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Liquid Crystalline Behaviour of Some Azobenzene Dyes

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ABSTRACT

A number of 4-aminoazobenzene dye units have been synthesised and subjected to thermal analysis by differential scanning calorimetry and hot stage optical microscopy. It is observed that liquid crystalline phase behaviour exists for those dyes having a nitro group in the 4-position on the terminal phenyl ring and with a short hydrocarbon 'tail' at the amino site with a terminal alcohol. Other structures in the series were not liquid crystalline. It appears that a highly polar terminal group and short hydrocarbon tail is required to form thermotropic mesophases.

1 INTRODUCTION

Azobenzene dyes such as CI Disperse Red I are frequently employed in experimental work on non-linear optical (NLO) devices.[1] The dye, which has an intense absorption in the blue region of the spectrum, can be poled to give second harmonic generation when dispersed in a polymer film. Dyes of this type with a hydroxyl functionality can be converted into acrylic monomers which undergo homo- or co-polymerisation to give side chain NLO polymers.[2-4] We have attempted to graft various azobenzene dyes, of a type similar to CI Disperse Red I, to a poly (chloroethyl vinyl ether) backbone.[5] We noted that some of the polymers showed thermotropic behaviour, but we have been unable to report this aspect of the work because of difficulties encountered in purifying and characterising the polymers. This led us to study the thermotropic

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behaviour of a number of azobenzene dyes to establish any details of structure that could lead to mesophases being formed. Light-scattering problems associated with the formation of mesophases generally make side chain liquid crystal polymers and low molecular weight mesogens undesirable for NLO applications.

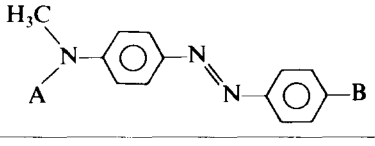
2 EXPERIMENTAL

2.1 Synthesis of 4-aminoazobenzene dyes (1a–g as in Table 1)

The general route to the synthesis of these dyes involves the initial preparation of a tertiary amine from an *N*-alkyl aniline and an ω-hydroxy alkyl chloride. This undergoes diazotisation with a tetrafluoroborate diazonium salt derived from a 4-substituted aniline. A typical procedure is given below.

*2.1.1 4′-[(2-hydroxyethyl)methylamino]-4-nitrobenzene (**1a**)*
A mixture of freshly distilled *N*-methylaniline (26·8 g, 0·252 mol), 2-chloroethanol (20·6 g, 0·256 mol), anhydrous potassium carbonate (35 g, 0·253 mol), potassium iodide (0·6 g) and 1-butanol (150 ml) was stirred and refluxed under nitrogen for four days. The cooled solution was filtered and the solvent removed. The residue was distilled under reduced pressure to give 18·7 g (50%) yield of *N*-2-hydroxyethyl-*N*-methylaniline

TABLE 1
Elemental Analyses of **1a–g**



	A	*B*	*C (%)*	*H (%)*	*N (%)*
1a	$(CH_2)_2OH$	NO_2	60·0 (60·0)	5·1 (5·4)	18·7 (18·7)
1b	$(CH_2)_3OH$	NO_2	61·5 (61·7)	5·5 (5·8)	17·8 (17·8)
1c	$(CH_2)_6OH$	NO_2	64·5 (64·0)	7·0 (6·8)	14·9 (15·7)
1d	$(CH_2)_2OH$	OCH_3	67·5 (67·3)	6·2 (6·7)	14·8 (14·7)
1e	$(CH_2)_3OH$	OCH_3	68·5 (68·2)	7·5 (7·1)	14·8 (14·1)
1f	$(CH_2)_6OH$	OCH_3	69·9 (70·3)	8·3 (7·9)	11·9 (12·3)
1g	$(CH_2)_6OH$	H	73·0 (73·3)	7·6 (7·81)	14·2 (13·5)

For elemental analysis, the expected amounts based upon empirical formulae are given in brackets.

(b.p. 123–127°C at 0·5 mm Hg); ^{1}H NMR ($CDCl_3$) δ = 1·8 (quint, 2H), 2·1 (s, 1H), 2·9 (s, 3H), 3·4 (t, 2H), 3·7 (t, 2H), 7·0 (dt, 5H). The above product (11·4 g, 48·3 mmol) as a solution in aqueous acetic acid (50% by vol) was added to a stirred suspension of 4-nitrobenzene diazonium tetrafluoroborate (10 g, 48·3 mmol) in 100 ml of aqueous acetic acid (50% by vol) at room temperature. After stirring for four hours the deep red solution was neutralised with ammonia solution and the product filtered off, washed with water and dried. It was then recrystallised from toluene to yield 8·7 g of crystals (50%). The product gave one spot on a TLC plate. ^{1}H NMR ($CDCl_3$) δ = 2·1 (s, 1H), 3·1 (s, 3H), 3·6 (t, 2H), 3·9 (t, 2H), 6·8 (d, 2H), 7·9 (dd, 4H), 8·3 (d, 2H). ^{1}H NMR spectra were determined using a Jeol 90 MHz NMR spectrometer. Visible absorption spectra were obtained using a Kontron 860 spectrophotometer.

