Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Synthesis and characterization of guest-host azo dyes with broad absorption bands

A. M. Lackner[a]; E. Sherman[a]; S. -Y. Wong[a]; S. -M. Wong[a]
[a] Hughes Research Laboratories, Malibu, California, U.S.A.

To cite this Article Lackner, A. M. , Sherman, E. , Wong, S. -Y. and Wong, S. -M.(1993) 'Synthesis and characterization of guest-host azo dyes with broad absorption bands', Liquid Crystals, 14: 3, 763 — 771
To link to this Article: DOI: 10.1080/02678299308027753
URL: http://dx.doi.org/10.1080/02678299308027753

LIQUID CRYSTALS, 1993, VOL. 14, NO. 3, 763–771

Synthesis and characterization of guest–host azo dyes with broad absorption bands

by A. M. LACKNER*, E. SHERMAN, S.-Y. WONG and S.-M. WONG
Hughes Research Laboratories, 3011 Malibu Canyon Road, Malibu, California 90265, U.S.A.

Three groups of dyes were synthesized and characterized in order to examine their solubility, absorption spectrum, and order parameter in liquid crystal hosts. Our synthesis method allowed the formation of the diazonium salts and the diazo coupling in ethyl acetate instead of an aqueous medium, permitting the formation of long and neutral azo dyes. In the liquid crystal BDH-E7, they showed order parameters in the range of 0·52 to 0·76. The two dyes with the longest molecular lengths were particularly interesting due to their very broad absorption spectra in the visible region. Each of these two compounds behave as single component black dye guest/host systems, which generally require a mixture of two or three dyes in the liquid crystal host. These dyes were also evaluated for use in polymer dispersed liquid crystal films.

1. Introduction

Pleochroic dyes are defined as dye structures with maximum absorbance along their principal axis and minimum absorbance along their minor axis. The primary use of these dye molecules is for guest/host interaction in nematic or in cholesteric to nematic phase transition liquid crystal systems. Pleochroic dyes vary in structure, but most can be characterized as azo, anthraquinone, or naphthoquinone dyes. The later two structures are more bulky than the azo dyes; therefore, they greatly increase the viscosity of the guest/host liquid crystal (LC) mixtures. The viscosity is also dependent on the total dye concentration. Dye/liquid crystal displays have several advantages such as use in colour displays, they have a wider viewing angle for monochrome displays, improved grey scale capability, and a higher brightness by eliminating one or both of the polarizers used in twisted nematic (TN) cells.

The use of a pleochroic dye dissolved in a liquid crystal to make an electrically controlled transmission mode display device was first described in 1969 by Heilmeier [1]. In 1974 White and Taylor [2] reported displays using improved dyes in cholesteric/nematic liquid crystal mixtures. However, the absorption bandwidth of most of these dyes is too sharp, hence only a small part of the incident light is absorbed by the dye. To correct for this problem three or more single dyes have been used in most guest/host display devices. Many research groups have synthesized new, more stable pleochroic dyes for various applications, and studied their properties, such as photo-, and electro-chemical stabilities, as summarized in a 1987 review by Ivashchenko and Rumyantsev [3]. Here, we report three groups of dyes synthesized at Hughes Research Laboratories, and characterized regarding their absorption properties, order parameter, and applications in liquid crystal hosts.

* Author for correspondence.

2. Pleochroic dyes

2.1. *Dye structures*

A number of pleochroic azo dyes were synthesized possessing the three basic groups shown in table 1. Homologues were synthesized with an extended molecular length by increasing the number of repeat units (*n*) from one to three. The properties of the newly synthesized dyes were compared to a known dye structure IIb, reported by White and Taylor [2]. As we have predicted, the longer molecular length in each pleochroic dye structure shifted the absorption peak to longer wavelength and increased the dye's absorption bandwidth.

2.2. *Dye synthesis and purification*

Compound I was synthesized by reacting equimolar amounts of terephthaldehyde with *N*,*N*-dimethyl-4-phenylenediamine, according to (1) of figure 1. The intermediate product was then reacted with an equimolar amount of 4-amino-benzonitrile to give the final product which was purified by recrystallization from benzene.

