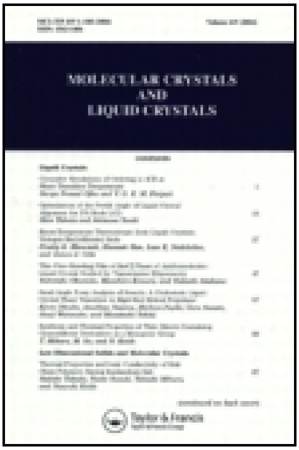

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N,N'-Disubstituted Naphthyl(Azo)-2,3-Dihydroperimidine Blue Dyes Exhibiting High Solubility in Ferroelectric Liquid Crystal Hosts

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The synthesis of N,N'-disubstituted naphthyl(azo)-2,3-dihydroperimidine blue dyes and a comparison of their absorption maxima and solubility in ferroelectric liquid crystal (FLC) hosts is described. The N,N'-disubstituted azo perimidines exhibited a much higher absorption maxima (20–50 nm) than their unsubstituted counterparts. In addition, the absorption maxima of the naphthyl(azo) perimidines was significantly higher than their phenyl(azo) analogues. Although the FLC solubility of the N,N'-dimethyl substituted dyes was similar to that measured for analogous unsubstituted dyes, the N,N'-dibutyl substituted bis(azo) dyes exhibited solubilities in excess of 8%.

INTRODUCTION

The concept of ferroelectric liquid crystal (FLC) displays was first demonstrated by Clark and Lagerwall.[1,2] Because of their inherent bistability and fast electrooptic switching capability, ferroelectric displays offer potential advantages over the widely used twisted and supertwisted nematic displays.

The utility of dichroic dyes in the fabrication of guest-host displays has been investigated since the late 1960's for nematic systems[3–5] and the early 1980's for ferroelectric systems.[6–8] In principle, dyes dissolved in ferroelectric liquid crystal hosts enable the generation of devices which do not suffer thickness constraints or poor viewing angle characteristics typical of birefrigence displays.[8]

With guest-host liquid crystal displays, it is generally desired to provide a device which appears neutral black in the absence of an electric field and clear or non-black in the presence of an electric field. In order to absorb strongly throughout the region between 400 and 700 nm, the display system requires at least three dichroic dyes having their absorption maxima centered at approximately 450, 550 and 650 nm.[9] Suitable dyes for guest-host applications must exhibit a reasonable solubility in the host liquid crystal (smectic or nematic) matrix. Typically, blue dyes

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are the most difficult to obtain due to the low electronic energy transitions necessary for the absorption of red light.[9] In addition, dissolution of dichroic dyes (particularly those absorbing light in the 600–650 nm range) into ferroelectric liquid crystals is often difficult due to the low FLC solubility of many of the candidates.[10]

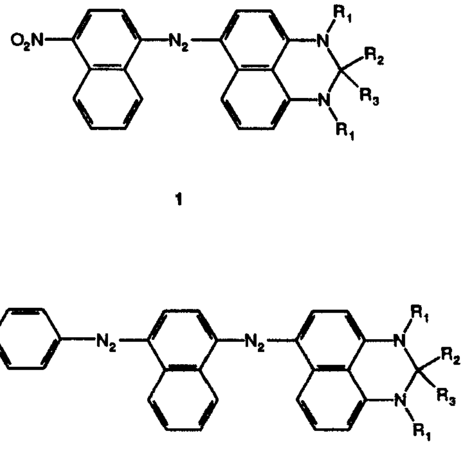
We reported previously on the synthesis of tetra(azo) dyes for *nematic* liquid crystals[11] which exhibited the necessary absorption maxima of >600 nm (blue dye component). Black guest-host nematic formulations employing these dyes have been successfully generated. Unfortunately, these same tetra(azo) dyes have generally shown low solubility (<1%) in most *ferroelectric* liquid crystal hosts which we have utilized. While certain bis(azo) dyes are soluble in a range of FLC hosts, their absorption maxima generally fall short of the desired 600–650 nm goal.

