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The influence of intramolecular hydrogen bonding on the order parameter and photostability properties of dichroic azo dyes in a nematic liquid crystal host

John Griffiths* and Kai-Chia Feng

Department of Colour Chemistry, University of Leeds, Leeds, UK LS2 9JT. E-mail: J.Griffiths@leeds.ac.uk

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It has been demonstrated that intramolecular hydrogen bonding in two classes of dichroic azo dyes has a generally detrimental effect on order parameter in a nematic liquid crystal host. Derivatives of 4-(*N*,*N*-diethylamino)-4′-nitroazobenzene with hydroxy groups intramolecularly hydrogen bonded to the azo group show lower order parameters in E7 nematic liquid crystal than the parent dye, but higher order parameters than corresponding methoxy dyes. 1-Arylazo-2-naphthols with a hydrogen bonding carboxamide group in position 3 exist exclusively in the hydrazone form and show even lower order parameters. Intramolecular hydrogen bonding also has a deleterious effect on photochemical stability.

Introduction

Dyed phase change liquid crystal displays are dependent on dichroic dyes with very specific characteristics, notably high order parameter, high solubility in the host, and good photostability.[1] Consequently there are relatively few such compounds that find commercial use, and these are largely restricted to the anthraquinones and, to a lesser extent, the azo dyes.[1,2] In general the azo dyes would be preferred to the anthraquinones because of their better order parameter and solubility characteristics, but the superior photostability properties of the anthraquinones have been the major factor leading to their dominance. In the anthraquinone dyes, photostability is influenced markedly by intramolecular hydrogen bonding, and this may be attributed to protection of the chromophore by rapid deactivation of the excited state by proton transfer.[3]

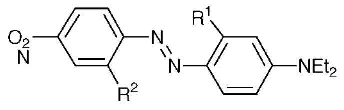
The effects of intramolecular hydrogen bonding on the properties of azo dyes in liquid crystal media have not been investigated. In addition to a possible influence on photostability, there may also be a significant effect on order parameter, although it is not clear if this would be beneficial or detrimental. On the one hand, a strongly hydrogen bonded dye molecule would be more rigid and planar (as evidenced by their generally higher extinction coefficients and narrower absorption bands than non-bonded analogues), and thus could orient more strongly with the mesogenic groups of the host. Alternatively, intramolecular hydrogen bonding may block sites of high and low electron density in the dye molecule which would otherwise be available for intermolecular interactions with the mesogens, or could reduce the overall dipole moment of the dye molecule, both effects having the potential to lower the observed order parameter.

In order to answer these questions, several azo and azo–hydrazone tautomeric dyes have been synthesised containing representative types of intramolecular hydrogen bonding, and their photostability and order parameter properties in a nematic liquid crystal host measured. The results have been compared with those for analogous dyes lacking such hydrogen bonding.

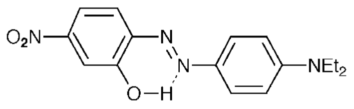
Results and discussion

Dye synthesis and characterisation

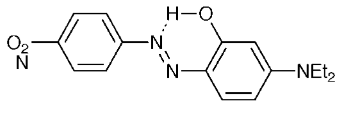
(a) Derivatives of 4-(*N*,*N*-diethylamino)azobenzene. Derivatives of 4-(*N*,*N*-diethylamino)-4′-nitroazobenzene **1** may be regarded as true azo structures. Thus the possibilities for conversion to hydrazone tautomeric forms are restricted to those derivatives with hydroxy groups *ortho* or *para* to the azo group, and even in these cases it is known that such tautomerism is generally negligible. The methoxy-substituted derivatives **2a,b** were prepared as examples of dyes with no hydrogen bonding and with no ability to undergo tautomerism. The hydroxy dyes **3a,b** then provided analogues with a single intramolecular hydrogen bond involving the azo group, and



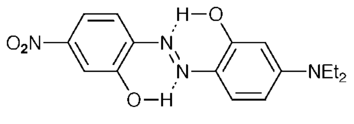
	R^1	R^2
1:	H	H
2a:	OMe	H
2b:	H	OMe



3a



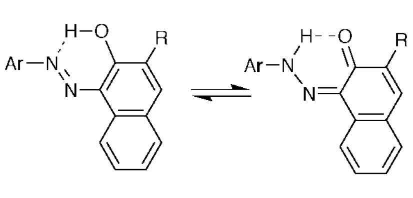
3b



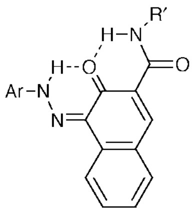
4

could be compared directly with **2**. Dye **4** was also prepared as an example of a dye with two hydrogen bonds to the azo group. The dyes were synthesised by diazotisation of 4-nitro-, 2-methoxy-4-nitro- and 2-hydroxy-4-nitro-aniline followed by coupling to the appropriate *N*,*N*-diethylaniline, and were characterised by microanalysis and mass spectrometry.