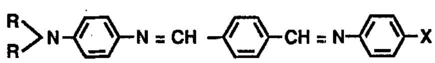
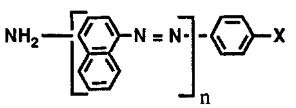
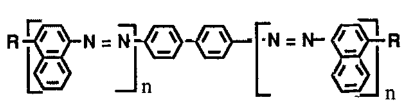
Compounds IIa and IIb were synthesized by a coupling reaction (using sodium nitrite) of 4-nitroaniline (or 4-cyanoaniline) and α-aminonaphthalene, as shown in (2) of figure 1. The final product was purified by recrystallization from ethanol. Compounds IIc and IId were synthesized by a coupling reaction (using isoamyl nitrite) of IIa or IIb and α-aminonaphthalene (see (3) in figure 1). The final product was purified with benzene.

Pleochroic dyes with structure III were synthesized according to the procedure shown in (2) for dye IIa. Compound IIIa was synthesized by a coupling reaction (using sodium nitrite) of one mole of benzidine and 2 moles of α-aminonaphthalene. Compound IIIb was synthesized by a coupling reaction (using isoamyl nitrite) of 1 mole of IIIa and 2 moles of α-aminonaphthalene. Compound IIIc was synthesized by a coupling reaction (using isoamyl nitrite) of 1 mole of IIIb and 2 moles of α-aminonaphthaline. The final products were purified with methanol.

2.3. *Pleochroic dye properties*

The new pleochroic dyes were characterized by measuring their absorption properties with a Perkin–Elmer Lambda 9 spectrophotometer. Spectral grade methylene chloride was used as a reference and as a solvent for the dye solution in 1 cm path length cells. The absorption maxima (λ_{max}), absorption bandwidths (at half

Table 1. The structures of the synthesized pleochroic dyes.

Compound	Dye structure	*n*	*X*	*R*
I		—	CN	CH_3
IIa		1	NO_2	—
IIb		1	CN	—
IIc		2	CN	—
IId		2	NO_2	—
IIIa		1	—	NH_2
IIIb		2	—	NH_2
IIIc		3	—	NH_2

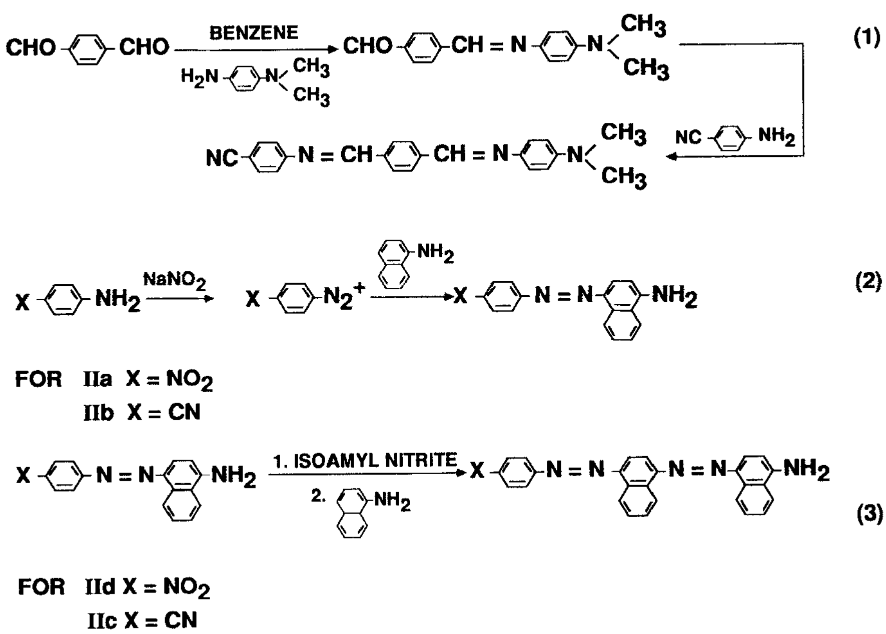


Figure 1. The synthesis procedure for the pleochroic azo dyes.

