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Liquid Crystal Guest-Host Systems

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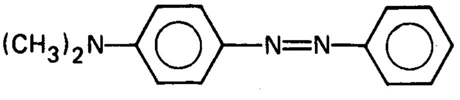
The guest-host interactions of pleochroic dyes dissolved in nematic liquid crystals has been reviewed, particularly with respect to the application in electrooptic displays. The role of the dye structure and the liquid crystal mixture is considered with respect to factors such as order parameter, absorption spectra and solubility.

The purpose of this review is to summarize the literature concerned with the use of dichroic dyes dissolved in nematic liquids. Such systems have found applications in two important areas, one to obtain information concerning the electronic spectra of the dyes, and the other as electrooptical displays. This latter application will receive greater emphasis in this review.

Liquid crystals are widely used in display applications, which exploit the electrooptical effects of dynamic scattering or the twisted nematic configuration. A display technique in which a dye was dissolved in a liquid crystal matrix was first suggested by Heilmeier and Zanoni[1] of the R.C.A. laboratories in 1968; however, vigorous commercial interest took some years to develop.[2] In this first report Heilmeier coined the name "guest-host interaction cells" and this has remained until the present.

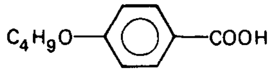
The principle behind the display is very simple and has not changed substantially since its inception in 1968. A small abount (0.1–1.0%) of a dichroic dye dissolved in a nematic liquid will be aligned with its long axis parallel to the long axis of the liquid crystal. This solution is then aligned either homeotropically or parallel to transparent electrodes depending upon the electrode surface treatment. If, for example, the nematic liquid is aligned in a parallel mode and has a positive dielectric anisotropy, the cell will be colored in the off position and become colorless on application of a field across the electrodes.

The original paper by Heilmeier and Zanoni demonstrated the effect by using 1 % by wt. of an azo dye, methyl red (**1**), dissolved in *p*-*n*-butoxybenzoic acid, a compound with a nematic range between 147° and 161°C. The electrodes were Nesa coated and spaced 12 μm apart. The cell showed a red to yellow color change in 1–5 msec. on the application of 4×10^4 V/cm. The relaxation time was about 100 msec.



(1)

This was followed by a more detailed study in which a greater variety of guest dyes and nematic hosts were investigated, and more quantitative measurements obtained.[3] Three nematic liquids (**2**), (**3**) and (**4**) were chosen as host materials and



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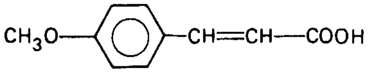

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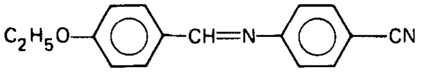
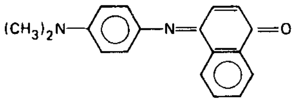


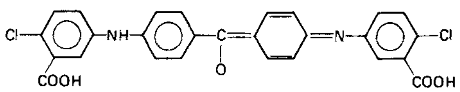
(4)

a variety of dye structures, (**1**), (**5**), (**6**), (**7**) and (**8**), were investigated as guest molecules.



Indophenol blue

(5)



Insolar green

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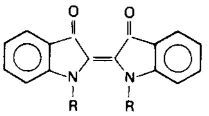
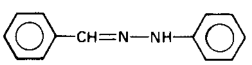


Indigos

(7)

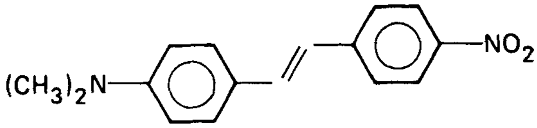


Hydrazones

(8)

Quantitative spectrophotographic measurements at 6000 Å of a system of (**5**) in (**4**) gave an optical density of 0.4 with no field applied and 1.9 with a field of 1.4×10^4 V/cm. It was determined that 10 % by wt. was a maximum dye concentration above which no further change in optical density was seen.

The next publication appeared three years later. In this study a trans-stilbene dye (**9**) was used as a guest in a compansated mixture of



(9)

cholesteryl chloride (CC) and cholesteryl nonanoate (CN).[4] The compensated ratio and temperatures were CC/CN 1/0.7 (T_N 55°C) and CC/CN 1/0.8 (T_N 60.5°C). Treatment of quartz plates with lecithin and sandwiching the guest-host mixture (10^{-3} wt. %) produced a cell in which the liquid crystal at $T° < T_N^\circ$ and $T° > T_N^\circ$ was oriented parallel but at T_N° was perpendicular to the plates. Thus by heating the cell from $T° < T_N^\circ$ to $T° = T°$ a color change could be seen. The optical density change in this case was from a maximum of 0.4 to a minimum of 0.05 at 4320 Å. Subsequently, the use of the same dye dissolved in two different nematic liquids, 4-methoxybenzylidene-4′-butylaniline (MBBA) and a commercial mixture of esters designated Merck W1, was described. In this case the liquid crystals were oriented with their long axis' parallel to a treated surface and both the absorption and fluorescent spectra of the guest molecule were measured. Measurements were made with lightpolarized parallel to and perpendicular to the long axis of the dye molecule.

To understand these results, the following introduction is necessary. The order parameter, S, is given by the formula

$$S = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle$$

where θ is the angle between the long molecular axis and the optical axis of the liquid crystal. Measurement of the absorption spectra of the guest with light parallel and then perpendicular to its long molecular axis will allow calculation of the dye order parameter. For molecules such as 4-dimethylaminonitrostilbene, in which the transition moment is parallel to the long axis, S can then be determined from the formula

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

where F is the dichroic ratio of the dye.

In terms of absorptivity the order parameter can be expressed as

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

The dichroic or contrast ratio (CR) is a related parameter and has also been used to evaluate the effectiveness of a dye in a guest-host cell.

$$\mathrm{CR} = \frac{A_{\parallel}}{A_{\perp}}$$

An examination was recently made[34] of these criteria as methods for evaluation of the merits of practical guest-host displays. It was found that not only was the ratio of parallel to perpendicularly transmitted light important, but that a number of other factors should be considered. These include the relative sensitivity of the human dye to various wavelengths of visible light and the width of the absorption band at half height. A value designated as the perceived contrast ratio (PCR) was suggested,

$$\mathrm{PCR} = \frac{\int_{4000\,\text{Å}}^{1000\,\text{Å}} T_{\perp}(\lambda)R(\lambda)\,\mathrm{d}\lambda}{\int_{4000\,\text{Å}}^{1000\,\text{Å}} T_{\perp}(\lambda)R(\lambda)\,\mathrm{d}\lambda}$$

where $T_{\perp}$ is the fraction of incident light transmitted in the on state, $T_{\parallel}$ is the light transmitted in the off state and R is the CIE standard relative spectral luminous efficiency for phototropic vision of the human eye at wavelength λ. Dyes with absorption at 550 nm, corresponding to a purple calor, were found to have the highest PCR. Although the perceived contrast ratio is undoubtedly a more valid figure of merit for a display cell than order parameter or contrast ratio, the literature to date has evaluated the cells in terms of order parameter and that is the method of comparison that will be used in this review.

