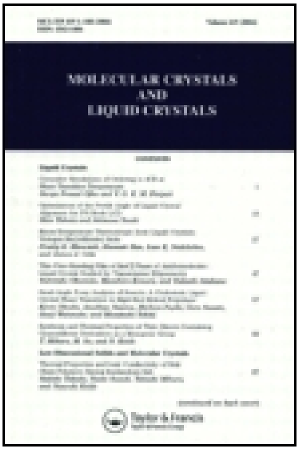

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: P. J. Shannon & S. T. Sun (1992): Synthesis and Characterization of Tetra(azo)2,3-Dihydroperimidine Dyes for Guest-Host Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 213:1, 43-49

To link to this article: http://dx.doi.org/10.1080/10587259208028715

Mol. Cryst. Liq. Cryst., 1992, Vol. 213, pp. 43–49
Reprints available directly from the publisher

Printed in the United States of America

Synthesis and Characterization of Tetra(azo)2,3-Dihydroperimidine Dyes for Guest-Host Liquid Crystals

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(Received August 25, 1991)

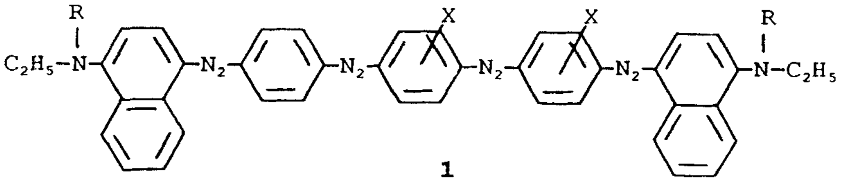
The synthesis and characterization of several tetra(azo)-2,3-dihydroperimidine dyes with alkyl substituents in the 1, 2, and 3 positions are described. The dyes have intense blue colors, high order pararmeters and high solubilities in liquid crystal host solvents. Order parameters are enhanced with longer alkyl substituents at the 2-position. Two of the dyes exhibit thermal transitions consistent with formation of liquid crystal phases.

INTRODUCTION

In 1974 White and Taylor described a twisted nematic version of Heilmeier and Zanoni's guest-host nematic display concept that accommodated all polarizations of light.[1,2] A guest-host display with high contrast, high brightness, and wide viewing angle, without the use of polarizers, became feasible. Since then, dichroic dyes for use in guest-host liquid crystal displays have been of significant interest.[3–5] A wide variety of azo, anthraquinone, and other dichroic dyes have been synthesized and characterized in liquid crystal host solvents.[6–12]

Requirements of the dyes include high order parameters, high extinction coefficients, good solubility in liquid crystal host solvents, high purity, photochemical and thermal stability and colors covering the whole visible range. Poly(azo) dyes have advantages in that they usually possess higher order parameters and much higher extinction coefficients than anthraquinone dyes. Increasing the number of azo groups increases the length to diameter ratio of the dye and usually results in an increase in the order parameter.[6–8,11] However, the solubilities of the higher poly(azo) dye molecules are claimed to be low.[4,8] Anthraquinones are noted for their photochemical stability but relatively low order parameters.[4,10]

In our development of new black dye mixtures for liquid crystal displays we had a need for a high performance blue dye. Poly(azo) dyes **1**, comprising N-ethylamino terminal moieties ($R = H$), exhibited blue colors but were not sufficiently soluble in many liquid crystal hosts. The N,N,N′N′-tetraalkyl analogs of **1** had improved solubility, but the maximum absorption was shifted to lower wavelength. This indicated that the nitrogen lone pairs were out of the plane of the chromophore. To circumvent this problem, tetra(azo) dyes **2**, incorporating the 2,3-dihydroperimidine moiety, were considered. Poly(azo) dyes where $R_1 = H$ are known,[13,14] but we anticipated that the N—H moieties would result in low solubilities. Thus 1,3-dialkyl analogs were desired.



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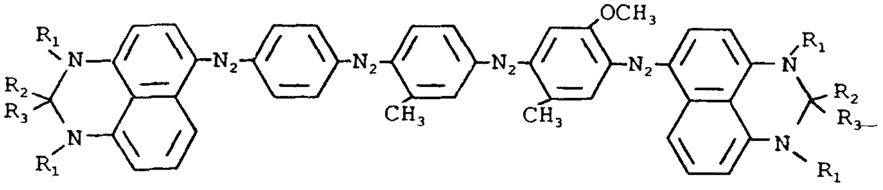

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We report here the synthesis and characterization of several tetra(azo)-2,3-dihydroperimidine dyes, **2**, with alkyl substituents at the 1, 2 and 3 positions, that have intense blue colors, high order parameters, and high solubilities in liquid crystal host solvents.