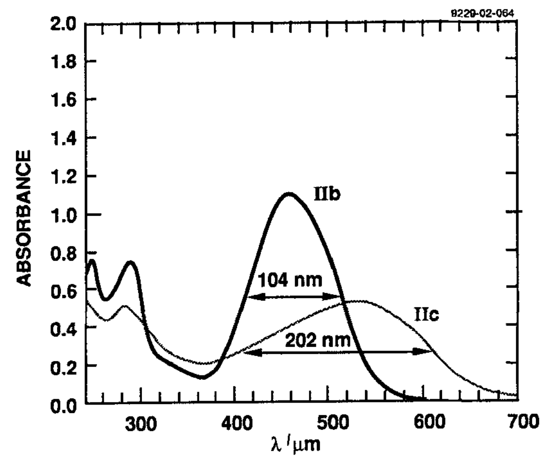


Figure 2. The absorption spectra of azo dyes IIb and IIc in methylene chloride.

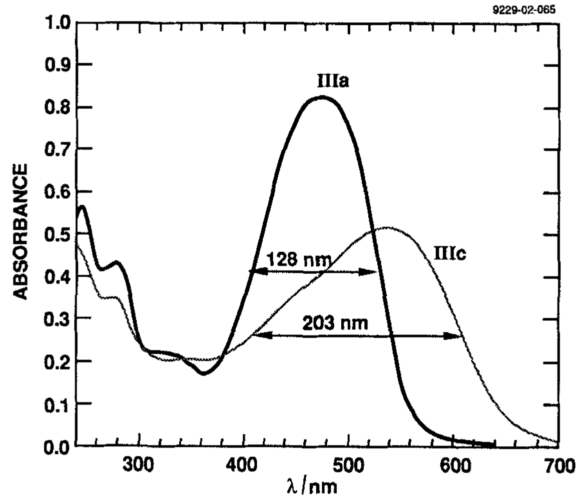


Figure 3. The absorption spectra of azo dyes IIIa and IIIc in methylene chloride.

Table 2. Pleochroic dye absorption in methylene chloride.

Compound	MW	Colour in CH_2Cl_2	ε in CH_2Cl_2	λ_{max}/nm	FWHM/nm
I	352·4	Yellow	$1{\cdot}6\times10^4$	434	96
IIa	291·3	Orange	$1{\cdot}6\times10^4$	476	123
IIb	272·3	Dark yellow	$2{\cdot}5\times10^4$	456	104
IIc	426·5	Magenta	$2{\cdot}7\times10^4$	528	202
IIIa	492·6	Dark yellow	$3{\cdot}6\times10^4$	474	122
IIIb	800·9	Magenta	$5{\cdot}7\times10^4$	536	199
IIIc	1109·3	Magenta	$5{\cdot}4\times10^4$	540	203

height), and extinction coefficients (ε) are summarized in table 2. The effect of the molecular length on the wavelength shift is shown in figures 2 and 3 for two different pleochroic dye structures. By extending the number of azo groups from 2, in dye structure IIIa, to six in dye structure IIIc, we have shifted the λ_{max} by 66 nm, and widened the FWHM bandwidth (FWHM defined as full width at half maximum transmittance), from 122 nm to 203 nm, respectively.

The magenta colour of the pleochroic dye IIIc in methylene chloride was changed to a dark grey colour by dissolving it in a liquid crystal mixture. Correspondingly, the dye's absorption band became wider in the LC solvent, as indicated in figure 4. In a BDH-E7 solution 80 per cent of the maximum absorption is retained in the 470 to 630 nm visible band.