The order parameter was determined as a function of temperature, as thermal motions of the liquid crystal host will decrease the apparent order parameter as the temperature increases. For the stilbene in W1 the order parameter decreased from 0.7 at $T/T_N = 0.85$ to 0.43 just below T_N. Similar measurements were made using 2,4-undecadienoic acid as the liquid crystal host and methyl red and pheophytine as the guest dyes.[6] The results show that this aliphatic acid is as good an aligning host as MBBA, however, it is less stable and tends to crystallize.

Russian workers[7] did the same experiment using as the guest-host couple N-dimethyl-4-nitrophenylazoaniline in 4-ethoxybenzylidene-4-cyanoaniline. They showed that the order parameter was constant over the band width of the absorption envelope and did not very with concentration. By independent methods the order parameter of the liquid crystal was measured and found to be the same as the value obtained for the dye. Thus they concluded that this was a simple method for measuring the order parameter of a liquid crystal. Larrabee[8] has suggested a display in which a pleochroic dye is aligned in a liquid crystal matrix in the usual manner; however, instead of

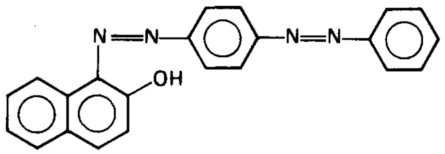
TABLE I

Dye	Ratio of on-to-off Fluorescence Intensities
Brilliant Phosphine	3.0/1
Primulin 0	1.7/1
1,8-Diphenyl-1,3,5,7-octatetrenol	1.5/1
Samaron Brilliant Yellow H6 G.L.	1.3/1

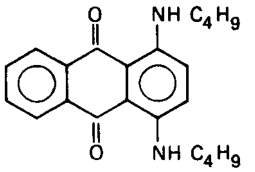
a change in the absorption spectrum of the dye as the liquid crystal is electrically switched, the change is in the fluorescence spectrum. The nematic host was *p*-*n*-butoxybenzoic acid and of the nearly 200 commercial dyes that were tested only four had enough variation in fluorescence to be of interest. These are shown in Table I with the ratio of intensities that were observed.

There was no further work using this concept until a recent paper by Coles[36] in which acridine orange, a cationic dye and a heterocyclic analogue of Michler's Hydrol Blue, was dissolved in a cyanobiphenyl host and tested as a fast optical shutter, making use of the fluorescence spectrum of the dye. A cell 2 mm thick was shown to have response times of several milliseconds compared to 100–200 ms for 20–50 μm cells in conventional systems. The contrast ratio, as Larrabee observed,[8] was not very high, due possibly to depolarization effects within the cell, however this remains a relatively unexplored area for investigation.

A patent[9] issued to the Matsushita Electric Industrial Company claimed a display using as nematic host a mixture of *p*-butoxybenzylidene-*p*′-cyanoaniline, *p*-heptyloxybenzylidene-*p*′-cyanoaniline and *p*-methoxybenzylidene-*p*′-heptylaniline. The pleochroic material which changed from red to blue in an electric field was a mixture of dyes (**10**) and (**11**).



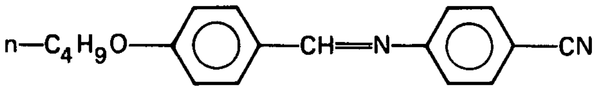
(**10**)



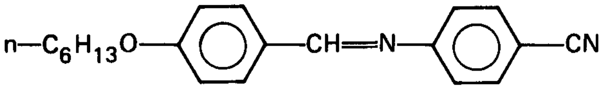
(**11**)

Thiacarbocyanine dyes dissolved in a liquid crystal host have also been used as color displays.[10]

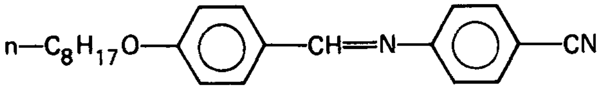
All of these devices used the change in orientation of a nematic host by an electric field as the switching mechanism. For good contrast between the on and the off state this configuration requires a polarizer in front of the cell, which decreases the brightness of the device. White and Taylor[11,12] suggested instead the use of the cholesteric to nematic transition. In this case the dye absorbs all of the incident light and not just one component of the polarization, and the requirement for a polarizer is eliminated. The host used was a mixture of equal parts of the liquid crystals **(12)**, **(13)** and **(14)**, with the addition of 5–15 % of the optically active ester **(15)**.



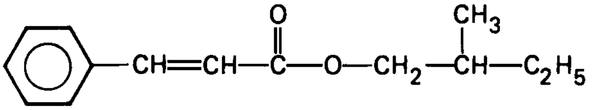
(12)



(13)



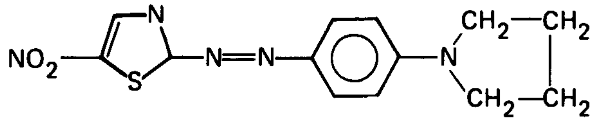
(14)



(15)

This mixture had a positive dielectric anisotropy and was cholesteric.

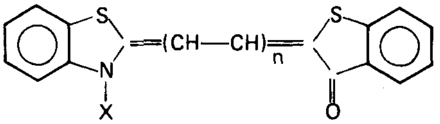
As guest dyes they used azo dyes of the aminothiazole type. An example is **(16)**.



(16)

Dyes of this type were found to be unstable if the device was operated with a DC field, but showed only small deterioration after three months operation in an AC mode. The authors described the model mathematically and concluded that the contrast ratio of such a device will increase inversely with the helical pitch of the cholesteric host; however, the shorter the pitch the more voltage required to switch to the nematic state. The validity of this relationship was confirmed experimentally by Cole and Aftergut,[13] who used as the cholesteric host a commercial formulation of *p*-cyanobiphenyl derivatives (E–7) plus an optically active *p*-cyanobiphenyl derivative (CB–15). The guest was a proprietary dichroic dye, G.E.–3.

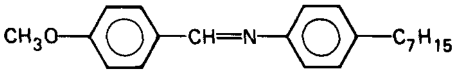
The original papers of Heilmeier and co-workers[1,3] used a nematic host with a positive dielectric anisotropy. Morita and co-workers;[14] however, at the Broadcasting Science Research Laboratories in Japan used MBBA as the aligning host. This is a well known room temperature nematic liquid with a negative dielectric anisotropy. The alignment is with the molecular axis perpendicular to the cell walls, and the application of a field, below the threshold voltage required for the onset of dynamic scattering, reorients the molecules to a parallel configuration, making the guest dyes visible. The dyes that were used were merocyanines such as (**17**).