2.2 Thermal analysis

2.2.1 Differential scanning calorimetry
This was carried out on a Perkin-Elmer DSC-7 instrument with heating/cooling rates of 20°C/min.

2.2.2 Hot stage microscopy
This was carried out using a Nikon Labophot polarising microscope fitted with a Linkam THMS 600 hot stage controlled by a Linkan TMS 91 system.

3 RESULTS

3.1 Optical microscopy

All samples were examined by hot stage microscopy between crossed polars. Only two samples showed any mesophases (**1a**, **b**). Both samples showed smectic A fan texture.

3.2 Differential scanning calorimetry

The two samples mentioned above (**1a**, **b**) were examined by DSC. Figure 1 shows the thermal traces for **1b** on first heating and subsequent cooling. The second heating cycle (not shown) was identical to the first. The transition temperatures for the endotherms agree closely with the optical observations and are given in Table 2, together with the enthalpies for the phase changes. The exothermic transitions on the first cooling cycle are also given.

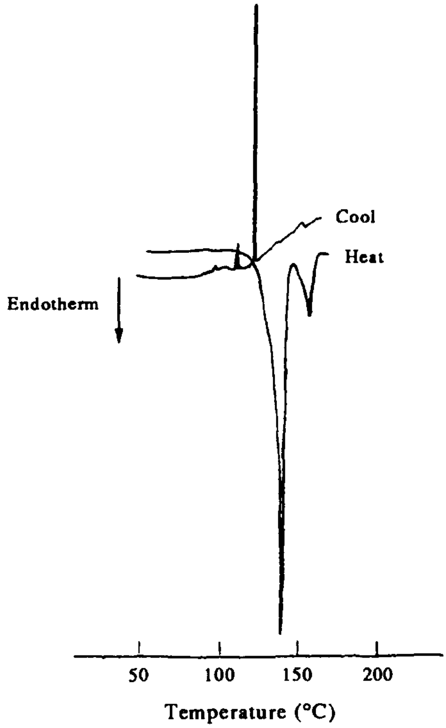


Fig. 1. Differential scanning calorimetry trace for compound **1b** on heating and cooling (first cycle). The exotherm is truncated on cooling.

TABLE 2
DSC Thermal Data for **1a–g**

Sample	*First heating cycle*	*Cooling cycle*
1a	128 (2·3)*	175
	161 (42·3)[a]	143
	175 (6·8)[b]	
1b	140 (65·0)[a]	119
	158 (10·1)[b]	156
1c	139·3 (34·2)	135·2
1d	137·5 (37·7)	137·1
1e	125·4 (38·2)	124·2
1f	40·2 (25·2)	39·6
1g	−24·6 (23)	−25·2

Thermal transitions given in °C.
Figures in parentheses are enthalpies in $J\ g^{-1}$.
* Not observed optically.
[a] Assigned optically as crystalline to smectic A transition.
[b] Assigned optically as smectic A to isotropic melt transition.

TABLE 3
Maximum Absorbance Characteristics

Compound	*λmax/nm*	*ε/dm^3 mol^{-1} cm^{-1}*
1a	485	29,600
1b	485	29,000
1c	485	27,600
1d	412	17,700
1e	412	17,600
1f	412	15,600
1g	416	10,600

3.3 Visible absorption spectrophotometry

The visible absorption spectrum in tetrahydrofuran was determined for a selection of these compounds and the molar extinction coefficients determined. A single broad band was observed in the blue region of the spectrum. The data are given in Table 3.

4 DISCUSSION

From the results it is clear that the two compounds which have a terminal nitro group and a short hydrocarbon chain (two or three methylene units) with a terminal alcohol group show liquid crystalline behaviour over the temperature ranges shown. It appears that increasing the length of the hydrocarbon 'tail' destroys the thermotropic behaviour since the dye with a six methylene unit (**1c**) shows no liquid crystalline behaviour. Attempts at producing a dye with a hydrocarbon tail of four methylene units were unsuccessful due to the cyclisation of 4-chlorobutanol in the early stages of the synthesis. Replacement of the 4'-nitro group by a methoxy functionality resulted in a complete absence of mesomorphic behaviour (in dyes **1d–f**).

