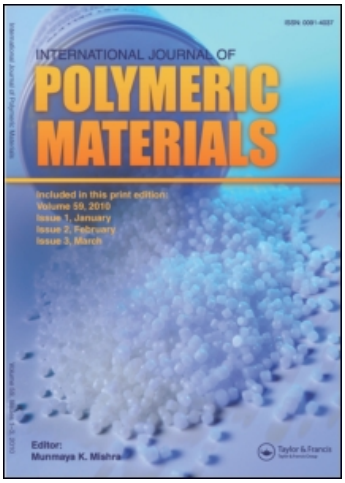

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Arylene Azo 1,5-dihydroxy Naphthalene-formaldehyde Oligomeric Dyes

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A series of oligomeric acid azo dyes has been prepared by coupling various aromatic diazonium salts to 1,5-dihydroxy-naphthalene formaldehyde (1,5-DHNF) oligomer. They were evaluated in terms of their softning point, yield, colour, solubility, IR and UV-Vis spectra. Structure property relationships are discussed and dyeing on wool, silk and nylon-6,6 were assessed. Dyeing on wool, silk and nylon-6,6 resulted in yellow, orange and brown to red colorations having excellent light fastness and washing fastness.

Keywords: Oligomers; Azo dyes; Diazo salts; IR-UV-Vis spectroscopy; Light fastness; Wash fastness

INTRODUCTION

Whilst napthols are well established intermediates for the synthesis of dyes, the use of napthol-formaldehyde condensates as coupling components in the formation of azo dyes and pigments has received little attention. However the use of phenolic resins as a coupling components in the formation of azo dyes has been reported [1–3] and the products are stated to be useful in the dyeing of synthetic and natural fibres, and also for leather. They are stated to have good fastness properties. One of the authors (HSP) recently studied the

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oligomeric dyes in this direction [4–6]. Hence in continuation of this work [4–6] the present work comprises some acid azo dyes based on the use of 1,5-dihydroxy naphthalene-formaldehyde condensates as a coupling components.

EXPERIMENTAL

Materials

1,5-dihydroxy naphthalene was of analytical grade and was crystallized from ethanol prior to use. Formaldehyde was of laboratory grade. For diazonium salt preparation, analytical grade arylamines were used (see footnote, Tab. II). Wool, silk and nylon-6,6 were gifted by Kiran Threads, Vapi.

Synthesis of 1,5-dihydroxy Naphthalene-formaldehyde (1,5-DHNF) Oligomer

In a round bottom flask (250 ml) a mixture of 1,5-dihydroxy naphthalene (0.2 mole), formaldehyde (0.1 mole), potassium carbonate (0.5 gm) was stirred until a solid mass was obtained. Generally the reaction proceeds at room temperature. The solid resin was washed with large amount of water and was dried. The brownish black colored solid product was kept in the desicator. The yield was 80% and it was designated as (1,5-DHNF) oligomer.

Synthesis of Oligomeric Azo-naphthalene-formaldehyde Dyes

1,5-DHNF oligomer (0.1 mole) was dissolved in 10% aq. NaOH (75 ml) and the pH of the liquor was adjusted to 10–10.5. The solution

TABLE I Characterization of 1,5-dihydroxynapthalene formaldehyde (1,5-DHNF) oligomer

	Softning point	*Elemental analysis* (%)				$\overline{Mn}$ *estimated by*
		C		*H*		
Colour	(°C)	*Calcd*	*Found*	*Calcd*	*Found*	*VPO*
Brown	> 230	77.41	77.3	5.37	5.30	744

where VPO = Vapour Pressure Osmometry.