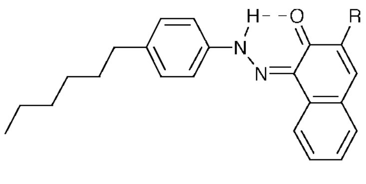
(b) 1-Arylazo derivatives of 2-hydroxy-3-naphthamides. 1-Arylazo-2-naphthols **5a** are typical examples of azo dyes, which in most cases exist predominantly in their hydrazone tautomeric forms **5b**.[4] This has important implications for the dipole moment and transition dipole moment directions of the chromophore, both properties having a major influence on order parameters. Such dyes already contain one strong intramolecular hydrogen bond, as shown in **5b**, and by introducing a primary or secondary carboxamide group in the 3-position of the naphthalene ring one can introduce a second hydrogen bond involving the 2-carbonyl group, as shown in **6**.[5]



5a **5b**



6



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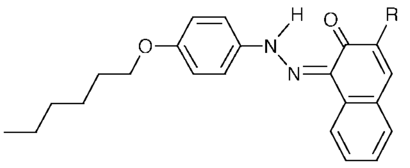


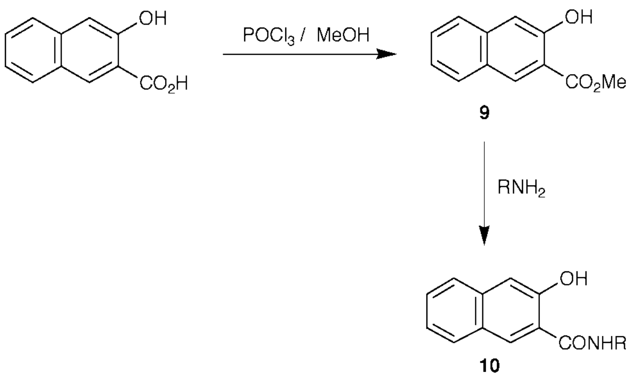
8

a: R = H

b: R = -CONHCH$_2$CH$_2$OH

c: R = -CONHCH$_2$CH$_2$CH$_2$OCH$_3$

As the additional hydrogen bond in **6** is known to improve photochemical stability and molecular packing properties in the azoic dyes and related pigments,[6] it was of interest to prepare representative dyes of this type in order to observe their behaviour in a liquid crystal host. One of the main problems with this class of dye is their low solubility in organic solvents, and this was overcome by using *N*-methoxypropyl and *N*-hydroxyethyl groups as side chains attached to amide nitrogen. Long chain substituents were introduced into the *para* position of the arylazo residue in order to extend the long axis of the dye molecule and improve alignment with the host mesogens. These groups had the added advantage of increasing further the solubility of the dyes in the liquid crystal host. Thus two series of dyes were prepared, namely the 4-*n*-hexyl series **7**, and 4-*n*-hexyloxy series **8**.



a: R = –CH$_2$CH$_2$CH$_2$OMe
b: R = –CH$_2$CH$_2$OH

Scheme 1

The dyes **7** and **8** were prepared by coupling diazotised *p*-hexylaniline or *p*-hexyloxyaniline respectively to the relevant 2-hydroxy-3-naphthamide in aqueous solution at pH *ca.* 9. The amide couplers were prepared as summarised in Scheme 1. Thus 2-hydroxy-3-naphthoic acid was reacted with phosphorus oxychloride in methanol to give the methyl ester **9**, and this was then heated under reflux in neat amine to give **10**. The dyes were purified by recrystallisation from ethanol and/or column chromatography until they showed a single spot on TLC analysis, and were characterised by microanalysis.