EXPERIMENTAL

Methods

Solubility was determined by a modification of the procedure of Haase.[15] Each dye was weighed into a Reacti-vial (Pierce Chemical Co.) containing a conical magnetic stirrer. ZLI 1982 (EM Chemicals) nematic host was added to give a 10 wt% mixture of dye in host. The mixture was sealed and stirred for six days at 25°C. The dye solution was filtered through a disposable syringe filter (Arco LC 13, 0.45 micron, Gelman Sciences). The filtered dye solution was weighed in an iodine cup and then transferred to a volumetric flask and diluted with chloroform. The UV-Vis spectrum of the filtered dye solution in chloroform was compared with those of solutions of known concentration. Comparing the extinctions, the solubility of the dye in the liquid crystal host was calculated.

Order parameters were measured using 11 micron gap cells containing buffed polyimide aligning layers. A Varian Cary 2300 Spectrophotometer was used to record the visible spectra. The filled cells were inserted into an Oriel 360° rotator with a stepper motor drive (#13049) mounted in the light path of the spectrophotometer. Between the light source and the rotating sample was inserted a Harrick depolarizer (#DPS-R4V, Harrick Scientific, Inc., Ossining, New York) and a Polaroid HN 32 polarizing film. A reference cell filled with liquid crystal solvent alone was used for calibration. An absorbance against wavelength scan was carried out to determine the wavelength of maximum absorption and the sample rotated to obtain a maximum value of A_{11} at lambda max. After realigning the sample through 90° a second adsorption spectrum was obtained and the minimum value, $A_{\perp}$, was obtained.

Infrared spectra were obtained on a Perkin Elmer 983G spectrometer. NMR spectra were recorded on a Varian EM-390 90 MHz CW spectometer using tetramethylsilane as an internal standard.

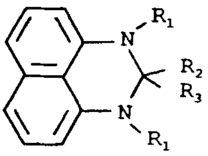
Differential scanning calorimetry was performed on a DuPont 2100 Thermal Analyzer at a heating rate of 20°C/min under a nitrogen atmosphere.

Materials

The 2,3-dihydro-1,3-dialkylperimidines were prepared by condensation of the desired aldehyde or ketone with N,N′-dimethyl-1,8-naphthalenediamine at room temperature in tetrahydrofuran with a catalytic amount of *p*-toluenesulfonic acid. Table I lists the melting points of several 2,3-dihydroperimidines prepared in this manner. The preparation of N,N′-dimethyl-1,8-naphthalenediamine has been described by Pozharskii, *et al.*[16] An alternative route was developed using direct methylation of 2,3-dihydro-2,2-dimethylperimidine followed by hydrolysis to give N,N′-dimethyl-1,8-naphthalenediamine.[17]

TABLE I

Melting points of 2,3-dihydroperimidines **4**



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	R_1	R_2	R_3	MELTING POINT (°C)
4a	H	CH_3	CH_3	114-115
b	CH_3	CH_3	CH_3	53-57
c	CH_3	H	C_3H_7	70-71
d	CH_3	H	C_8H_{17}	62-63
e	CH_3	H	$C_{12}H_{25}$	30-32

Tetra(azo) dye **2b.** The diazodiamine 3 (0.75 g, 2 mmol) was mixed with 5 N HCl (2.8 mL) and water (3.6 mL) to give a fine suspension. Sodium nitrite (2 M, 2.2 mL, 4.4 mmol) was added over 3 min at room temperature. The stirring was continued for 2 min and the mixture cooled to 0°C. The diazonium solution was added to a mixture of 2,3-dihydro-1,2,2,3-tetramethylperimidine, **4b**, (1.27 g, 5.6 mmol), sodium acetate (1.0 g) and acetic acid (8 mL) cooled to 0°C. A thick black suspension formed immediately. The mixture was stirred occasionally for 1 hr at 0°C. The mixture was basified by pouring into saturated potassium carbonate solution. The solid was washed twice with warm water and recrystallized twice from THF-ethanol (40 mL, 1:1) to give **2b** (0.60 g, 35%): mp 217°C; NMR ($CDCl_3$) 8.35 (*d*, 2H), 8.0–7.3 (*m*, 13H), 6.55 (*m*, 4H), 4.04 (*s*, 3H), 3.05–2.70 (4*s*, 18H), 1.5 (*s*, 12H); IR (KBr) 1588 cm^{-1}; solubility = 8.01 wt% in ZLI 1982; λmax ($CHCl_3$) = 600 nm, e = 6.50×10^4; order parameter = 0.70 (1.1 wt% in ZLI 1982).