TABLE II Characterization of oligomeric azo-1,5-DHNF dyes

Oligomeric azo-1,5-DHNF dyes a	*Colour*	*Nitrogen (%) Found*	*Cal.*	*Mean no. of azo groups*	*Yield (%)*	*$\overline{Mn}$ by VPO*	*λ max*	*log ε*	*Dyeing on wool LF*	*WF*	*Dyeing on silk LF*	*WF*	*Dyeing on nylon LF*	*WF*
1,5-DHNF-1	Dark Violet	7.81	7.80	1.94	85	1404	462	4.62	3 to 4	4	4	5	4 to 5	6
1,5-DHNF-2	Purple	9.55	9.50	1.92	88	1244	467	4.59	4	5	4	5	5	6
1,5-DHNF-3	Pinkish Brown	8.17	8.20	1.91	80	1364	470.5	4.46	4	5	4 to 5	5	5	5
1,5-DHNF-4	Dark Brown	9.55	9.50	2	91	1264	474	4.52	4 to 5	6	3 to 4	4	5	5
1,5-DHNF-5	Brown	10.31	10.30	1.95	92	1212	487.5	4.56	4 to 5	6	4	5	5	5
1,5-DHNF-6	Katthal Brown	10.31	10.20	1.93	86	1228	360	4.08	3 to 4	4	4	5	3 to 4	5
1,5-DHNF-7	Brownish Orange	10.31	10.20	1.96	84	1232	478	4.42	4	5	4 to 5	5	4	5

LF = Light Fastness; WF = Wash Fastness; a = Amines used as diazo components: (1) H-acid; (2) Y-acid; (3) Chicago-acid; (4) J-acid; (5) Tobias-acid; (6) Laurent's-acid; (7) Brooner-acid.

was then cooled to 0°C and the appropriate diazonium liquor was added to it drop wise maintaining the temperature 0°C and the required pH was maintained. The mixture was stirred and the resultant acid azo dyes were obtained by evaporation procedure. The product was Soxhlet-extracted with ether to remove any monoazo dye resultant from the presence of any residual naphthol in the oligomer.

Characterization

Elemental analysis of 1,5-DHNF oligomer and oligomeric azo 1,5-DHNF dyes was carried out on an Elemental Analyzer (Carlo Erba, Italy). The mean number of azo groups of the dyes was determined by the known method [7]. Visible spectra were recorded on Beckman DK-2A spectrophotometer and the thermal stability of the dyes were assessed on Du Pont 951 Thermal analyzer at a heating rate of 10°C/min. The number average molecular weight of all the oligomeric cid azo dyes were estimated both by VPO and nonaqueous conductometric titration method. The $\bar{M}n$ (by VPO) of 1,5-DHNF oligomer is represented in Table I. IR spectra were recorded on Nicolet 600 D using KBr matrix as reference.

Dyeing of Wool, Silk and Nylon-6,6 with Oligomeric Azo-1,5-DHNF Dyes

A known quantity of each oligomeric azo 1,5-DHNF dyes (Tab. II) was taken into water, together with required acid medium. Wool, silk and nylon-6,6 (2.0 gm) were colored at 2% depth using liquor ratio of 50 : 1 and a dyeing temperature of 90°C. Fastness properties of the dyes were determined according to recognized procedure [8].

RESULTS AND DISCUSSION

Infusible compounds of the type studied have been used as a pigments rather than dyes due to their poor dyeability properties [9]. Napthol-formaldehyde oligomers are known to have poor dyeability and it was therefore attempted to obtain oligomers of low molecular weight from the condensation of 1,5-dihydroxy naphthalene with formaldehyde.

Phenol formaldehyde oligomers can be utilized in various applications and many synthetic methods for their formation are available [10]. The synthesis of napthol-formaldehyde oligomers has received less attention. To provide suitable oligomer for the present study, a number of variable in the synthesis, *i.e.*, molar ratio of reactants, temperature, catalysts and reaction time were optimized. The 1,5-DHNF oligomer was obtained as a solid product, which remained in this form even after six to seven months of storage in vacuum desicator. The C and H contents (Tab. I) for 1,5-DHNF oligomer is in agreement with the proposed structure, which also emphasize the probable heterogeneous nature of the product due to the reaction proceeding at the para position.

All the oligomeric azo-1,5-DHNF dyes listed in Table II were soluble in solvents ethanol, 1,4-dioxane, DMF and DMSO. As 1,5-DHNF condensates are the mixtures of different molecular DHNF oligomeric chains the traces of free napthol, the resulting azo 1,5-DHNF dyes could be non-heterogeneous. On the premise [8–11] that the simple napthol based azo dyes are soluble in solvents like ether, ethanol, 1,4-dioxane, DMF and DMSO, the oligomeric azo 1,5-DHNF dyes were Soxhlet-extracted with ether-ethanol (1 : 1) to remove both the simpler dyes and traces of any low molecular weight oligomeric azo 1,5-DHNF dye. The values of nitrogen content of the azo 1,5-DHNF dyes indicate that there may be two azo groups present per oligomer chain. This is in agreement with the estimated azo group content of samples in the series of oligomeric azo 1,5-DHNF dyes.