We describe here mono(azo) and bis(azo) dichroic dyes, **1** and **2** respectively (Figure 1), which combine naphthyl moieties and 2,3-dihydroperimidines disubstituted at nitrogen, that have high absorption maxima and high solubility in a range of FLC hosts.

EXPERIMENTAL

Methods

To measure dye solubility in ferroelectric liquid crystal hosts, thin films of the guest-host mixture were fabricated as follows: Dye was dissolved into the liquid crystal at the desired weight percent in 1 ml Reacti-Vials (Pierce Chemical Co.) fitted with a conical magnetic stir bar. The vials were sealed and stirred on a hot block overnight at 80–100°C. A small amount of material was placed on a glass slide and sandwiched between the slide and a glass coverslip. The slides were stored for 30 days at ambient temperature unprotected from light and were periodically



1

2

FIGURE 1 Mono(azo) and bis(azo) dichroic dyes **1** and **2**.

inspected for phase separation with an optical microscope. If no phase separation was observed over 30 days, the dyes were considered to be soluble in the liquid crystal at that weight percent.

To determine the effect of dye loading on the Smectic C^* transition temperature, display cells were fabricated and a square wave signal was applied while monitoring switching as a function of temperature. Cells were fabricated from glass substrates coated with an indium tin oxide conducting surface and a silicone/polyimide parallel-rubbed alignment layer. Electrode spacing was maintained using 5 μm glass fibers and the cell was sealed using a quick curing epoxy resin. Six inch wire leads were attached to the exposed ITO surfaces using a conductive silver-based epoxy resin. The cells were capillary filled at elevated temperature with the desired ferroelectric guest-host mixture and sealed with epoxy resin to prevent leakage. The cells were placed on a Mettler hot stage and the temperature was ramped at 1 degree per minute (0.2°C/minute near the transition) while applying a 2 Hz square wave signal with a ±2.5 V amplitude to switch the FLC between its bistable states. The onset/cessation of switching was viewed through an optical microscope to determine the transition temperature.

Materials

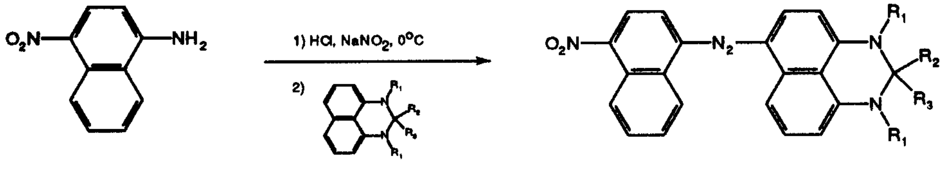
The preparation of the mono(azo) and bis(azo) dihydroperimidines are illustrated in Schemes I and II respectively.

All dyes were purified by column chromatography (Baker 40 μm silica gel, THF: Hexane as eluant) and recrystallization if crystalline at room temperature. Melting points of crystalline materials were determined with a Mel-Temp II (Laboratory Devices) capillary melting point apparatus.

We generally found that the mono and bis(azo) dihydroperimidines which were unsubstituted at nitrogen, were more difficult to purify than the N,N′-disubstituted analogues.