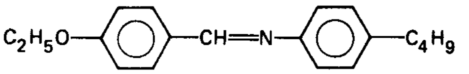
(**17**)

The cells had a rise time of 0.8 seconds at 10 r.m.s. volts, with a relaxation time of 2.5 seconds. The dye (**17**) for which x is a methyl group and $n = 2$ has a λ_{max} at about 6000 Å and a dichroic ratio of 1.93 on going from the colored to the clear state. This corresponds to an order parameter of 0.23.

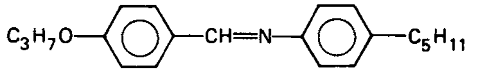
The Matsushita Electric Company in Japan has patented[15,16] electro-optical devices in which a 1 % solution of an anthroquinone dye in a mixture of Schiff base liquid crystals with negative dielectric anisotropy is used as the active element. The formulation was equal parts of (**18**), (**19**) and (**20**) and the dyes were (**21**) and (**22**)



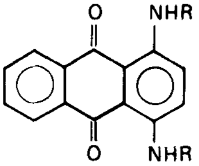
(**18**)



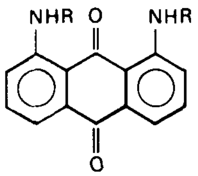
(**19**)



(**20**)



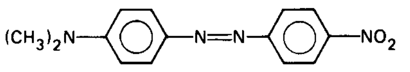
(**21**)



(**22**)

where R in (**20**) and (**21**) is an alkyl group, C_4—C_{20}. The example described was $R{=}C_4H_9$. These cells were blue in the absence of a field and colorless in a 1 KHz field of 20 volts. Demus Pelzl and Kuschel[17] reported still another display using a complex mixture of esters with a 1 % solution of methyl red as the guest dye.

Blinov and co-workers,[18] in an interesting twist, have chosen to use the guest host relationship of a dye in a liquid crystal matrix not as a light modulator for displays but as a convenient means for determining the liquid crystal order parameter. The dyes chosen have the direction of their absorption oscillator coinciding with their long molecular axis. Dissolving the dye in the liquid crystal and measuring the dichroic ratio, which has been corrected to take the local field anisotropy into account, allows the order parameter of the dye to be determined. These authors assume that the order parameter of the dye coincides with that of the liquid crystal. They used as guest molecules mostly azo dyes such as **(23)**, **(24)** and **(25)**.



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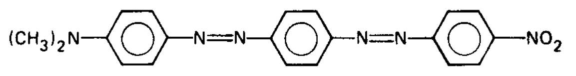

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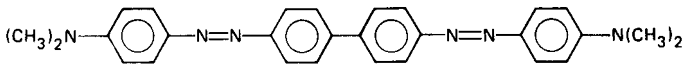
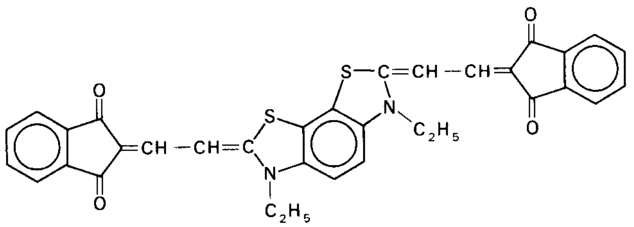


(25)

The order parameters of seven liquid crystals were determined by this method. The structures with the order parameters are shown in Table II. The value obtained for *p*-azoxyanisole (0.57) was compared to that obtained by N.M.R. (0.568) and by diamagnetic measurements (0.57) in order to confirm the validity of the method.

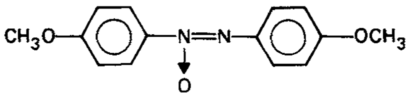
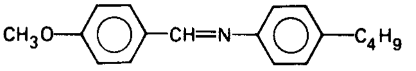
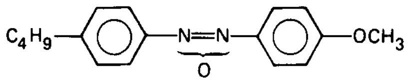
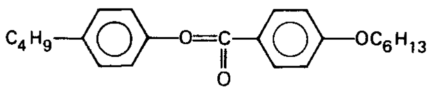
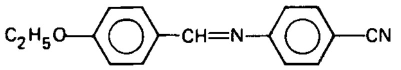
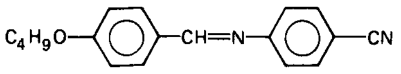
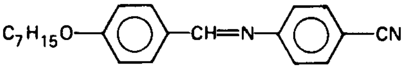
Other authors have used the orientation of a dye as a method for studying the polarization of its absorption bands. Meroxyanine dyes such as **(26)** dissolved in MBBA were investigated[19] and found to have two absorptions of opposite polarization, one along the molecular axis, at 5740 Å, and the other perpendicular to it at 4820 Å.



(26)

The same liquid crystal was used as host to investigate 4-nitro-4′-dimethylaminoazobenzene at 4950 Å.[20] The polarization of the electronic spectra of anthracene, pyrene, *p*-azoxyanisole and *β*-carotene was investigated[21] in two commercial liquid crystal hosts, ZL 612 and N-9 (Merck Co.). The order

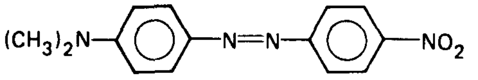
TABLE II

Dye	Order Parameter
	0.57
	0.63
	0.65
	0.745
	0.485
	0.625
	0.565

parameter of *p*-azoxyanisole was 0.66 in N-9 and 0.57 in ZL 612. *β*-Carotene has values of 0.69 and 0.59 in those same hosts. This technique has also been used to interpret the electronic absorption spectra of two porphyrins,[22] mesoporphyrin dimethyl ester and tetraphenylporphyrin, along with their manganese III salts. The host for this experiment was a compensated nematic mixture of cholesteryl chloride and cholesteyl laurate (27.7–72.3% by wt.). Orientation was by a DC electric field of 4 KV applied to silver electrodes. The results obtained disagree with previous work and show that all the transitions from 3500–9000 Å have the same in plane orientation. Previous work had indicated an out of plane transition at 4000 Å. The order parameter for the tetraphenylphorphyin free base was 0.13. These authors[23] improved the technique through the use of an AC field to orient the liquid crystal and studied a number of azo aromatic compounds in order to demonstrate the usefulness of the method as a means of assigning the polarizations of electronic transitions in organic molecules.

Another group[24] has measured the decrease in order parameter of MBBA by dissolving a variety of solutes with different shapes and sizes in this liquid crystal. The additions of the identical mole fractions of anisotropic molecules were found to lower the order parameters by identical amounts, the effect with isotropic molecules, on the other hand, increases with solute size.