Visible absorption spectra and order parameters of the azo dyes in E7 liquid crystal host

The host chosen for this study was E7, a commercially available nematic eutectic mixture of 4-cyano-4″-*n*-pentyl-*p*-terphenyl, 4-alkyl-4′-cyanobiphenyls and 4-alkoxy-4′-cyanobiphenyls. Spectral data and order parameters in E7 for all the dyes studied are summarised in Table 1. The aminoazobenzene dyes **1**–**4** show a single absorption band in the visible region, and demonstrate the usual positive solvatochromism for this type of dye. Thus absorption maxima in acetone occur at longer wavelengths than in the less polar solvent toluene. In the protic solvent ethanol, however, there are anomalies, and those dyes with intramolecular hydrogen bonding, *i.e.* **2b**, **3b** and **4**, absorb at shorter wavelengths in this solvent than in toluene, whereas the non-hydrogen bonded methoxy counterparts show the opposite effect. If one considers the spectra of dyes **2** and **3** measured in toluene, in which specific solvent interactions will be minimal, then it is apparent that the hydroxy groups in **2b** and **3b** exert a somewhat greater bathochromic effect than corresponding methoxy groups in **2a** and **3a**. This may be attributed to the hydrogen bonding in the former dyes, which will increase chromophore planarity and orbital overlap. However the effect is not additive and in the case of dye **4** with two hydrogen bonds, the absorption maximum falls between those of **3a** and **3b**.

In E7 liquid crystal there is a pronounced positive solvatochromism for all the dyes and the bathochromic effect of hydrogen bonding is significantly enhanced, so much so that dye **4** now absorbs at the longest wavelength (λ_{max} 545 nm). Absorption maxima calculated by the PPP-MO method[7] reproduce most of the general λ_{max} trends observed in toluene, although absolute agreement between theory and experiment is only moderate.

The order parameters of the dyes **2**–**4** in E7 were disappointing, in that they were all slightly lower than that of the parent dye **1**. Thus intramolecular hydrogen bonds *per se* and the concomitant increase in molecular coplanarity do not confer enhanced alignment between the dye chromophore and the host mesogens. However, the methoxy-substituted dyes **2a,b** show order parameters *ca.* 0.05–0.06 units lower than their

Table 1 Visible absorption spectra and order parameters in E7 of dyes **1–4**, **7** and **8**

Dye	λ_{max}(ethanol)/nm	λ_{max}(acetone)/nm	λ_{max}(toluene)/nm	λ_{max}(calc.)/nm	λ_{max}(E7)/nm	Predominant tautomer in E7	Order parameter S
1	482	486	474	444	504	azo	0.62
2a	497	502	484	444	515	azo	0.52
3a	470	500	490	436	512	azo	0.58
2b	488	491	482	466	509	azo	0.54
3b	512	516	514	504	532	azo	0.59
4	488	512	500	507	545	azo	0.56
7a	474	415	418	492	476	hydrazo	0.46
7b	502	499	522	491	530	hydrazo	0.20
7c	501	499	524	491	530	hydrazo	0.13
8a	464	415	463	438	418	azo	0.32
8b	519	514	513	501	524	hydrazo	0.27
8c	518	514	513	501	522	hydrazo	0.20

hydroxy-substituted counterparts **3a,b**, reflecting the greater planarity and reduced rotational mobility of the latter dyes. Thus it can be concluded that if it is necessary to introduce electron donor groups into an azo dye chromophore in order to produce a specific λ_{max} shift, then hydroxy groups are preferable to methoxy groups because of the higher order parameters and greater bathochromic shifts they induce. The order parameter for **4** lies between that for the hydroxy dyes **3a** and **3b**, again demonstrating the minimal influence of intramolecular hydrogen bonding on dye alignment characteristics in comparison with dye **1**.

The 1-arylazo-2-naphthol dyes **7** and **8** are more complex systems than **1–4**, as they can show significant azo–hydrazone tautomerism. Thus their visible absorption spectra sometimes show two absorption bands attributable to the two tautomers, and the ratio of the tautomers at equilibrium depends both on substituents in the dye and the nature of the solvent. In the case of parent dye **7a,** roughly equal amounts of the two tautomers could be detected in toluene, the azo form dominating slightly [λ_{max} (azo) *ca.* 418 nm, λ_{max} (hydrazone) *ca.* 476 nm, relative absorbance values *ca.* 1.2 : 1]. In ethanol and E7 the hydrazone form was much more predominant, demonstrating the known stabilising effect of strong solvent–solute interactions on hydrazone tautomers.[8] The *p*-hexyloxyphenylazo dye **8a** showed a greater propensity to exist as the azo tautomer, which was consistent with the known effects of electron donating groups in the arylazo residue,[8] and in toluene the azo tautomer was the dominant species [λ_{max} (azo) 463 nm, λ_{max} (hydrazone) *ca.* 510 nm, relative absorbance values *ca.* 1.0 : 0.4]. Even in ethanol and E7 the azo tautomer was predominant.