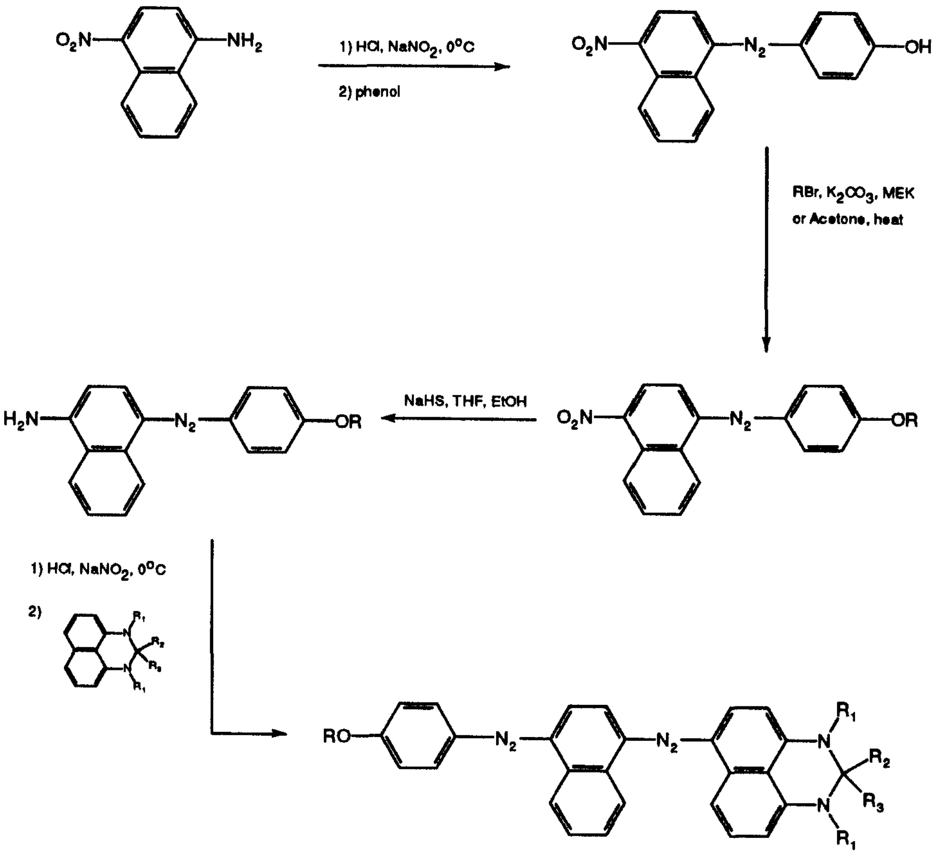
Structural determination of the dyes and intermediates was made through the interpretation of ^{1}H NMR, IR and UV-Vis spectra. All ^{1}H NMR spectra were run on a Varian EM 390 continuous wave spectrometer. IR data was collected on a Perkin-Elmer 983 spectrophotometer and UV-Vis data was collected on Cary 2300 UV-Vis/Near-IR spectrophotometer.

The 2,3-dihydro-1,3-dialkylperimidines employed in the azo coupling reactions were synthesized according to the procedures of Shannon and Sun[11] and the unsubstituted 2,3-dihydroperimidines were synthesized according to the procedures



1

SCHEME I Synthesis of mono(azo)dihydroperimidines **1**.



2

SCHEME II Synthesis of bis(azo)dihydroperimidines **2**.

outlined by Buell.[12] 1-amino-4-nitronaphthalene was purchased from Aldrich Chemical Co. and used without further purification. The ferroelectric liquid crystals SCE11 and ZLI-3654 were purchased from BDH Limited, (Poole, England) and EM Industries Inc., (Hawthorne, NY) respectively.

Described below are the experimental procedures for a representative mono(azo) and bis(azo) dye.

Mono(azo) dye **1d** *(1,3-di-n-butyl-2,3-dihydro-2-octyl-6-(4-nitronaphthylazo)perimidine):* 1-amino-4-nitronaphthalene (500 mg, 2.7 mmol) was placed in a small beaker and 4 ml of glacial acetic acid was added. The slurry was stirred at room temperature for 15 minutes before adding 3 ml of 5N HCl and cooling to 0°C. Sodium nitrite (210 mg, 3 mmol) dissolved in 2 ml of distilled water was added to the beaker with constant stirring over 15 minutes. The mixture was stirred at 0°C for 1 hour. Urea (50 mg) was added, and stirring was continued for an additional 15 minutes. The mixture was then filtered to remove insoluble material and cooled to 0°C. In a separate beaker was combined 1,3-di-n-butyl-2,3-dihydro-2-octylperimidine (1.1 g, 2.8 mmol) and 8 ml of glacial acetic acid. Upon cooling to 0°C, the diazonium salt solution was added to the second beaker with stirring. The resulting black slurry was stirred at 0–5°C for 1 hour before adjusting the pH to 8.0 with saturated sodium carbonate solution. The organic material was extracted with ethyl acetate, washed with water, dried over anhydrous magnesium sulfate and filtered to yield 1.4 g as a blue/black semi-solid. Flash chromatography (20:80 THF:hexane) yielded 500 mg as a viscous oil. ^{1}HNMR ($CDCl_3$) δ 9.1 (1H, m, aromatic); 8.8–6.2 (8H, m, aromatic); 6.6 (1H, *d*, *J* = 7 Hz, aromatic); 6.4 (1H, *d*, *J* = 7 Hz, aromatic); 4.4–4.2 (1H, m, CH); 3.8–2.8 (4H, m, —CH_2N—); 2.0–0.8 (30H, m). IR (CH_2Cl_2) ν_{max} 2960, 2930, 2860, 1588, 1300, 1250, 1135, 765 cm^{-1}. UV-Vis (CH_2Cl_2); λ_{max} = 618 nm, ε = 12,945 L/Mol·cm.