The first work on the effect of dye structure was undertaken by Constant and co-workers.[25] They investigated the effect of structure change for four azo dyes **(27)**, **(28)**, **(29)** and **(30)** on the order parameter, and on the stability of the dye in a display cell. They also evaluated the dyes with respect to parameters such as color and solubility.



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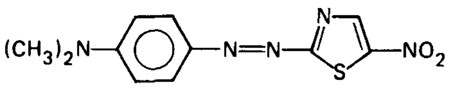

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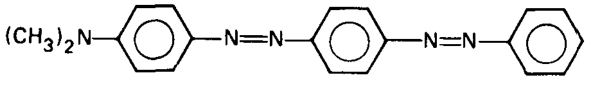
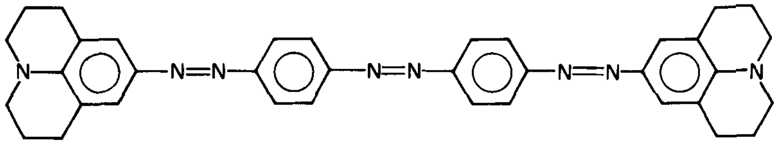
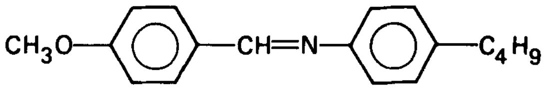


(29)

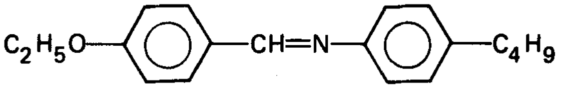


(30)

The liquid crystal hosts used in these investigations were commercial mixtures of 4-alkyl-4'-cyanobiphenyls and 4-alkyl-4'-cyanoterphenyls (E3, E7, E8 and E9). The order parameters were calculated from the dichroic ratios of layers which were aligned parallel to the electrode, and had dye concentrations of 0.5 wt. %. As had been anticipated, the order parameter increased with the length of the molecule. The dye stability was good for compounds **(27)** and **(29)** and poor for **(28)** and **(30)**. The absorbance of these latter two decreasing to 50 or 60% of their original absorbance after 12 to 16 × 10^3 hours running time. Dyes **(27)** and **(29)**, on the other hand, showed almost no decrease in absorbance after 16 × 10^3 hours. These results are corroborated by some initial work done in this laboratory[26] in which a 1% solution of dye **(30)** in 4-pentyl-4'-cyanobiphenyl was tested. The resistivity decreased from 5×10^{10} to 10^9 ohm cm^{-1} in two days and the initial purple color had deteriorated in the same time. Uchida and co-workers[27] also did an investigation of dyes suitable for display cells by determining the order parameters for 30 dyes using a single liquid crystal host. The host was a mixture of three Schiff base liquid crystals **(31)**, **(32)** and **(4)** in a ratio of 50/35/15 wt. % and had a positive dielectric anisotropy

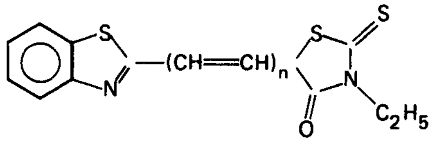


(31)

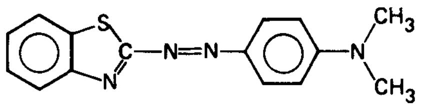


(32)

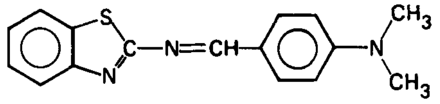
The dyes investigated can be divided into three main categories, as examplified by (33), (34) and (35).



Methine dyes (33)



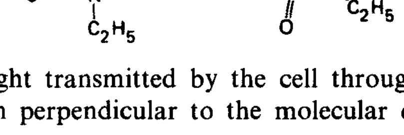
Azo dyes (34)



Azomethine dyes (35)

The cells were prepared from glass which had been treated with N-methyl-3-aminopropyltrimethoxysilane, an orienting agent which promotes parallel alignment. The results confirmed once again that the longer dyes had higher order parameters, and comparing the three types of dyes it was found that the order parameters of the azo and azomethines were greater than comparable methine dyes. Surprisingly it was noted that in comparing dyes with N-alkyl groups the shorter the alkyl chain, the higher the order parameter. Dyes with heterocyclic rings had lower order parameters upon replacement of a sulfur in the ring with an oxygen atom.

These same workers[28] using the same liquid crystal host and alignment technique next investigated the effect of varying several cell parameters using a single merocyanine dye (36) as the guest.



(36)

They plotted the light transmitted by the cell through a polarizer, first parallel to and then perpendicular to the molecular orientation initially against electrode spacing at constant concentration, and then with various dye concentrations and constant electrode spacing. These experiments confirmed the Beer-Lambert relationships.

$$\text{Log } T_{\parallel} = -k_{\parallel}cd$$

$$\text{Log } T_{\perp} = -k_{\perp}cd$$

Where c is the dye concentration, d the cell spacing, T the light transmission and k the absorption coefficient. If a field is applied to the cell with the polarizer parallel, the light transmission is modified and the Beer-Lambert relationship can be written

$$\text{Log } T_{\parallel}' = -k_{\parallel}'cd$$

Where $k_{\parallel}'$ is an apparent absorption coefficient. Due to the influence of the cell walls on the orientation $T_{\parallel}' < T_{\perp}$ and the measured cell thickness, d has to be modified by a factor ds which depends on the depth of influence of the wall orientation into the cell. They showed that the ratio ds/d for an applied voltage is independent of d and above 15 volts the ratio of ds/d is less than 0.04. Thus, above this voltage the surface layers can be neglected. If the product of the dye concentration and cell thickness is kept constant, variations in the cell thickness will not alter the color switching characteristics. They also measured the relationship between the rise and recovery time as a function of voltage and cell thickness and showed:

$$t_{\text{rise}}\,\alpha(d/V)^2$$

$$t_{\text{rec.}}\,\alpha d^2$$

Where d is the cell thickness and V the applied voltage.

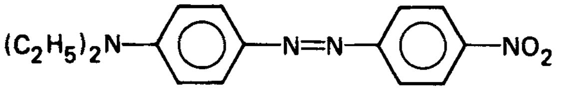
Another investigation into the effect of dye structure on order parameter was carried out[29] by determining the order parameter in the usual manner, i.e., measuring the dye absorption parallel and perpendicular to an aligned nematic host through a plane polarizer. The alignment was achieved by evaporation of an SiO_x layer at an angle of 30° on to indium doped tin oxide coated glass plates. The dye concentrations were 0.3 wt. %. The host liquid crystal was the same mixture of **(30)**, **(31)** and **(4)** used by Uchida.[27] Thirty-five azo dyes were investigated. Substitution on the benzene ring either in the form of a hydrogen bonding substituent or simply a broadening substituent such as methyl, lowers the order parameter. The substitution of a pyrrolidine ring in place of N-dialkylamine on the benzene ring has the effect of increasing the order parameter quite markedly. The exception to this is dimethylamino which also imports a high order parameter. The series once again confirms the fact that for equivalent substituents the longer the dye molecule the higher the order parameter.