However, the dyes **7b,c** and **8b,c** which have a 3-carboxamide substituent hydrogen bonded to the hydrazone carbonyl group, showed exclusive hydrazone formation in all solvents. Thus they showed a single relatively narrow band in the 520–530 nm range in E7. In this medium the 3-carboxamide substituent had a pronounced effect on the colour of the dyes, and whereas **7a** and **8a** were orange in E7, dyes **7b,c** and **8b,c** were red–purple. X-Ray crystallographic studies have also shown that 3-carboxamide substituents contribute to a bifurcated hydrogen bond and favour the hydrazone tautomeric form.[5]

Although **7b,c** and **8b,c** exist as discrete tautomers in E7, and have planar strongly hydrogen bonded structures, their order parameters were very low, and significantly less than for the parent dyes **7a** and **8a**. The reason for this was first sought by application of molecular orbital theory. A dye chromophore will try to align itself with respect to the host mesogenic groups so that its permanent dipole moment is parallel to that of the mesogen, and its spatial overlap with the mesogen is maximal. The E7 host used in this study comprises a mixture of 4-*n*-pentyl-4″-cyano-*p*-terphenyl, 4-alkyl-4′-cyanobiphenyls and 4-alkoxy-4′-cyanobiphenyls, all such mesogens having a strong permanent dipole moment as well as a rigid rod-like shape. A compromise situation will hold if the dipole moment direction and the long axis of the dye differ, and the greater the deviation between the two, the poorer will be the degree of alignment. In addition, if the transition moment direction for the visible band of the dye chromophore differs significantly from the molecular alignment axis, the measured order parameter will be lowered further. As the permanent π-dipole moment (μ_π) and the transition moment (M) directions can be calculated readily by PPP-MO theory,[7,9] it is possible to examine if either of these factors contributes to the low order parameters for the dyes.

Fig. 1a and 1b show calculated μ_π and M directions for the two parent dyes **7a** and **8a** respectively. For the purposes of the calculations a hydrazone structure was assumed in the former case, and an azo structure in the latter (see Table 1). For both systems the same approximate molecular alignment axis (MAA) was assigned by considering the longest axis through the molecule that encompassed both the dye π-chromophore and its terminal long alkyl chain (see Fig. 1). In both the case of **7a** (hydrazone) and **8a** (azo), the deviation of the calculated μ_π and M directions from the MAA was reasonably large, thus accounting for the moderate order parameters for these dyes. Interestingly, the calculations revealed that the 3-carboxamide groups in dyes **7b,c** and **8b,c** had only a small effect on the M direction, but caused a larger deviation of μ_π from the MAA (Fig. 1c and 1d). This explains in part why the amido-substituted dyes have a lower order parameter than the unsubstituted dyes. However, another factor must be the greater indeterminacy of the MAA in the substituted dyes. As can be seen in Fig. 2, the methoxypropyl side chain on the nitrogen of the carboxamide group of dye **8c** provides an elongation of the molecule in a direction almost perpendicular to the previously assumed MAA. Thus the true MAA is less well defined and the dye will be poorly aligned with the host mesogens. This explains why the dyes **7c** and **8c** have even lower order parameters than corresponding dyes **7b** and **8b**, as they have a longer chain attached to the amide nitrogen. Unfortunately, it was essential to include these side chains in order to ensure adequate solubility of the dyes in the host.

Photostability properties in E7

It is well known that intramolecular hydrogen bonding in a dye molecule will often lead to a marked improvement in photochemical stability. For example, in the anthraquinone dyes, hydroxy, primary and secondary amino groups in the 1-position of the anthraquinone ring will provide a strong hydrogen bond to the adjacent carbonyl group, and thus they have high light fastness.[2] For this reason, all commercial anthraquinone dyes have such a substitution pattern. It is believed that the improvement in stability is due at least in part to facile proton transfer in the photoexcited state, leading to a reduction in the excited state lifetime. As photostability is one of the most important features of dichroic dyes used in liquid crystal displays, it was of interest to see if the hydrogen bonding present in dyes **3**, **4**, **7** and **8** could also confer improved resistance to photochemical fading.