Bis(azo) dye **2e** *(1,3-di-n-butyl-2,3-dihydro-2-octyl-6-[4′-(4″-hexyloxyphenyl(azo))naphthyl(azo)]perimidine).* This compound was synthesized in four steps as described below:

1-Amino-4-nitronaphthalene (10.0 g, 53.2 mmol), 5N HCl (63 ml, 315 mmol) and 42 ml of distilled water were mixed in a 200 ml beaker. After cooling the yellow suspension to 0°C, 2M $NaNO_2$ (28.9 ml, 57.8 mmol) was added dropwise over 30 minutes. The suspension was stirred an additional 30 minutes at 0°C and 6 hours at room temperature. The mixture was again cooled to 0°C and added to a second beaker containing phenol (5.9 g, 62.7 mmol), glacial acetic acid (126 ml) and sodium acetate (16.8 g) at 0°C. The orange/red suspension was stirred at 0°C for 1 hour and then slowly basified to a pH of 7 with saturated Na_2CO_3. The red solid was filtered and washed with water. Flash chromatography (40:60 THF/hexane as eluant) yielded 10.2 g (65%) of monoazo nitronaphthyl phenol as an orange solid: mp = 180°C; ^{1}H NMR ($CDCl_3$) δ 9.0–6.8 (10H, m). IR ($CHCl_3$) ν_{max} 3370, 1608, 1600, 1515 cm^{-1}.

The above monoazo phenol (3.5 g, 11.9 mmol), acetone, potassium carbonate (3.36 g, 17.0 mmol) and 1-bromohexane (2.0 ml, 10.2 mmol) were mixed and refluxed for 16 hours under a nitrogen atmosphere. The reaction was cooled, extracted with ether, washed with water, 2N HCl, water and saturated sodium bicarbonate, dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to yield 4.4 g (98%) of 4-(4′-hexyloxyphenylazo)-1-nitronaphthalene as an orange/red solid. This was used in the next step without further purification. mp = 68–70°C. ^{1}H NMR ($CDCl_3$) δ 8.8–6.6 (10H, m); 3.85 (2H, *t*); 2.0–0.5 (11H, m). IR ($CHCl_3$) ν_{max} 1600, 1582, 1520, 1298 cm^{-1}.

The 4-(4′-hexyloxyphenylazo)-1-nitronaphthalene (4.4 g, 11.7 mmol) was dissolved in THF (77 ml) and absolute ethanol (150 ml) and heated with stirring under a nitrogen atmosphere to *ca.* 70°C. Sodium hydrogen sulfide (6.2 g, 110 mmol) dissolved in distilled water (22 ml) was added in one portion. After stirring 5 hours, the solution was poured into distilled water (200 ml) and the resulting red crystals were filtered and dried (3.81 g, 94% yield). Recrystallization from THF: ethanol yielded 3.2 g: mp = 87–88°C; ^{1}H NMR ($CDCl_3$) δ 8.9 (1H, *d*); 8.8–6.7 (9H, m); 4.45 (2H, br s); 3.9 (2H, t); 2.0–0.6 (11H, m).