In the azobenzene series the effect of substitution in the benzene rings is additive and by assigning group values for order parameter the order parameter for an unknown molecule could be predicted. Substitution of thiazole rings for the benzene rings lowers the order parameter, and the λ_{max} is shifted to a lower energy. A benzothiazale, however, increases the order parameter once again. A few dyes were prepared with other five membered nitrogen sulfur heterocycles and these were found to have lower order parameters when compared to the thiazoles. The same authors[30] then selected three azo dyes from the group tested in their first study[21] and measured the effect of a variety of nematic hosts. The cell preparation and measuring techniques were the same as in the previous paper although they did note that the calculation of the order parameter should include the refractive indices $\eta_{\parallel}$ and $\eta_{\perp}$.

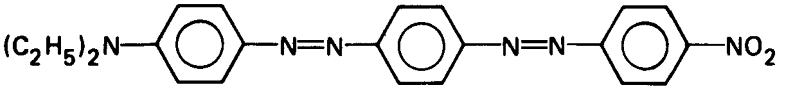
$$S = \frac{A_{\parallel}\eta_{\parallel} - A_{\perp}\eta_{\perp}}{2A_{\perp}\eta_{\perp} + A_{\parallel}\eta_{\parallel}}$$

Calculations using this formula increased the value of S by 0.03–0.05.

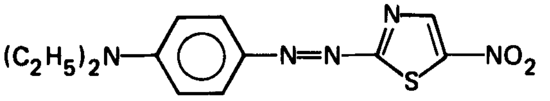
The dyes selected for testing were **(37)**, **(38)** and **(39)**.



(37)



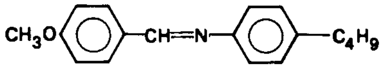
(38)



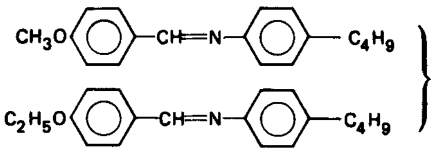
(39)

The nematic hosts selected were the following:

1.

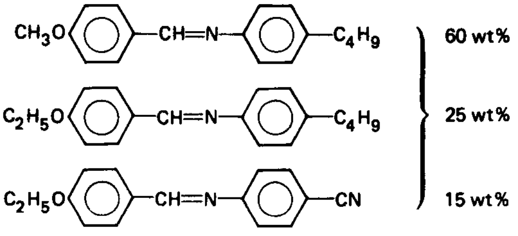


2.



1:1 wt%

3.

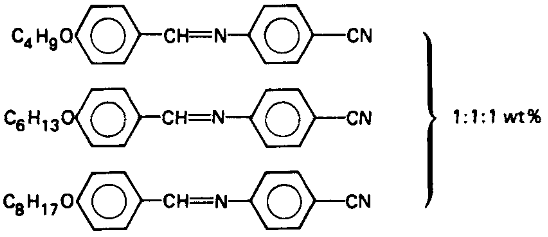


4. Hoffman-La Roche 101 – Ester Mixture

5. Hoffman-La Roche 200 – Schiff Base Mixture

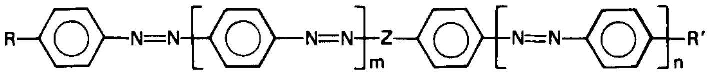
6. B.D.H E-7 Cyanobiphenyls and Terphenyls

7.



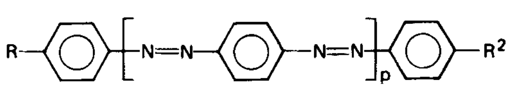
One of the factors which of course will affect the order parameter is the temperature, and how close the temperature of the measurement is to the clearing temperature of the host. The fact that in this set of experiments the order parameter is not directly proportional to the difference between room temperature and the clearing temperature shows that there are other factors involved when comparing effects of different hosts. The conclusion was that there is no ready correlation between the physical properties of the hosts and the order parameters of the dyes, and consequently it was hazardous to infer the order parameter of the host from that of the dye.

A patent issued to Coates Gray and McDonnel[31] claimed azo dyes such as **(40)**, **(41)** and **(28)** to have high order parameters and good chemical stability when dissolved in cyanopolyphenyl type liquid crystals.



(40)

$R{=}R'{=}H$, alkoxy, dialkylamino $Z{=}N{=}N,\underbrace{N{=}N}_{O}$ $m{=}n{=}0\ldots 4$

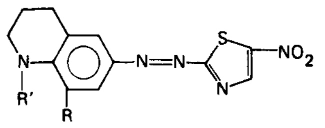


(41)

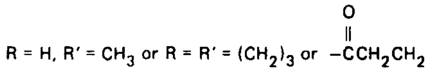
$R{=}H$, alkoxy, dialkylamino $R^7{=}NO_2CN$ $P{=}0\ldots 4$

The example cited was (**27**) which in a mixture of cyanobiphenyls, has a λ_{max} of 5940 Å and an order parameter of 0.70.

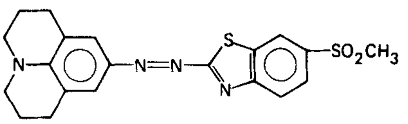
Another patent[32] claims the use of azo dyes such as (**42**) and (**43**). No details concerning the cells are given.



(**42**)

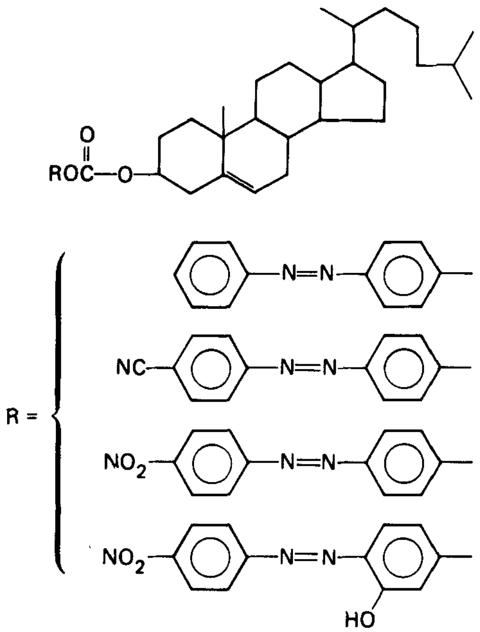


$R = H, R' = CH_3$ or $R = R' = (CH_2)_3$ or $-\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2-$



(**43**)

An investigation of the properties of a series of cholesteryl azo dyes which themselves are liquid crystalline was recently carried out. These are not very highly colored compounds, having λ_{max} ranging from 3220 to 4300 Å and with melting points from 137° to 226°C. Their structures are shown below; (**44**) to (**48**).