An additional advantage of the intramolecular hydrogen

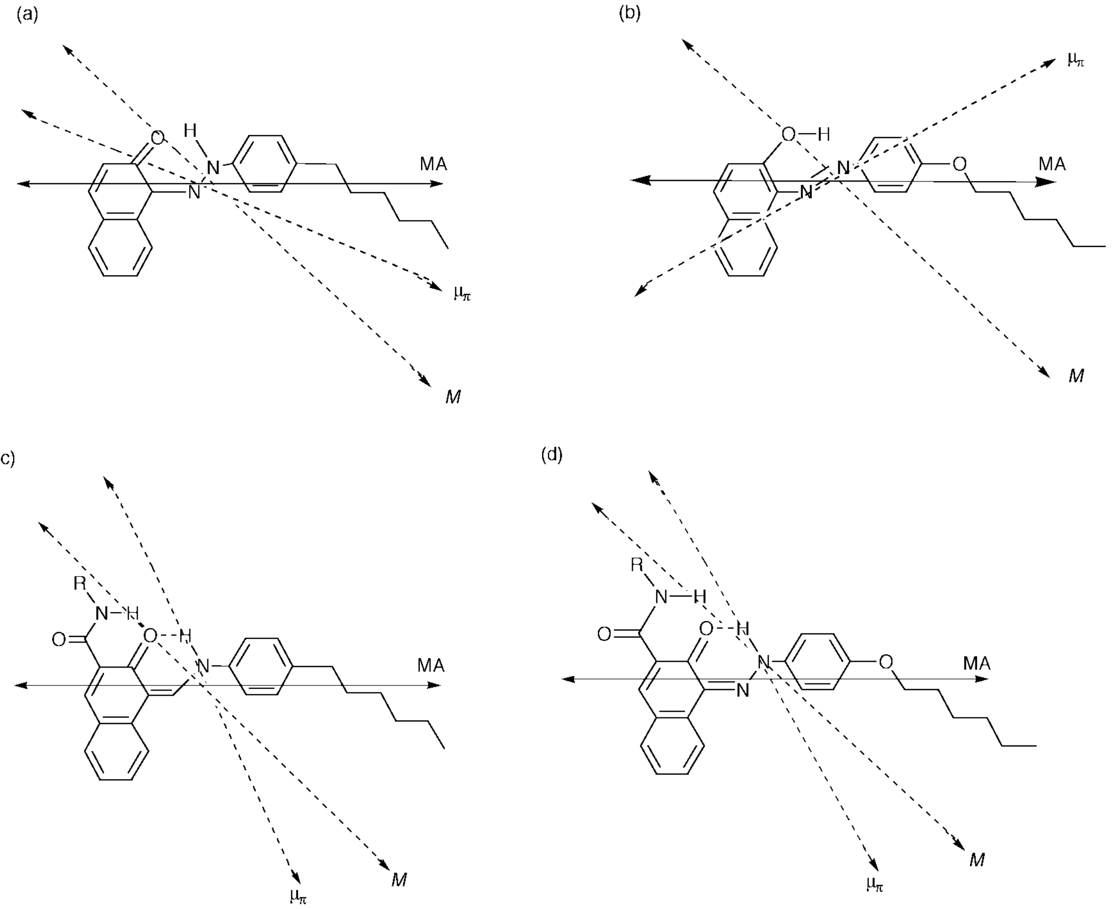


Fig. 1 Assumed molecular alignment axes (MAA) and MO calculated π-dipole moment (μ_π) and transition moment (M) directions for (a) **7a**; (b) **8a**; (c) **7b,c**; (d) **8b,c**.

bond in azo and hydrazone dyes is that photochemical $E \rightarrow Z$ isomerisation is not a complicating factor, as the rate of thermal $Z \rightarrow E$ reversion is so high that it is not possible to detect any of the Z isomer under steady state illumination conditions at ambient temperatures.[10–12]

Glass cells (gap 25 μm) containing aligned solutions of the dyes in E7 were exposed to the radiation from a phosphor-coated 500 W mercury–tungsten filament lamp, designed to simulate accelerated daylight fading. The cells were unsealed, so ensuring aerobic conditions, and fading was measured spectrophotometrically at the λ_{max} of the dye at intervals over a period of 1500 hours, and at an ambient temperature of 40 ± 5 °C. It was found that fading kinetics were approximately first order over the initial stages of the fading process but then became more complex. A useful empirical measure of the photostability was provided by the time for 50% fade ($t_{1/2}$), which could be measured directly from the fading curve, or determined by extrapolation in the case of those dyes with very slow fading rates. The $t_{1/2}$ values and initial first order rate constants are summarised in Table 2.

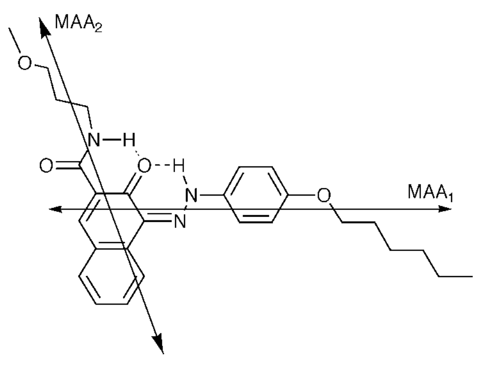


Fig. 2 Two potential molecular alignment axes for **8c**.