4-(4′-hexyloxyphenylazo)-1-nitronaphthalene (1.4 g, 4.0 mmol) and 12 ml of 5N HCl was stirred at room temperature. After cooling to 0°C, $NaNO_2$ (260 mg dissolved in 5 ml distilled water, 3.8 mmol) was added slowly over 15 minutes with constant stirring. After 30 minutes, the mixture was added to a second beaker containing 2,3-dihydro-1,3-dibutyl-2-octyl perimidine (1.5 g, 3.8 mmol), glacial acetic acid (12 ml) and sodium acetate (1.6 g) at 0°C. After 30 minutes, the blue/black suspension was basified to a pH of 7, extracted with methylene chloride, washed with water, dried over anhydrous magnesium sulfate, filtered and concentrated to yield 3.5 g as a viscous blue oil. Purification via repeated flash chromatography (20:80 THF:hexane) yielded a dark blue viscous oil which would not crystallize. ^{1}H NMR ($CDCl_3$) δ 8.9 (2H, m); 8.4 (1H, *d*, J = 9 Hz); 8.2–7.1 (8H, m); 6.9 (2H, *d*, J = 9 Hz, aromatic); 6.5 (2H, m, aromatic); 4.3 (1H, bt, CH); 4.0 (2H, *t*, J = 6 Hz, CH_2O—); 3.9–3.4 (2H, m, Ch_2N—); 3.4–2.9 (2H, m, CH_2N—); 2.0–0.7 (42H, m). IR (CH_2Cl_2) ν_{max} 2930, 2860, 1588, 1300, 1140, 765 cm^{-1}. UV-Vis (CH_2Cl_2): λ_{max} = 600 nm, ε = 27,148 L/Mol·cm.

RESULTS AND DISCUSSION

Absorption Spectra

All dyes represented in Tables I and II were dark blue in color and showed a maximum absorption of between 560 and 620 nm. In general, as can be seen from a comparsion of the absorptions of **1b** to **1c** and **2d** to **2b**, the N,N′ disubstituted azo perimidines exhibited absorption maxima at longer wavelengths (30–50 nm)

TABLE I

Absorption data and melting points for mono(azo)-2,3-dihydroperimidines **1**

Dyes	R_1	R_2	R_3	mp (°C)	$\lambda_{max}{}^a$ (nm)	ε X 10^3
1a	H	Me	Me	176–178	568	15.4
b	H	H	C_8H_{17}	oil	568	8.9
c	Me	H	C_8H_{17}	105–107	600	26.5
d	C_4H_9	H	C_8H_{17}	oil	618	12.9

TABLE II

Absoprtion data and melting points for bis(azo)-2,3-dihydroperimidines **2**

Dye	R	R_1	R_2	R_3	mp (°C)	$\lambda_{max}{}^a$ (nm)	ε X 10^3
2a	C_6H_{13}	Me	H	C_6H_{13}	62–67	582	28.7
b	C_6H_{13}	Me	H	C_8H_{17}	122–125	592	31.9
c	$C_{12}H_{25}$	Me	H	$C_{12}H_{25}$	98–99	594	38.0
d	C_6H_{13}	H	H	C_8H_{17}	51–52	560	35.4
e	C_6H_{13}	C_4H_9	H	C_8H_{17}	oil	600	27.1

a. UV-Vis spectra run in dichloromethane.

than their unsubstituted counterparts. In addition, higher homologues (i.e., R_1 = C_4H_9) exhibited absorption maxima at longer wavelengths than their methyl substituted counterparts. The magnitude of the shift in λ_{max} as one goes from methyl substitution to n-butyl substitution (**1c**/**1d** and **2b**/**2e**) ranged between 10 and 20 nm.

The bis(azo)-2,3-dihydroperimidine **3** (Figure 2) previously synthesized in our laboratories, exhibited a λ_{max} in chloroform of 553 nm (ε = 28,100 L/Mol·cm). PPPMO[13,14] calculations had predicted that replacement of one of the phenyl rings with a naphthyl moiety would increase the wavelength of absorption approximately 30 to 40 nm. We can see from Table II that the lambda max of **2b** does indeed exhibit a UV-Vis bathochromic shift of *ca.* 40 nm[15] relative to **3**.