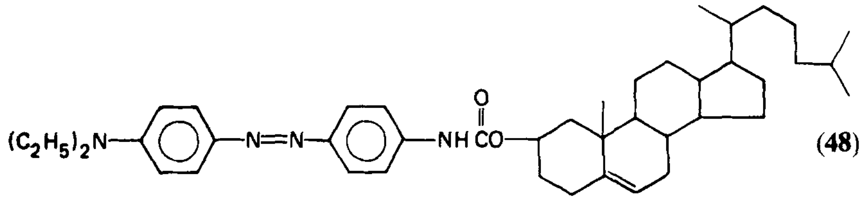


(**44**)

(**45**)

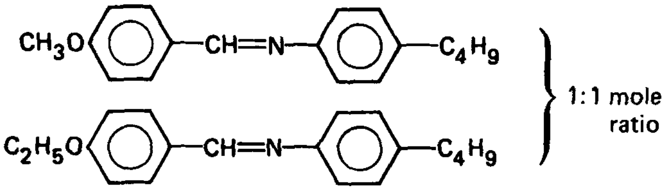
(**46**)

(**47**)

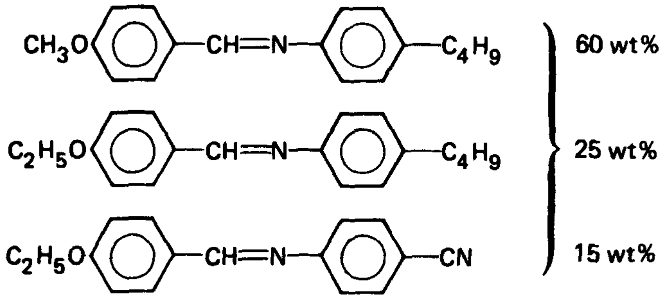


(48)

They were used as 0.3% additives to two different nematic mixtures, and the order parameters determined. The cell preparation and method for determination of the order parameters was the same as described in Ref. 20. The nematic hosts had the following compositions.

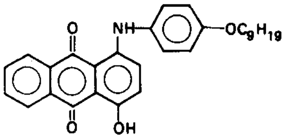


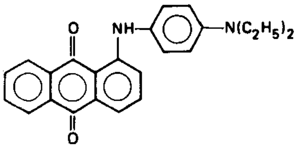
and

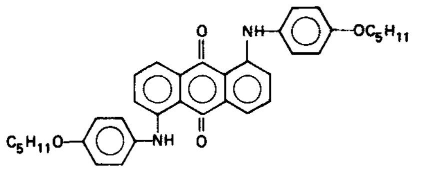


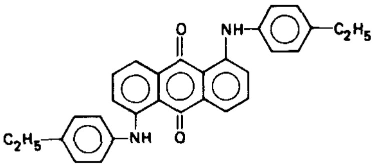
The order parameter was only measured for (**48**), and as would be anticipated this is quite different for the two hosts. The two component mixture giving a value of 0.51 and the three component mixture 0.61. These values are not much different than is found for a number of monoazobenzenes, despite the additional length due to the cholesteryl moiety. The authors conclude that this similarity can only be due to steric interactions between the dye and the host molecules.

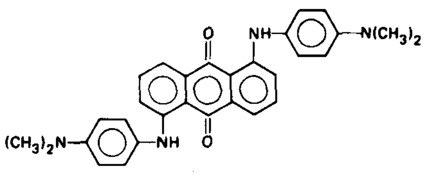
A recent publication[2] claims vast improvement in photochemical stability for a series of anthraquinone dyes compared to azo dyes. The structures of these dyes are shown as (**49**) to (**53**).


(49)


(50)


(51)


(52)


(53)

The hosts used in this study were commercial cyanobiphenyl and terphenyl mixtures (E7 and E9), and the cells were aligned by using a rubbed polyvinyl alcohol coating on glass substrates. The order parameters were quite consistant for the five materials, varying only from 0.63 to 0.68. The photostability tests were carried out using two types of lamps, GE F20T12 Black Light and Hanovia OVS 500 arc lamp. Resistivities which started at about 10^{11} ohm cm^{-1} dropped about an order of magnitude over a period of two months. Azo dyes which were tested under the same conditions dropped about an order of magnitude over a period of two months. Azo dyes which were tested under the same conditions dropped about two orders of magnitude during the same time. The order parameters of the anthraquinone dyes remained essentially constant during two months exposure, azo dyes, on the other hand, dropped about 0.6 to 0.7 units in 400 to 1800 hours.

Tables III to VI summarize the individual dyes that have been investigated as guest molecules in liquid crystal hosts and give the order parameter and

TABLE III

Anthraquinone dyes

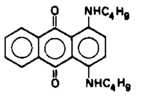
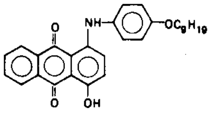
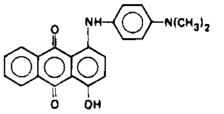
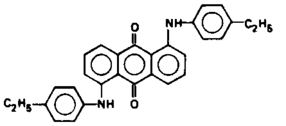
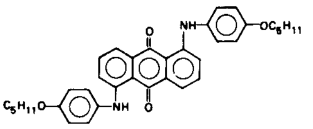
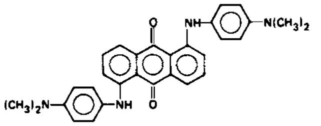
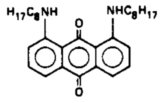
Structure	Order parameter	Absorption (λ nm)	References (Liquid crystal mixtures)
	—	blue	15(2) 9(19)
	0.65	596	2(12)
	0.63	612	2(12)
	0.67	554	2(12)
	0.68	557	2(12)
	0.65	546	2(12)
	—	purple	16(19)

TABLE IV
Merocyanine dyes

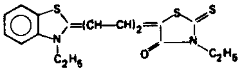
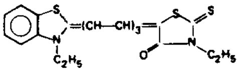
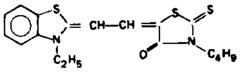
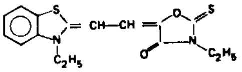
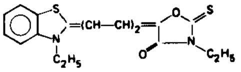
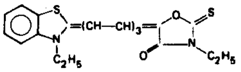
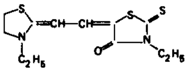
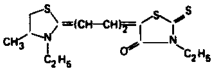
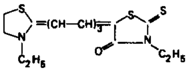
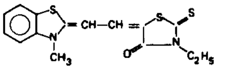
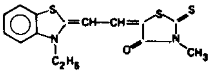
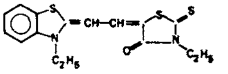
Structure	Order parameter	Absorption (λ nm)	References (Liquid crystal mixtures)
	0.55 —	610 610	27(7) 28(7)
	0.64	640	27(7)
	0.50	530	27(7)
	0.46	505	27(7)
	0.51	578	27(7)
	0.59 —	613 640	27(7) 28(7)
	0.23	487	27(7)
	0.36 —	563 603	27(7) 28(7)
	0.48	603	27(7)
	0.54	529	27(7)
	0.52 —	529 530	27(7) 28(7)
	0.50 —	532 530	27(7) 28(7)