IR spectra of the 1,5-DHNF oligomer and oligomeric dyes are furnished in Figures 1 and 2. Upon careful observation, a sharp peak around $1600\,cm^{-1}$ is found for substituted naphthalene, a band at $\sim 2850\,cm^{-1}$ of $—CH_2—$ group, a sharp band around $1380-1400\,cm^{-1}$ of aromatic hydroxyl group are observed in the spectra of 1,5-DHNF.

The UV-Visible spectra of the azo-1,5-DHNF dyes were recorded in DMF. It is apparent that the wavelength of maximum absorption is related to the azo groups in the compounds and it is observed within the region 360–488 nm, variations in λ_{max} being attributed to structural variations in the oligomer and to the nature of aryl amine used as a diazo component. The thermal stability of the azo 1,5-DHNF dyes was also assessed in terms of the loss of weight at different

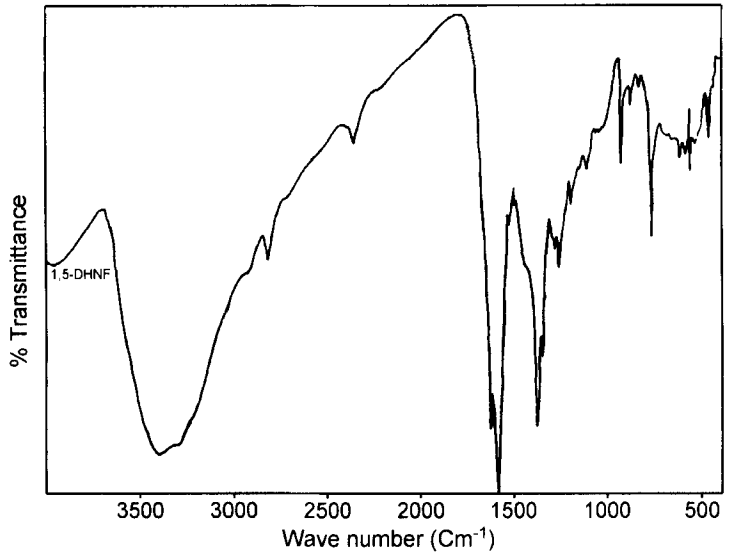


FIGURE 1 IR spectrum of 1,5 DHNF oligomer.

temperatures (figure not shown) at a constant heating rate of 10°C/min in air. This showed that the azo 1,5-DHNF dyes began to decompose at around 190°C, with weight loss being complete at around 220°C depending upon the structural variations.

The oligomeric azo 1,5-DHNF dyes were dyed on wool, silk and nylon-6,6 fibres at 2% depth of shade and gave yellow to brown shades implied in Table II. The dyebath exhaustion of the oligomeric dyes in the dyeing of wool, silk and nylon-6,6 fibres was low (30–50%) as compared with the values of 70–80% of simple aryl azo-phenols, -cresols, -resorcinols or -napthols [8–11]. This difference was probably attributed to molecular size considerations. Results for the percentage fixation of the oligomeric dyes in the dyeing of the wool, silk and nylon-6,6 indicated that the oligomeric dyes showed higher values (70–90%) than simple azo dyes (60–80%).

The light fastness of the oligomeric azo 1,5-DHNF dyes is shown in Table II. The light fastness of the azo 1,5-DHNF dyes on wool, silk and nylon-6,6 fibres varied from moderate to good on wool and silk and good to very good on nylon-6,6. The majority of the dyes are having higher ratings. The washing fastness (neutral detergents) varied from very good to excellent on wool, silk and nylon-6,6 fibres.