The variation in melting temperatures is indicated in Fig. 2.

Robello[4] has used dye **1c** to produce an acrylic monomer by esterification of the alcohol functionality with acryloyl chloride. We found **1c** to be more difficult to purify than **1a** or **b** and the elemental analysis indicates that our sample is not as pure as that reported by Robello. The melting point of **1c** obtained by Robello was 3–5 degrees higher than ours. Like us, however, Robello failed to observe any liquid crystallinity in **1c**. Interestingly, Robello reported that upon homopolymerisation, the acrylic ester did show smectic behaviour with a clearing temperature of 180°C;

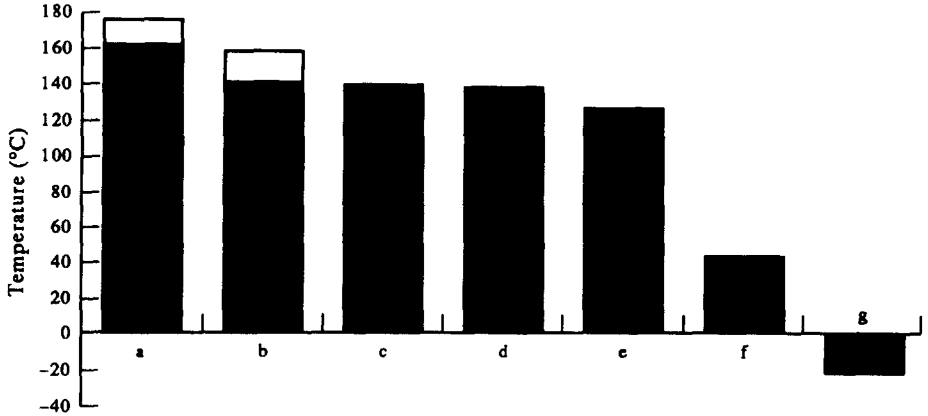


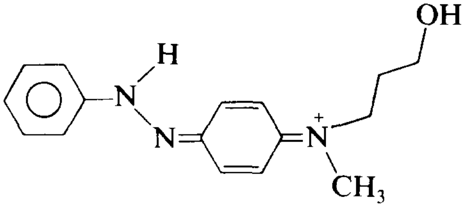
Fig. 2. Variation in isotropic melt temperature for azobenzene dyes. The unshaded area represents the smectic A phase in compounds **1a** and **1b**.

copolymers with methyl methacrylate were not liquid crystalline. Hill *et al.*[3] have used **1a** to prepare acrylic homopolymers in exactly the same way as Robello and chose this dye precursor because it presents a short spacer length and therefore would reduce light scattering in NLO devices. They do not report whether or not the dye precursor was liquid crystalline but it appears that the homopolymer was not.

The presence of a terminal methoxy group rather than a nitro group alters the visible absorption characteristics by decreasing the wavelength slightly and reducing the extinction coefficient. There is also a significant decrease in the melting temperature compared to the nitro-substituted dyes. The effect of having only hydrogen as the substituent in the 4-position (**1g**) is to reduce the melting temperature dramatically such that the product is a yellow oil.

It has been reported that UV irradiation of CI Disperse Red I in chlorinated solvents or in a poly (vinyl chloride) matrix results in a colour change from orange to magenta.[6] This has been attributed to protonation of the dye by degradation of the solvent or matrix, and the UV/^{1}H NMR spectrum of protonated CI Disperse Red I appears to confirm this interpretation.[6] We wished to see if the protonated form of **1b** exhibited any thermotropic behaviour. After dissolution of **1b** in acetonitrile, concentrated hydrochloric acid was added and the expected colour change (orange to magenta) was observed. Addition of water gave a clear magenta solution. Addition of dichloromethane resulted in partitioning of the magenta coloration between the two layers and some of the organic layer was removed and cast on a glass slide.

Examination of the film, after evaporation of solvent, by polarised light microscopy revealed that the material did not melt or show any thermotropic mesophases up to 280°C. This material is presumed to be the protonated form of the dye as shown below:



In summary, we have found that for the azobenzene dyes described, there are two features that militate against liquid crystalline behaviour, viz. having a terminal substituent of polarity less than that of a nitro group, and having a hydrocarbon tail of six methylene units or more. The latter observation is particularly surprising and we are not able to offer a rationalisation at the present. Since CI Disperse Red I is not liquid crystalline it can also be concluded that the presence of an *N*-ethyl substituent on the terminal amino groups also destroys liquid crystallinity. Addition of acid to give what is presumed to be the protonated form of the dye destroys any liquid crystalline behaviour.

ACKNOWLEDGEMENT

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