, Plenum, New York, Chapter 15 (1990).
7. Mitsui Toatsu Chem. Inc., Japan Kokai Tokkyo Koho, JP 81, 169, 885 (1981).
8. ———, Japan Kokai Tokkyo Koho, JP 82, 105, 457 (1983).
9. Agfa-Gevaert, European Patent EP 687, 674 (1995).
10. Eastman Kodak, UV Patent 5, 179, 207 (1993).
11. S.N. Naik, Synthesis of Heterocyclic Compounds, M.Sc. (Tech.) Thesis, University of Mumbai (1984).

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