TABLE IV (continued)

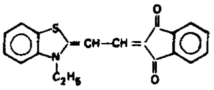
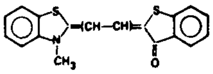
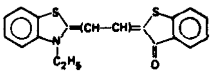
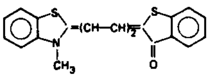
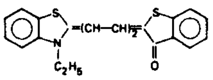
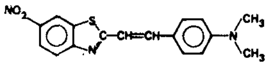
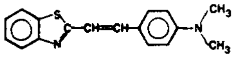
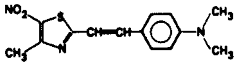
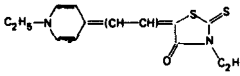
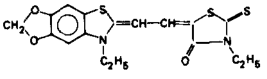
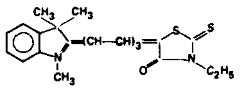
Structure	Order parameter	Absorption (λ nm)	References (Liquid crystal mixtures)
	0.375	500	19(1)
	0.17	—	14(1)
	0.14	—	14(1)
	0.24	600	14(1)
	0.16	—	14(1)
	0.7	457	27(7)
	0.59	413	27(7)
	0.57 —	510 510	27(7) 28(7)
	0.59	582	27(7)
	0.57	551	27(7)
	0.55 —	608 612	27(7) 19(7)

TABLE IV (continued)

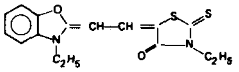
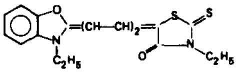
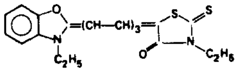
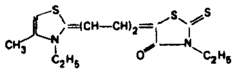
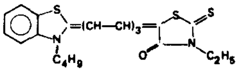
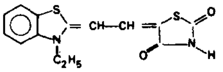
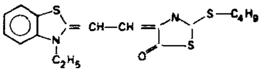
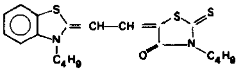
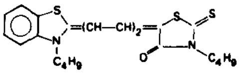
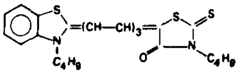
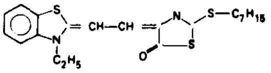
	0.36	497	27(7)
	0.42	577	27(7)
	0.54 —	624 624	27(7) 28(7)
	—	632	28(7)
	0.57	640	27(7)
	0.41 —	474 475	27(7) 28(7)
	0.41	534	27(7)
	0.39	531	27(7)
	0.45	611	27(7)
	0.56	637	27(7)
	0.39	535	27(7)

TABLE V
Azo dyes

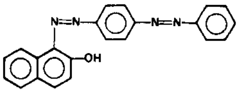
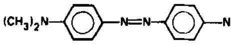
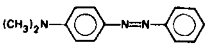
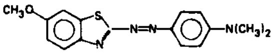
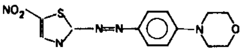
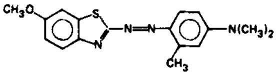
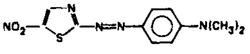
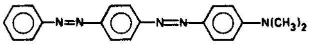
Structure	Order parameter	Absorption (λ nm)	References (Liquid crystal mixtures)
	—	—	9(2)
	0.565	490	18(25)
	0.625	490	18(24)
	0.485	490	18(23)
	0.745	490	18(22)
	—	495	20(1)
	0.5	500	7(3)
	0.62	500	29(7)
	0.70	508	25(16)
	0.60	—	25(15)
	0.70	—	25(12)
	0.77	—	25(13)
	0.57	490	18(20)
	0.63	490	18(1)
	0.65	490	18(21)
	0.14	495	6(29)
	—	—	3(3)
	0.17	482	1(6)
	—	—	17(18)
	0.66	512	27(7)
	0.66	570	27(7)
	0.63	523	27(7)
	0.70	594	25(16)
	0.70	594	31(16)
	—	blue	26(17)
	—	orange	26(17)
	0.75	505	25(16)
	0.67	—	25(15)
	0.74	—	25(12)

TABLE V (continued)

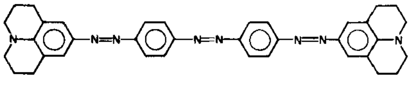
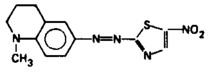
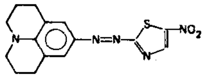
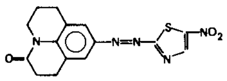
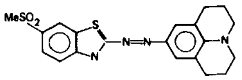
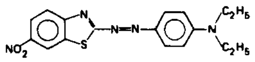
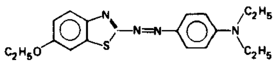
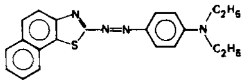
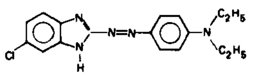
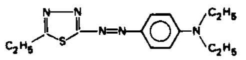
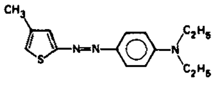
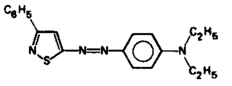
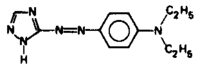
	0.79 0.78 0.78 0.80 —	568 — — — purple	25(16) 25(12) 25(15) 25(13) 27(17)
	—	—	32
	—	—	32
	—	—	32
	—	—	32
	0.58	551'	29(7)
	0.57	522	29(7)
	0.54	539	29(7)
	0.46	507	29(7)
	0.48	502	29(7)
	0.47	491	29(7)
	0.45	528	29(7)
	0.16	456	29(7)

TABLE V (continued)

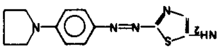
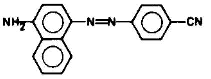
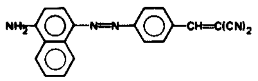
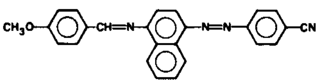
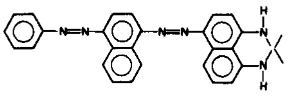
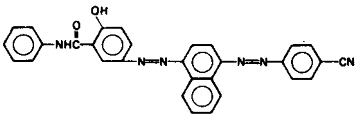
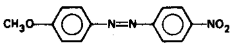
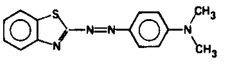
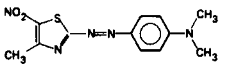
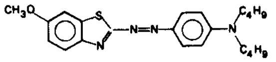
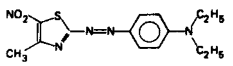
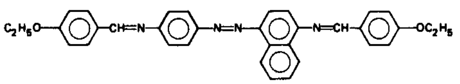
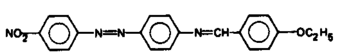
Structure	Order parameter	Absorption (λ nm)	References (Liquid crystal mixtures)
	0.71 0.54	595 607	11(8) 29(7)
	0.67	500	11(8)
	0.65	470	11(8)
	0.77	450	11(8)
	0.63	620	11(8)
	0.71	490	11(8)
	0.69	430	29(7)
	0.63	512	27(7)
	0.60	585	27(7)
	0.56	517	27(7)
	0.53	508	27(7)
	0.77 —	451 yellow	27(7) 28(7)
	0.72 —	413 yellow	27(7) 28(7)

