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Azo Dyes Based on Phenolic Oligomers: Part 2. Arylene Azo-Naphthol-Formaldehyde Oligomer Dyes

Hasmukh S. Patel & Babu D. Lad

Department of Chemistry, Sardar Patel University,
Vallabh Vidyanagar 388120, India

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ABSTRACT

A series of oligomeric azo dyes has been prepared by coupling various aromatic diazonium salts to 1-naphthol–formaldehyde (1-NF) and 2-naphthol–formaldehyde (2-NF) oligomers. They were evaluated in terms of their softening points, yields, colour, solubility and UV–Vis spectra. Structure–property relationships are discussed and dyeings on polyester PET and nylon-6,6 assessed. Dyeings on polyester and nylon-6,6 resulted in yellow, orange and brown to red colorations having excellent fastness to light and washing.

1 INTRODUCTION

Whilst naphthols are well established intermediates for the synthesis of dyes, the use or naphthol–formaldehyde condensates as coupling components in the formation of azo dyes and pigments has received little attention. However, the use of phenolic resins as coupling components in 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 of leather. They are stated to have good fastness properties. It was therefore of interest to investigate some azo dyes based on the use of naphthol–formaldehyde condensates as coupling components.

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2 EXPERIMENTAL

2.1 Materials

1- and 2-naphthols were of analytical grade and were crystallized from ethanol prior to use. Formalin and oxalic acid were of laboratory grade. For diazonium salt preparation, analytical-grade arylamines were used (see footnote, Table 2).

Polyester PET (100%) was supplied by Mafatlal Fabrics, Ahmedabad, India, and nylon-6,6 by Vareli Fabrics, Surat, India.

2.2 Synthesis of naphthol–formaldehyde oligomers

1-Naphthol–formaldehyde (1-NF) and 2-naphthol–formaldehyde (2-NF) oligomers were prepared by the following methods.

2.2.1 1-Naphthol–formaldehyde (1-NF) oligomer
A mixture of 1-naphthol (1 mol), formalin (0·5 mol), oxalic acid (2·0 g) and benzene (500 ml) was refluxed for 3 h. The reaction mixture was then distilled under reduced pressure to remove benzene and water and the resulting liquor was washed with petroleum ether (b.p. 40–60°C). The oligomer was collected as a viscous material.

2.2.2 2-Naphthol–formaldehyde (2-NF) oligomer
To a solution of 2-naphthol (1 mol) in benzene (500 ml), formalin (0·5 mol) and oxalic acid (2·0 g) and the mixture was refluxed until the solid oligomeric product was formed. This was filtered, washed with hot water and air-dried; it decomposed at 156–165°C.

Characterization data for these oligomers are reported in Table 1.

2.3 Synthesis of oligomeric arylene azo-naphthol–formaldehyde dyes

1-NF (or 2-NF) oligomer (0·1 mol) was dissolved in 10% aq. NaOH (75 ml) and the pH of the liquor was adjusted to 10–10·5. The solution was then cooled to 0°C and the appropriate diazonium liquor was added to it dropwise whilst maintaining a temperature of 0°C and a pH 10–10·5. After coupling was complete the reaction mixture was stirred for 1 h at 0°C and then acidified to pH 5·5. The precipitated product was filtered, washed with water, dried, and Soxhlet-extracted with ether–methanol (1:1, v/v) to remove any monoazo dye resultant from the presence of any residual naphthol in the oligomer.

TABLE 1
Characterization of Naphthol–Formaldehyde(NF) Oligomers

Naphthol–formaldehyde oligomer	*Appearance*	*Softening point* (°C)	*Elemental analysis* (%)				*Efflux viscosity time* (*s*) *at room temperature* (~32°C)
			C		*H*		
			Calcd	*Found*	*Calcd*	*Found*	
1-Naphthol-F (1-NF)	Dark brown liquid	—	84·6	84·4	5·1	5·1	102
2-Naphthol-F (2-NF)	Light solid	156–158	84·6	84·5	5·1	5·2	—

2.4 Characterization

Elemental analyses of the NF oligomers and oligomeric azo-NF dyes was carried out on an Elemental Analyzer (Carlo Erba, Italy). The efflux viscosity time of the 1-NF oligomer was measured at room temperature (~32°C) using a B:5-1733 flow cup. The mean number of azo groups of the dyes was determined by known methods.[4] Visible spectra were recorded on a Beckman DK-2A spectrophotometer and the thermal stability of the dyes was assessed on a Du Pont 951 Thermal Analyzer at a heating rate of $10°C\,min^{-1}$.