The order parameter, S, of the pleochroic dyes was measured by dissolving dyes with broad absorption bands in liquid crystal mixtures with positive dielectric anisotropy. The dye/LC mixture was sandwiched between electrodes whose surface was treated to achieve uniform parallel alignment, by angle deposition of a thin layer of SiO_2. In the unexcited state the pleochroic dye was aligned by the liquid crystal and strongly absorbed one plane of polarization. Activating the cell with a sufficiently high

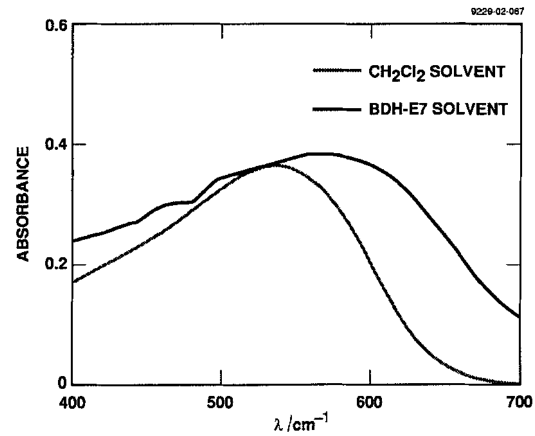


Figure 4. Comparison of dye IIIc absorption spectra in methylene chloride and the liquid crystal BDH-E7.

very small. Typical electric field activated transmission curves are shown in figure 5 for 0·5 per cent dyes dissolved in a BDH-E7 liquid crystal mixture. The guest/host mixture, including the newly synthesized blue pleochroic dye IId, showed more favourable electrooptical properties than the commercially available indophenol blue dye dissolved in the BDH-E7 LC host. Our single dye/LC mixture had a lower off-state and at the same time a higher on-state transmission than the indophenol blue/LC mixture, resulting in a higher contrast ratio of 9·3 as opposed to 4·9. Each of the newly synthesized dyes were dissolved in a BDH-E7 LC mixture for comparison of their absorption maximum, λ_{max}-E7, contrast ratio (CR = transmission at 10 V/transmission at 0 V) and order parameter, as tabulated in table 3. The optical order parameters of the dye host mixtures have been defined [2] as

$$S=\frac{A_{\parallel}-A_{\perp}}{A_{\parallel}+2A_{\perp}},$$

where $A_{\parallel}$ is the dye/BDH-E7 absorbance in a 0·5 mm thick test cell measured parallel to, and $A_{\perp}$ measured perpendicular to the director of parallel aligned LC layer. In BDH-E7, the new dyes showed order parameters in the range of 0·52 to 0·76. The two dyes with the longest molecular lengths in this group were particularly interesting due to their very broad absorption spectra in the visible region. The absorption spectrum of the longest single component black dye in the BDH-E7 LC was compared to the corresponding azo dye with $n=1$ in figure 6. Each of these two compounds behave as single component black dye guest/host systems, which generally requires a mixture of two or three dyes in the LC host.

3. New pleochroic dye applications

3.1. *Guest/host systems*

The grey scale response time of the best pleochroic dye, with the widest absorption band in the visible region, has been measured [4] and compared to the commercially available guest/host LC mixture, ZLI 2455, containing several dye components. Response time data were obtained with a step function of 10 kHz sine wave signals at different voltages corresponding to 4 distinct grey shade levels: 30 per cent, 50 per cent, 70 per cent, and 90 per cent of the maximum transmission level at 15 V. The turn-on electric field reoriented the LC/dye to a perpendicular state where the dye absorption is

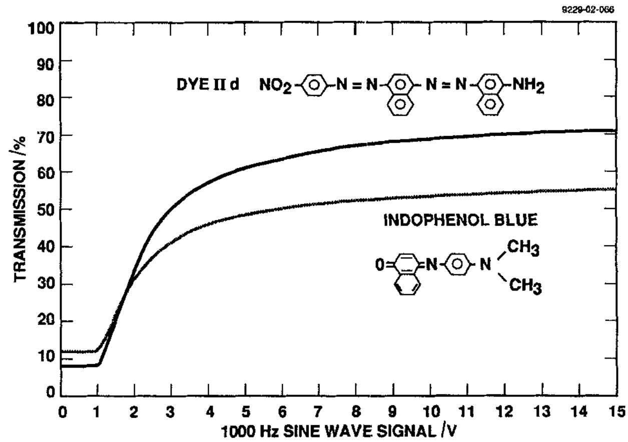


Figure 5. The field activated transmission curve for 0·5 per cent dye dissolved in a BDH-E7 liquid crystal mixture.