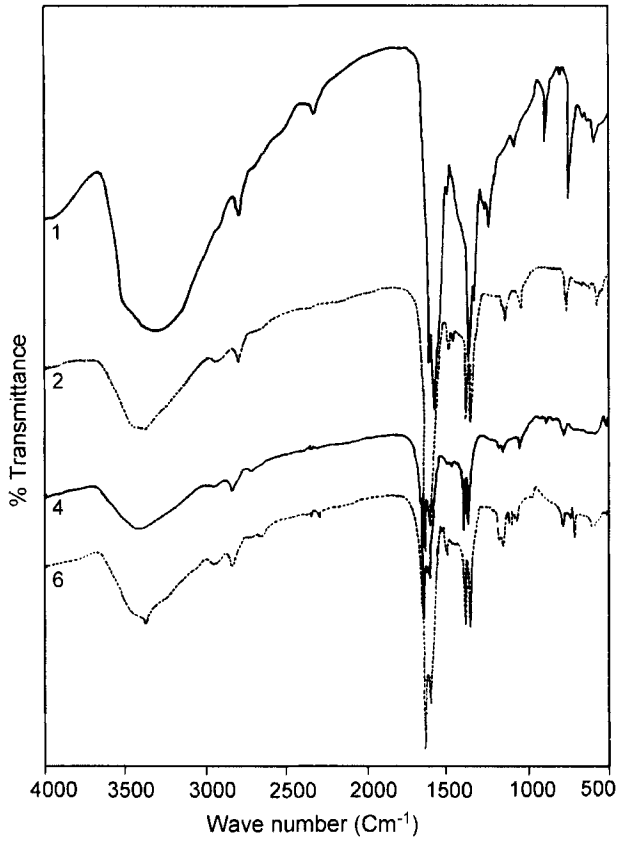
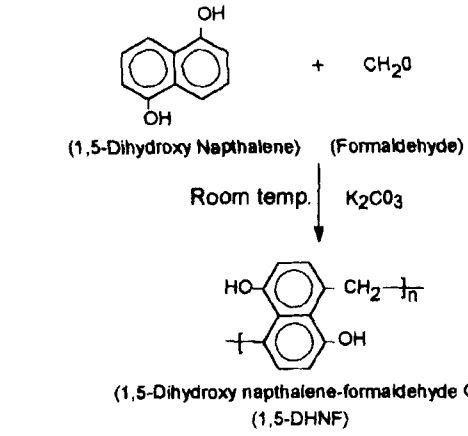
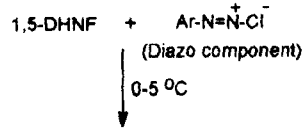


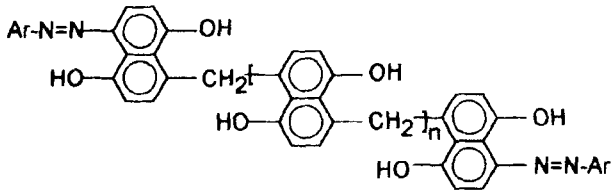
FIGURE 2 IR spectra of 1,5-DHNF-1, -2, -4, -6 (Tab. II).

Compared with the simple azo-phenol dyes, the dyeing produced from the oligomeric azo 1,5-DHNF dyes had moderate light fastness, but slightly higher washing fastness.

It is of interest to note that most of the polymeric dyes previously reported [10–11] when dyed on various textiles, gave somewhat unlevel colorations. But with the azo 1,5-DHNF dyes described in the present work, particularly when the dyeing were carried out for relatively short periods (1.5 hrs on wool and silk, 45 mins on nylon-6,6) and at low temperatures, better dyeings were obtained. The results of the work showed excellent fastness properties of the produced dyes and helps to minimize the greatest problem of pollution.



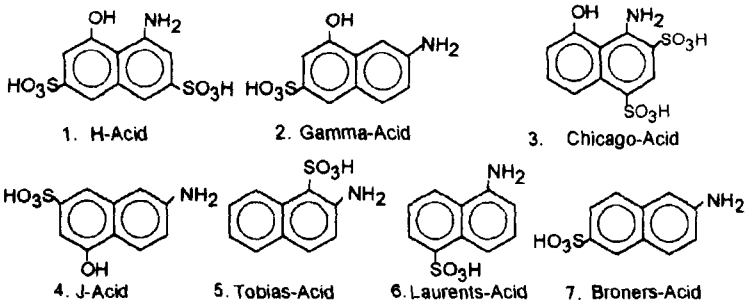




(Oligomeric Acid Azo Dyes)

Where: n=2,3

Diazo-Components are as under:



SCHEME 1

Acknowledgements

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