Surprisingly it was found that intramolecular hydrogen bonding had a significant deleterious effect on photochemical stability. This can be seen most dramatically with the doubly hydrogen bonded azo dye **4**, which has a $t_{1/2}$ of 125 hours, in comparison with the parent dye **1**, which is more than 30 times more stable with a $t_{1/2}$ of 3900 hours. To place these stabilities in context, it should be noted that 1,4-bis(methylamino)anthraquinone, a blue dye belonging to a general group of anthraquinone dyes used in LC displays, was found to have a $t_{1/2}$ of *ca.* 5000 hours under identical exposure conditions. Thus dyes **1** and **7a** may be considered to approach the minimum technical requirements for LC display applications, whereas all the other derivatives have unacceptably low photostabilities.

The source of the low photostability in the hydrogen bonded derivatives may be attributed in part to azo–hydrazone

Table 2 Photofading parameters for dyes **1–4** and **7**, **8** in E7

Dye	Initial first order rate constant/10^{-7} s^{-1}	$t_{1/2}$/h[a]
1	0.5	3900
2a	1.5	1100
2b	1.2	1600
3a	2.7	600
3b	1.7	1100
4	1.6	125
7a	0.4	4700
7b	3.2	700
7c	1.7	1100
8a	1.9	1000
8b	5.4	350
8c	3.4	570

[a] Time for 50% fade.

tautomerism. It is well known that hydrazone tautomers are more susceptible to photooxidative degradation than azo tautomers.[13] The degradation process is initiated by peroxide radical hydrogen abstraction from the hydrazone N–H group, or by an "ene" reaction between the hydrazone and singlet oxygen, both pathways producing the same unstable hydroperoxide which thermally degrades to a quinone and a diazonium species.[13] In the aminoazobenzene series **3** and **4**, although such dyes exist predominantly in the azo form, there will be a small amount of a hydrazone structure present in equilibrium, and this will undergo such a photodegradation process, leading ultimately to a rapid fading of the azo dye. The importance of this process can be inferred by comparing the fading rates of the hydroxy dyes **3** with those of the corresponding methoxy dyes **2**, which are unable to produce a hydrazone tautomer. Considering empirical $t_{1/2}$ values, it is found that **2a** is almost twice as stable as **3a**, and **2b** is *ca.* 40% more stable than **3b.** However, hydrazone formation is not the whole story, as the methoxy dyes themselves are significantly less photostable than the parent dye **1**. This may reflect the general oxidative nature of azo dye photodegradation, when electron donating groups will be expected to facilitate such a process.

With the exception of **7a**, all the dyes in the series **7** and **8** exist in their hydrazone forms in E7. It is significant therefore that only **7a**, present predominantly in the azo form, shows a high photostability in this medium. Thus it appears that the hydrogen bonding 3-carboxamide group in dyes **7b,c** and **8b,c** serves principally to force the dyes to adopt the hydrazone structure and consequently cause a decrease in photostability. Any beneficial effects that the additional hydrogen bonding from this group might have on excited state lifetimes are more than offset by this factor.

Conclusions

Although 2- and 2′-hydroxy groups in the 4-(*N*,*N*-diethylamino)-4′-nitroaminoazobenzene chromophoric system will intramolecularly hydrogen bond to the azo group, so affording increased planarity and reduced rotational mobility of the molecule, this does not lead to enhanced order parameters in comparison with the parent non-hydrogen bonded dye. It appears that the additional hydroxy substituents inhibit dye–mesogen interaction, presumably by a combination of increased lateral molecular size and prevention of specific interactions between the azo group and the host mesogens. However, when the hydroxy derivatives are compared with their methoxy-substituted analogues, they do show slightly enhanced order parameters.

In the 1-arylazo-2-hydroxynaphthalene system the situation is complicated by azo–hydrazone tautomerism, and the introduction of a hydrogen bonding carboxamide group in the 3-position causes the dyes to adopt exclusively the hydrazone form, whereas in the absence of this substituent the azo form is present in significant amounts. The carboxamide-substituted dyes showed low order parameters, and this was attributed partly to the unfavourable change in the permanent π-dipole moment direction caused by the carboxamide group, and partly to the lateral extension of the molecule introduced by the side chain attached to the amide group. These side chains were essential, however, to provide adequate dye solubility in the liquid crystal host.