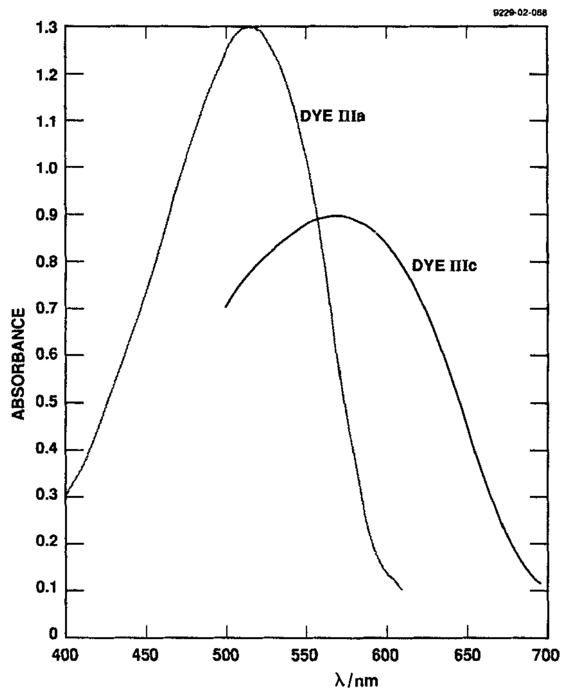
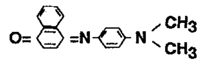
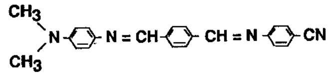
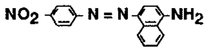
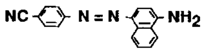
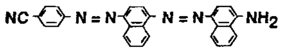
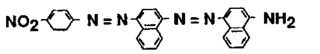
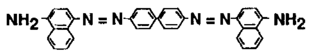
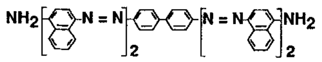
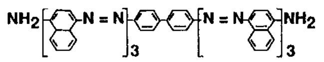


Figure 6. The absorption spectra of azo dyes IIIa and IIIc in a BDH-E7 liquid crystal mixture.

Table 3. Pleochroic dye properties in BDH-E7 liquid crystal mixtures.

	Dye structure	λ_{max}-E7/nm	*CR*	*S*
	 Indophenol blue	600	3·1	0·39
I		450	8·8	0·76
IIa		553	3·6	0·52
IIb		515	3·0	0·64
IIc		595	5·1	0·58
IId		606	4·4	0·55
IIIa		520	6·7	0·67
IIIb		575	5·9	0·63
IIIc		565	6·5	0·65

time (τ_{on}) was reported as the time interval between the start of the signal and 90 per cent of the maximum transmission, while the decay time (τ_{decay}) was measured from the termination of the step function signal to the decrease of the transmission to 10 per cent of its maximum level. From the data summarized in table 4 we can see a definite relationship between host viscosity and guest/host mixture response times. The single black dye response times and grey scale properties are comparable to the multi-component black dye mixture used in ZLI 2455. The *p* value included in table 4, $P_x = (V_x - V_{10})/V_{10}$, is a figure of merit indicating multiplexing limitations or grey scale capabilities. High P values are needed for good grey scale, whereas low P values are favourable for multiplexing. The single black dye, IIIc, demonstrated excellent grey scale capability with a figure of merit close to two times higher than that of the commercial guest/host mixture's *p* value.

Guest/host cells are much less sensitive to viewing angle distortions than standard TN cells [5], as we have demonstrated for the commercial black guest/host mixture ZLI 1841. We have observed a similar viewing angle improvement by using our single pleochroic dye IIIc in a nematic guest/host LC mixture.

3.2. *Dyes in polymer dispersed liquid crystal films*

Pleochroic dyes were added to liquid crystal mixtures used for polymer dispersed liquid crystal (PDLC) films to increase the on/off contrast ratio. Dyes which separate preferentially in the LC droplet should decrease the film off-state transmission by combining the light absorption with the light scattering effect. However, dyes also limit the film's on-state transmission due to their limited order parameter in the LC droplet, and especially due to any retention of the dyes in the polymer matrix. Selected new azo dyes ($\sim$1 per cent concentration) were dissolved in BDH-E7, mixed with the Norland NOA65 monomer system and photopolymerized with 14·6 mW cm^{-2} exposure. The

Table 4. Guest/host response times.