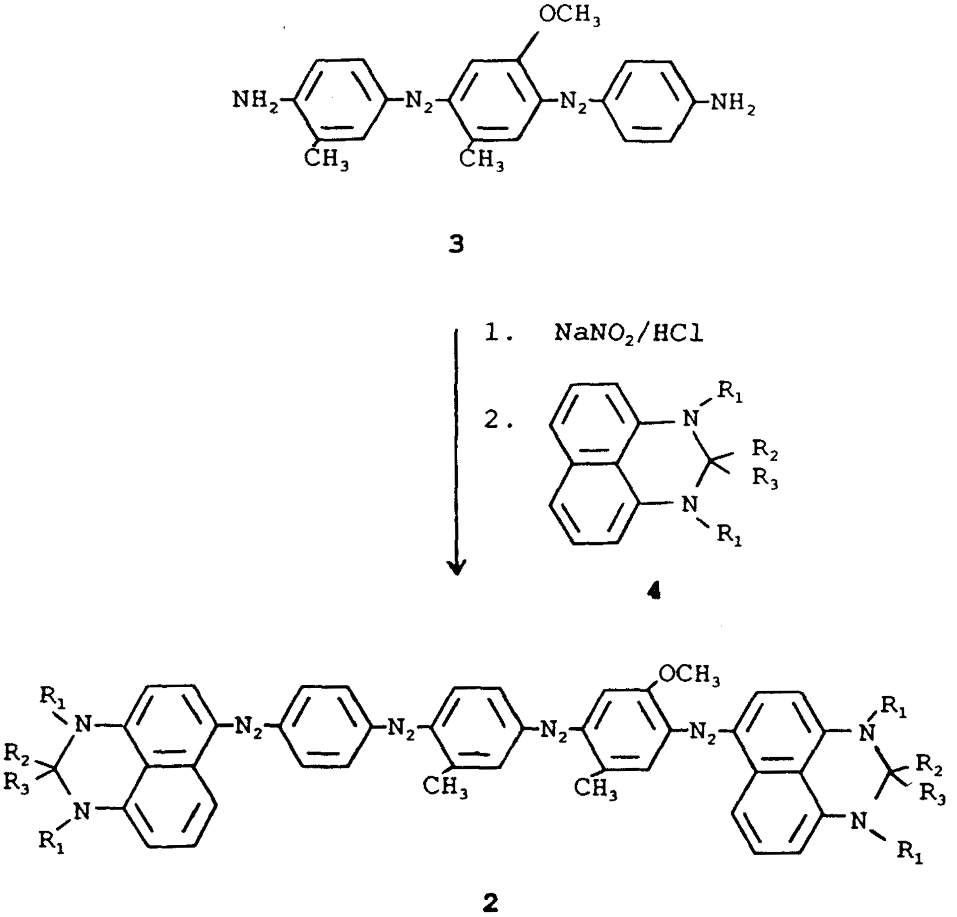
RESULTS AND DISCUSSION

The synthesis of the tetra(azo)-2,3-dihydroperimidine dyes is similar to that described by Cole and Aftergut for making poly(azo) dichroic dyes.[13,14] A bis(azo) diamine **3** (Scheme I) was first prepared by sequential diazonium coupling reactions. The diamine **3** was diazotized to give a bisdiazonium salt that was coupled with the desired 2,3-dihydroperimidine in acetic acid or acetic acid-tetrahydrofuran solution. The products were purified by chromatography and recrystallization before characterization. Table II lists information on the dyes prepared by this method.

Lambda max of 1,3-dimethyl-2,3-dihydroperimidine dyes range from 600 to 614 nm. The 1,3-unsubstituted dye **2a** has a maximum absorption at 588 nm, indicating that the 1,3-substitution pattern results in a slight red shift of the dye, as would be expected with an increase in electron density in the chromophore. The extinction coefficients range from 6.5×10^4 to 7.2×10^4 for dyes **2b–e**. This is five times higher than many anthraquinone dichroic dyes.