2.5 Dyeing of polyester PET and nylon-6,6 with oligomeric azo-NF dyes

A known quantity of each oligomeric azo-NF dye (Tables 2 and 3) was taken into water, together with the same quantity of Dodemol (dispersing agent), 2–3 drops of wetting agent (2% lauryl sulphate solution) and a dispersion of the azo-NF dye was then prepared using ultrasonic vibration for 2 h. Polyester PET and Nylon-6,6 (2·0 g) were colored at 1% depth using a liquor ratio of 50:1 and a dyeing temperature of 90°C.

Fastness properties of the dyes were determined according to recognized procedures.[5]

3 RESULTS AND DISCUSSION

Infusible compounds of the type studied have been used as pigments rather than dyes due to their poor dyeability properties.[6] Naphthol–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- and 2-naphthols with formaldehyde.

TABLE 2
Characterization of Oligomeric Azo-1-NF Dyes

Oligomeric azo-1-NF[a]	*Yield (%)*	*Softening range (°C)*	*Found N (%)*	*Mean number of azo groups*	*Colour*	λ_{max} *(nm)*	log ε	*Dyeing on polyester*		*Dyeing on nylon*	
								Lightfastness	*Washing fastness*	*Lightfastness*	*Washing fastness*
1-NF-**1**	90	142–143	6·6	1·89	Reddish brown	480	4·43	4–5	5	5	4–5
1-NF-**2**	95	195–198	6·6	1·90	Brown	410	4·58	3–4	3	4–5	5
1-NF-**3**	79	252–255	6·5	2·00	Red	490	4·74	3	3	3–4	4
1-NF-**4**	88	117–120	6·0	1·90	Orange	4·90	4·43	3–4	4	4–5	4
1-NF-**5**	93	98–101	6·0	1·80	Red	370	4·88	3	3–4	4	3–4
1-NF-**6**	91	148–150	6·0	2·00	Brown	345	4·34	3	3–4	4	3–4
1-NF-**7**	91	103–106	6·0	1·90	Reddish	495	4·265	4	4–5	5	4–5
1-NF-**8**	92	88–90	6·3	1·90	Brown	425	4·52	3–4	3	3–4	4

[a] Amines used as diazo components: **1**, aniline; **2**, *p*-toluidine; **3**, 4-phenetidine; **4**, 4-nitroanilene; **5**, 1-naphthylamine; **6**, 4-anisidine; **7**, 4-chloroaniline; **8**, 3-nitroaniline.

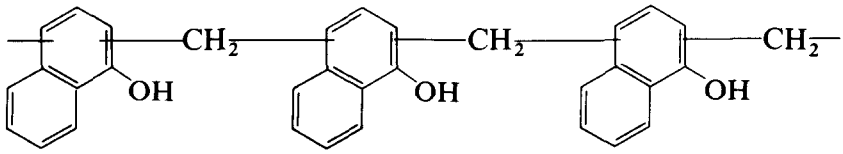
TABLE 3
Characterization of Oligomeric Azo-2-NF Dyes

Oligomeric azo dye[a]	*Yield (%)*	*Softening range (°C)*	*Found N (%)*	*Mean number of azo groups*	*Colour*	λ_{max} *(nm)*	log ε	*Dyeing on polyester*		*Dyeing on nylon*	
								Lightfastness	*Washing fastness*	*Lightfastness*	*Washing fastness*
2-NF-**1**	83	137–140	8·1	1·90	Orange	485	4·67	5–6	5	5	4–5
2-NF-**2**	76	180–182	8·0	2·00	Red	455	3·98	3	3	4–5	4
2-NF-**3**	89	94–98	8·0	1·90	Orange	450	4·55	5	5–6	5	5
2-NF-**4**	86	191–193	7·2	2·00	Orange	490	4·77	3–4	4	4	4–5
2-NF-**5**	89	93–96	7·2	1·80	Reddish brown	370	4·815	4	3–4	5	5
2-NF-**6**	83	172–174	7·2	1·80	Yellow	490	4·37	6	5–6	5–6	6
2-NF-**7**	90	116–119	7·1	1·83	Violet	495	4·37	4–5	4–5	5	4–5
2-NF-**8**	88	108–110	7·4	1·90	Brown	430	4·83	3–4	4	4–5	5

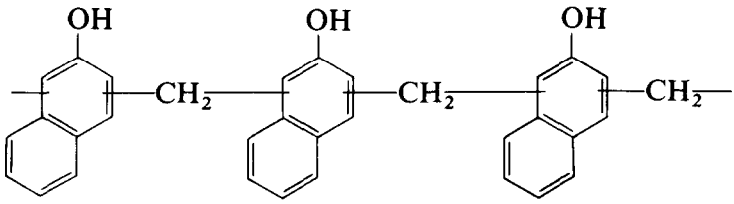
[a] See footnote to Table 2.