	Dye		
	IIIc	IIIc	ZLI 2455
Dye structure	Azo	Azo	Azo, naphthoquinone
Host LC	ZLI 2222-100	ZLI 1957/5	ZLI 1957/5
Host LC viscosity, at 20°C	12	18	18
Host LC voltage, *V*10	3·6	2·6	2·6
Grey level—30 per cent τ_{on}	117 ms	136 ms	132 ms
—30 per cent τ_{decay}	21 ms	29 ms	24 ms
Grey level—90 per cent τ_{on}	4 ms	5 ms	8 ms
—90 per cent τ_{decay}	21 ms	32 ms	28 ms
P_{80}–P_{20}	0·963	1·035	0·581

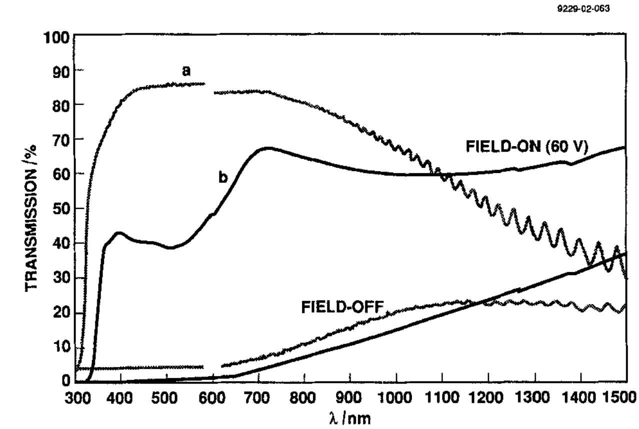


Figure 7. The wavelength effect on the PDLC film transmission, BDH-E7 in NOA65 with 1 : 1 volume ratio: (*a*) without dye; (*b*) with 1 per cent IIIc pleochroic dye.

long chain azo dye, IIIc, with flat absorption in the visible region was incorporated into a PDLC film and showed 40–50 per cent transmission in the 400–700 nm range, as shown by the spectrophotometer curves of the PDLC transmission in figure 7 for the field-on and field-off conditions. However, the guest/host PDLC has a lower transmission in the visible range than a comparable PDLC film without a dye, in the near IR region the guest/host PDLC showed higher transmission and contrast.

4. Conclusion

Several new pleochroic dyes were synthesized and evaluated for guest/host and PDLC applications. Our synthesis method permitted the formation of long and neutral azo dyes with order parameters as high as 0·76 in the LC BDH-E7. The two dyes with the longest molecular lengths in group III were particularly interesting due to their very broad absorption spectra in the visible region. Each of these two compounds behaved as single component black dye guest/host systems, which generally require a mixture of two or three dyes in the LC host, demonstrating good grey scale capability with a wide viewing angle. These dyes were also evaluated for use in polymer dispersed liquid crystal films, and were found to show improved properties in the near IR region.

The authors would like to thank Dr J. David Margerum for his assistance in many helpful discussions.

References

[1] HEILMEIER, G. A., CASTELLANO, J. A., and ZAZONI, L. A., 1969, *Molec. Crystals liq. Crystals*, **8**, 293.

[2] WHITE, D. L., and TAYLOR, G. N., 1974, *J. appl. Phys.*, **45**, 4718.

[3] IVASHCHENKO, A. V., amd RUMYANTSEV, V. G., 1987, *Molec. Crystals liq. Crystals*, A, **150**, 1.

[4] LACKNER, A. M., and MARGERUM, J. D., 1984, Flat panel liquid crystal display response time studies, Final Report, Contract No. N66001-83-C-0386.

[5] MARGERUM, J. D., LACKNER, A. M., and BAK, C. S., 1983, Flat panel liquid crystal display: gray scale and viewing angle studies, Final Report, Contract No. N66001-82-C-0297.