In addition to providing no order parameter advantages, hydrogen bonding groups in both the aminoazobenzene and 1-arylazo-2-naphthol series proved to have a pronounced accelerating effect on photochemical fading. This could be attributed to the hydrogen bonding groups influencing azo–hydrazone tautomerism. Thus in the aminoazobenzenes, the hydroxy groups permitted the existence of hydrazone forms, which were otherwise absent. In the 1-arylazo-2-naphthols the carboxamide group enforced exclusive adoption of the hydrazone form. The known sensitivity of hydrazone tautomers to photooxidation thus explains the observed decrease in photostability.

Experimental

Preparation of intermediates and dyes

General procedure for synthesis of 4-(*N*,*N*-diethylamino)-4′-nitroazobenzenes 2 and 3. *Diazotisation of nitroanilines.* The appropriate nitroaniline (0.02 mol) was dissolved in a mixture of concentrated hydrochloric acid (6 cm^3) and water (6 cm^3) and poured onto crushed ice (*ca.* 20 g) with stirring. A solution of sodium nitrite (0.02 mol) in water (20 cm^3) was added immediately and the mixture stirred at 0–5 °C for 30 minutes. The resultant diazonium solution was then used directly for the second step.

Coupling. The appropriate *N*,*N*-diethylaniline (0.02 mol) was dissolved in a mixture of acetic acid (12 cm^3) and water (6 cm^3), and sodium acetate trihydrate (15 g) was added with stirring, followed by sufficient acetic acid to give a clear solution. The diazo solution was added to the stirred solution at 0–5 °C over 30 minutes, maintaining the pH between 4 and 7 by addition of sodium hydroxide solution. The mixture was allowed to rise to room temperature over 3 hours and the precipitated product filtered off, washed with water and dried. The following purification procedures were used: **2a**: recrystallisation from cyclohexane; **2b**: recrystallisation from petroleum spirit (bp 80–100 °C); **3a**: column chromatography (neutral alumina/toluene–dichloromethane) followed by recrystallisation from toluene; **3b**: column chromatography (silica/dichloromethane) followed by recrystallisation from toluene. Yields and characterisation data are summarised in Table 3.

4-(*N*,*N*-Diethylamino)-2,2′-dihydroxy-4′-nitroazobenzene 4. 2-Hydroxy-4-nitroaniline (0.02 mol) was dispersed in water (50 cm^3) containing sodium nitrite (0.02 mol) and cooled to <5 °C by addition of ice. The suspension was poured into a solution of concentrated hydrochloric acid (6 cm^3) and water (6 cm^3) and stirred at 0–5 °C for 2 hours. The diazo solution was then added with stirring at 0–5 °C to a solution of 3-hydroxy-*N*,*N*-diethylaniline (0.02 mol) in water (60 cm^3) containing sodium hydroxide (0.8 g, 0.02 mol) and sodium carbonate (2.12 g, 0.02 mol) over a period of 90 minutes. Stirring was continued for 3 hours, allowing the temperature to rise to *ca.* 25 °C, and after adjusting the pH to 7 with hydrochloric acid the product was filtered off, washed and dried (98% yield). Purification was effected by recrystallising twice from toluene. Characterisation data are given in Table 3.

Synthesis of 1-arylazo-2-naphthol dyes 7a and 8a. *Diazotisation of 4-hexyl- and 4-hexyloxy-aniline.* A solution of the arylamine (6 mmol) in a mixture of water (25 cm^3) and hydrochloric acid (20 mmol) was cooled to 0–5 °C, and a solution of sodium nitrite (6 mmol) in water (25 cm^3) was added over 30 minutes with constant stirring, maintaining the temperature below 5 °C . After stirring at this temperature for a further 30 min. the clear solution of the diazonium chloride was used immediately for preparation of the appropriate azo dye.

Coupling. 2-Naphthol (6 mmol) was dissolved in a solution of sodium hydroxide (20 mmol) in water (150 cm^3) and cooled to 0–5 °C. The appropriate diazo solution was added dropwise with vigorous stirring over 30 min, maintaining the temperature below 5 °C. The pH of the solution was then adjusted to *ca.* 9 by addition of sodium hydroxide and stirring was continued at this temperature for a further hour. The suspension was then warmed to room temperature and after