In most cases, PPPMO calculations accurately predicted the values of λ_{max} for the various azo chromophores which were synthesized. For example, the predicted λ_{max} of 575 nm for **2a** compares reasonably well with the experimental value of 582 nm (Table II). However, an unexpectedly high value was observed for the experimental absorption of **1c** relative to its predicted value. MO calculations had predicted an absorption of *ca.* 530 nm which was considerably lower than the experimental value of 600 nm. The reasons for this anomaly are unclear at this time.

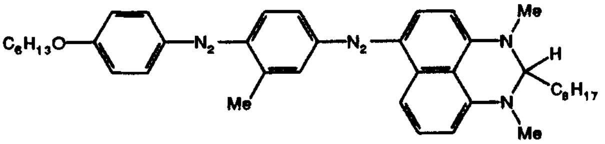
FLC Solubility

The FLC hosts SCE11 and ZLI-3654 which were used for solubility testing and device fabrication were both medium tilt liquid crystals (30° and 25° respectively). SCE11 has a phase sequence I to N^* (at 114°C) to S_c^* (at 60°C) to S_I (at −3°C), while ZLI-3654 has a phase sequence of I to cholesteric (at 86°C) to S_c^*/S_A (at 76°C) to S_c^* (at 62°C) and remains in the S_c^* to below 0°C.

Dye solubility was determined by increasing the concentrations at intervals of *ca.* 0.5% for all dye samples except **2e**. The percentages listed in Table III represent the highest dye concentration at which no phase separation was observed over a 30 day interval at ambient temperature unless otherwise noted.

Although the solubility of the N,N′-dimethyl substituted dyes was in some cases, about the same as that measured for the unsubstituted dyes, the di-n-butyl substituted dye **2e** exhibited solubilities greater than 8% in both liquid crystal hosts (9.5% in SCE11). In fact, since no upper limit was observed in SCE11, the maximum concentration has yet to be determined for this dye/host combination. Even after 11 months at ambient temperature, the slides containing the highest concentration of **2e** showed no deterioration in either liquid crystal host. The unsubstituted dyes generally discolored over time, particularly in the host ZLI-3654.

To determine the effect of dye loading on the S_c^* transition temperature, 5 μm



3

FIGURE 2 Bis(azo)-2,3-dihydroperimidine 3.

TABLE III

Percent solubility of 2,3-dihydroperimidine azo dyes in FLC hosts

	DYES					
FLC	**1a**	**1c**	**2a**	**2c**	**2d**	**2e**
SCE11	4.0	2.5	3.0	2.0	4.0	9.5[a]
ZLI-3654	1.5	3.0	2.0	-	1.0	8.0

a. Highest % loading which was investigated.

TABLE IV

S_c^* transition temperature of FLC guest-host mixtures as a function of dye **2e** concentration

Sample	% Dye []	FLC	S_c^* Transition (onset/cessation)
1	0	SCE11	57.6/57.8
2	2.1	SCE11	51.4/51.6
3	3.9	SCE11	45.5/45.7
4	7.3	SCE11	35.0/35.0
5	0	ZLI-3654	56.8/57.2
6	2.2	ZLI-3654	54.4/55.0
7	4.1	ZLI-3654	53.3/53.7
8	7.5	ZLI-3654	45.9/46.5

cells were fabricated and filled with FLC guest-host mixtures having a range of dye concentrations. The temperature at which switching commenced and ceased was then determined.

From the data in Table IV it can be seen that increasing the concentration of dye **2e** in the FLC hosts SCE11 and ZLI-3654 has the effect of lowering the upper S_c^* transition temperature. The effect is much less pronounced for ZLI-3654 than for SCE11. In the former case, a 7.5% loading of dye lowers the transition temperature only 10–11°C.

In summary, the mono(azo) and bis(azo) dyes described herein possess intense blue color and in some cases very high solubilities in ferroelectric liquid crystal hosts, making them viable candidates for high contrast FLC guest-host displays.

Acknowledgment

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15. The λ_{max} of **2b** when measured in chloroform in place of methylene chloride was 585 nm. This would represent an actual bathochromic shift of 32 nm.