The solubility of the dyes was measured in ZLI 1982 nematic host using a modification of the procedure described by Haase.[15] As expected the 1,3-unsubstituted dye **2a** has fairly low solubility. The 1,3-substituted dyes have much higher solubility in the nematic host. The solubility decreases as the chain length of the 2-alkyl substituent increases beyond three carbons. These results indicate that larger poly(azo) dyes have sufficient solubility in nematic hosts to attain high contrast guest-host displays. The lack of hydrogen bonding moieties (N—H groups) and the unsymmetrical substitution pattern of the chromophore play a dual role in solubility enhancement.

The order parameter is a measure of the ordering of a dichroic dye in the liquid crystal host.[2] It is obtained by measuring the adsorption of the guest-host cell combined with a single polarizer, positioned to maximize absorption (A_{11}), and the absorption when the polarizer is rotated 90 degrees from the initial position



SCHEME I Synthesis of tetra(azo)-2,3-dihydroperimidine dyes.

$(A_\perp)$. The ratio of these absorptions is the dichroic ratio, D. The order parameter, S, is defined as

$$S = \frac{D - 1}{D + 2}$$

and is a number ranging from 0 to 1.0.

Order parameter measurement assumes that the dye and liquid crystal have been aligned optimally in one direction by a uniform aligning layer. Measurements can vary considerably from one practicing group to another.[18] This may be a consequence of very subtle differences in the effectiveness of the alignment layers. Thus, order parameters of this series of dyes are reproducible; but comparison of absolute numbers to order parameters of dyes measured by other workers may not be valid.

Table II indicates that the order parameters of the tetra(azo) dyes are relatively high. The order parameter increases as the length of the alkyl tail increases from

TABLE II

Physical data for tetra(azo)-2,3-dihydroperimidines

	R_1	R_2	R_3	mp[a] (°C)	λmax nm	ε X10^4	Solubility (ZL1 1982)	O.P. (1 wt%)
2a	H	CH_3	CH_3	202-215	588	4.11	0.71	—
b	CH_3	CH_3	CH_3	217	600	6.50	8.01	0.70[b]
c	CH_3	H	C_3H_7	167	614	6.67	9.34	0.73
d	CH_3	H	C_8H_{17}	120[c]	612	6.89	4.96	0.76
e	CH_3	H	$C_{12}H_{25}$	157[c]	612	7.22	1.76	0.77
							1.21[d]	0.80[d]

[a] Thomas-Hoover capillary.
[b] 1.1 wt%.
[c] Multiple melting transitions in DSC observed.
[d] Measured in ZL1 2452.

C-3 to C-12. This would be expected if the alkyl tail contributes to the overall length of a rigid molecule. Uchida, *et al.*, have indicated that order parameters of azo chromophores having alkoxy tails level off at a two carbon chain length.[11] Order parameter is known to be dependent on the dye concentration.[19,20] In most cases the order parameter decreases with increasing dye concentration. However, one example of an increasing order parameter with dye concentration has been noted.[12] The dye order parameter also changes significantly in different hosts.[3,4] As an example of this, the C-12 perimidine **2e** has an order parameter of 0.77 and 0.80 in ZLI 1982 and ZLI 2452 nematic hosts, respectively.

Since the length to breadth ratio of the tetra(azo) dyes is large, one may expect the dyes to exhibit some liquid crystal phases of their own. Tetra(azo) dyes **2d** and **e** were investigated further by microscopy and DSC. Microscopy of **2d** indicated an initial melting at 116°C and a significant viscosity reduction at 145°C. The DSC of **2d** showed large endotherms at 85 and 98°C that appeared to be solid-solid transitions, a slight endotherm at 117°C corresponding to the first melting transition and a broad shallow endotherm at 138°C. Microscopy of tetra(azo) dye **2e** shows softening at 117°C and significant viscosity reductions at 147 and 155°C. DSC of **2e** showed endotherms at 143 and 158°C. Thus, dyes **2d**, **e** appear to exhibit liquid crystal phases at elevated temperature. Typical phase textures were not evident by microscopy due to the very high extinction of light by the dyes.

In summary, the tetra(azo)-2,3-dihydro-1,3-dimethyl-2-alkyl perimidine dyes described here exhibit high solubilities in nematic hosts, offer high order parameters, and have intense blue colors necessary for high contrast guest-host displays.

Acknowledgment

We thank Scott T. Schnelle for this technical assistance and R. C. Burnier for solubility measurement.

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