Table 3 Yields and characterisation data for dyes **2–4**, and **7**,**8**

				Microanalysis					
				Found/%			Calculated/%		
Dye	Yield/%	Mp/°C	Formula	C	H	N	C	H	N
2a	93	138–139[a]	$C_{17}H_{20}N_4O_3$	62.6	6.1	17.1	62.2	6.1	17.1
2b	33	140–141[b]	$C_{17}H_{20}N_4O_3$	62.2	6.0	17.1	62.2	6.1	17.1
3a	95	212–214	$C_{16}H_{18}N_4O_3$	60.9	6.0	17.6	61.1	5.7	17.8
3b	19	190–200	$C_{16}H_{18}N_4O_3$	61.3	5.8	17.8	61.1	5.7	17.8
4	98	268–270	$C_{16}H_{18}N_4O_3$	58.1	5.6	16.8	58.2	5.5	17.0
7a	58	65–67	$C_{22}H_{24}N_2O$	79.6	7.8	8.0	79.5	7.2	8.4
7b	77	145–148	$C_{25}H_{29}N_3O_3$	71.5	7.2	10.2	71.6	6.9	10.0
7c	61	69–72	$C_{27}H_{39}N_3O_3$	71.9	6.9	9.6	72.5	7.4	9.4
8a	93	78–80	$C_{22}H_{24}N_2O_2$	75.7	6.7	8.0	75.9	6.9	8.1
8b	71	160–163	$C_{25}H_{29}N_3O_4$	68.5	7.0	9.5	69.0	6.7	9.7
8c	74	106–108	$C_{27}H_{39}N_3O_4$	69.8	7.0	8.5	70.0	7.1	9.0

[a] Lit.,[15] 138–140 °C. [b] Lit.,[16] 139–140 °C.

30 minutes the product was filtered off, washed with water and recrystallised from ethanol. Yields and characterisation data are summarised in Table 3.

General procedure for 7b and 8b

Methyl 2-hydroxy-3-naphthoate (5×10^{-2} mol) was heated until melted and ethanolamine (0.1 mol) was added. The mixture was then heated under reflux for 15 minutes and then poured into warm water (200 cm^3) at 70 °C with thorough stirring. Hydrochloric acid was added to adjust the pH to *ca.* 1, and stirring was continued until the suspension had cooled to room temperature. The solid was filtered off, washed with water, dried and recrystallised from a mixture of petroleum ether and toluene (1 : 1) to give 2-hydroxy-3-[*N*-(2-hydroxyethyl)]naphthamide **10b** in 35% yield. A solution of **10b** (6 mmol) in aqueous sodium hydroxide (20 mmol in 150 cm^3) was then coupled to the appropriate diazo solution following the procedure outlined for dyes **7a** and **8a**. The dye was filtered off and recrystallised repeatedly from ethanol until pure by TLC. Characterisation data are given in Table 3.

General procedure for 7c and 8c

Following the method detailed for **10b**, methyl 2-hydroxynaphthoate (5×10^{-2} mol) was reacted with 3-methoxypropylamine (0.1 mol) to give 3-[*N*-(3-methoxypropyl)]-2-hydroxy-3-naphthamide **10a** in 52% yield. This was coupled to the appropriate diazo solution following the general procedure outlined for **7b** and **8b**. Yields and characterisation data for **7c** and **8c** are summarised in Table 3.

Measurement of order parameters

The liquid crystal host E7 (BDH-Merck), a eutectic mixture with a stable nematic mesophase over the range −10 to 60 °C, was used for the measurements. Cells were constructed according to the procedure detailed by Jones and Reeve,[14] using microscope slides coated with oriented polyvinyl alcohol. A cell gap of 25 µm was maintained with aluminium foil spacers, and the cells were sealed along three sides with epoxy resin. Cells were filled by capillary action with solutions of the dyes in E7, the concentration being adjusted to give an absorbance reading in the range 0.5–1.5 at the λ_{max} of the dye (corresponding to dye concentrations in the range 0.5–1.0%). After filling, the cells were heated to 15 °C above the N–I transition temperature and cooled slowly to room temperature before measurements were made. The cells were inspected microscopically to ensure that they were free from undissolved dye particles. The absorption spectra of the cells in the parallel and perpendicular orientation modes were measured using polarised light, and the order parameters *S* were calculated using eqn. (1):

$$S = \frac{A_{par} - A_{per}}{2A_{per} + A_{par}} \qquad (1)$$

where A_{par} and A_{per} are the absorbance values for light polarised parallel and perpendicular respectively to the alignment direction of the liquid crystal host.

Photofading measurements

Unsealed cells were irradiated in a Mark 1 MBTL Microscal Fadometer, using a phosphor-coated 500 watt mercury–tungsten filament lamp, and were situated at a distance of 15 cm from the lamp outer surface. The lamp output consisted of broad weak emission between 300 and 700 nm, with major lines at 348, 395, 438, 545, 585 and 666 nm, thus simulating high intensity daylight exposure. The cells attained an equilibrium temperature of *ca.* 40±5 °C throughout the exposure period. Absorption spectra were measured at appropriate intervals and the absorbance of the dye solution at the λ_{max} determined.

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