Phenol–formaldehyde oligomers can be utilized in various applications and many synthetic methods for their formation are available.[7] The synthesis of naphthol–formaldehyde oligomers has received less attention. To provide suitable oligomers for this present study, a number of variables in the synthesis, i.e. molar ratios of reactants, temperature, catalyst and reaction time, were optimized. The 1-NF oligomer was obtained as a viscous liquid, which remained in this form even after six to seven months' storage in a vacuum desiccator. The efflux time at toom temperature (~ 32°C) for the flow viscosity of 1-NF oligomer remained constant during this storage period.

The C and H contents (Table 1) for both the 1-NF and 2-NF oligomers are in agreement with the proposed structures (**I** and **II**), which also emphasize the probable heterogeneous nature of the products due to reaction proceeding of the *ortho* position, the more probable *para* position, or a combination of the two.



I 1-NF oligomer



II 2-NF oligomer

All the oligomeric azo-NF dyes listed in Tables 2 and 3 were soluble in solvents as ethanol, 1,4-dioxane, DMF and DMSO. As the NF condensates are mixtures of different molecular NF oligomeric chains and traces of free naphthol, the resulting azo-NF dyes could be non-homogeneous and, on the premise[8] that simple naphthol-based azo dyes are soluble in solvents such as ether, ethanol, 1,4-dioxane, DMF and DMSO, the oligomeric azo-NF dyes were Soxhlet-extracted with ether–ethanol (1:1) to remove both the simpler dyes resulting from traces of free naphthol and of traces of any lower molecular-weight oligomeric azo-NF dye. The resultant azo-NF dyes were solids, having softening points within the range 94–260°C depending upon the nature of the dye. The values of the nitrogen content of the azo-NF 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 this series of oligomeric azo-NF dyes.

The UV-visible spectra of the azo-NF dyes were recorded in DMF. Absorption maximum and extinction coefficients are shown in Tables 2 and 3. It is apparent that the wavelength of maximum absorption is relatable to the azo group in the compounds and it is observed within the region 370–543 nm, variations in λ_{max} being attributable to structural variations in the oligomer and to the nature of the arylamine used as diazo component.

The thermal stability of the azo-NF dyes was also assessed in terms of the loss in weight at different temperatures at a constant heating rate of 10°C min^{-1} in air. This showed that the azo-NF dyes began to decompose at around 190°C, with weight loss being complete at around 220°C depending on structural variations.

The oligomeric azo-NF dyes were dyed on polyester PET and nylon-6,6 fibres at 1% depth of shade and gave the yellow to brown shades implied in Tables 2 and 3. The dyebath exhaustion of the oligomeric dyes in the dyeing of polyester PET and nylon-6,6 fibres was low (30–50%) compared with the values of 70–80% of simple arylazo-phenols, -cresols, -resorcinols, or -naphthols).[8] These differences are probably attributable to molecular size considerations. Results for the percentage fixation of the oligomeric dyes in the dyeing of polyester PET and nylon-6,6 indicated that the oligomeric dyes showed higher values (70–90%) than simple azo dyes (60–80%).

The lightfastness of the oligomeric azo-NF dyes are shown in Tables 2 and 3. The lightfastness of both the azo-1-NF and azo-2-NF dyes on polyester PET and nylon-6,6 fibres varied from moderate (3) to good (4) on polyester PET and good (4) to very good (5) on nylon-6,6, the majority of the dyes having the higher rating. The washing fastness (neutral detergent) varied from moderate (3) to very good (5) on both polyester PET and nylon-6,6 fibres. Compared with simpler azo-phenol dyes,[8] the dyeings produced from the oligomeric NF dyes had more moderate lightfastness, but slightly higher washing fastness.

It is of interest to note that most of the polymeric dyes previously reported[8], when dyed on various textiles, gave somewhat unlevel colourations. With the azo-NF dyes described in this present work, and particularly when dyeings were carried out for relatively short periods (1·5 h on polyester PET, 45 min or nylon-6,6) and at lower temperatures, level dyeings were obtained.

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