TABLE V (continued)

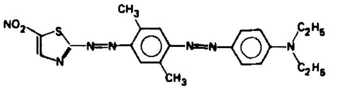
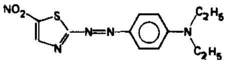
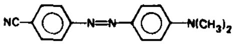
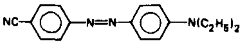
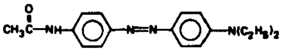
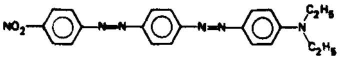
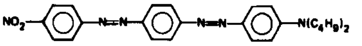
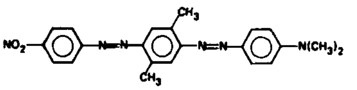
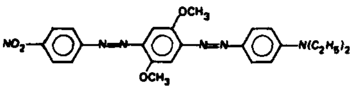
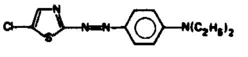
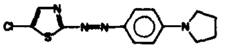
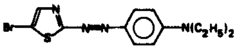
	0.73	595	11(8)
	0.48	595	30(1)
	0.46	595	30(9)
	0.48	593	30(7)
	0.38	595	30(10)
	0.67	592	11(8)
	0.46	595	29(7)
	0.52	603	30(11)
	0.59	600	30(12)
	0.60	603	30(8)
	0.60	464	29(7)
	0.52	474	29(7)
	0.50	425	30(8)
	0.50	425	33(7)
	0.66	550	29(7)
	0.65	538	33(9)
	0.72	550	30(1)
	0.73	545	30(9)
	0.70	542	30(7)
	0.54	540	30(10)
	0.65	538	29(7)
	0.65	538	30(11)
	0.66	545	30(12)
	0.70	542	33(7)
	0.61	544	29(7)
	0.59	579	29(7)
	0.52	585	29(7)
	0.46	520	29(7)
	0.58	526	29(7)
	0.45	522	29(7)

TABLE V (continued)

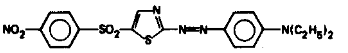
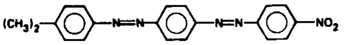
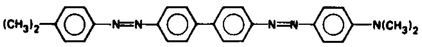
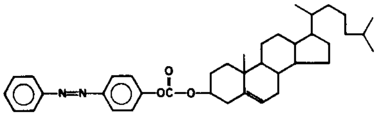
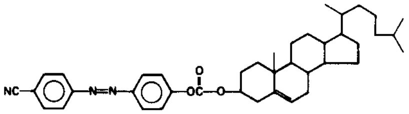
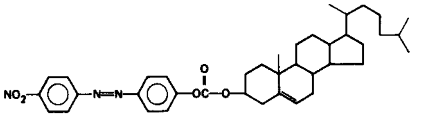
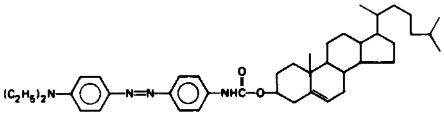
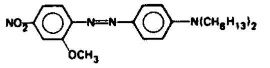
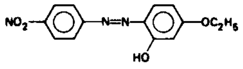
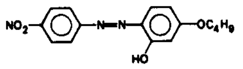
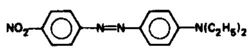
Structure	Order Parameter	Absorption (λ nm)	References (Liquid Crystal mixtures)
	0.27	526	29(7)
	—	490	18
	—	460	18
	—	322	33
	—	332	33
	—	340	33
	—	425	33
	0.51 0.61	423 420	33(9) 33(7)
	0.59	450	29(7)
	0.59	440	29(7)
	0.55 0.62 0.60 0.50 0.50 0.55 0.42 0.51 0.55 0.51	506 514 513 513 510 506 505 505 506 505	33(7) 30(8) 30(12) 30(11) 30(10) 29(7) 30(7) 30(1) 30(1) 33(9)

TABLE V (continued)

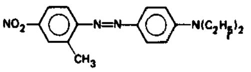
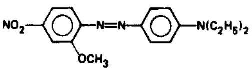
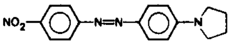
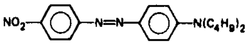
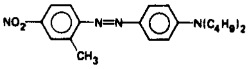
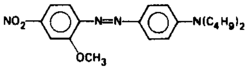
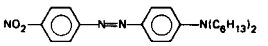
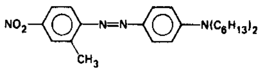
	0.46	506	29(7)
	0.43	514	29(7)
	0.62	515	29(7)
	0.51	508	29(7)
	0.40	506	29(7)
	0.34	516	29(7)
	0.48	507	29(7)
	0.42	509	29(7)

TABLE VI
Miscellaneous dyes

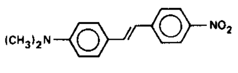
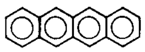
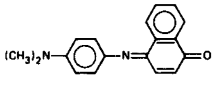
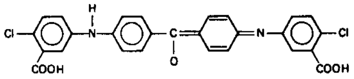
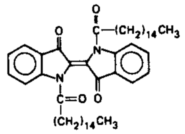
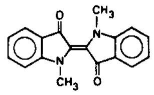
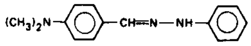
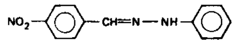
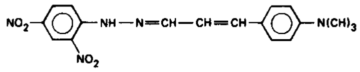
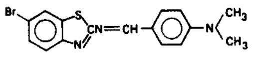
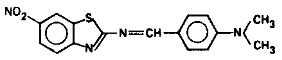
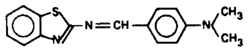
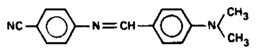
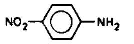
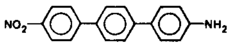
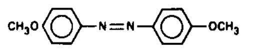
Structure	Order parameter	Absorption (λ nm)	References (Liquid crystal mixtures)
	—	—	24(4)
	0.7–0.43 0.7	445 432	5(5) 4(28)
	0.55–0.40	480	5(5)
Tetraphenylphorphyin	0.13 0.09	— —	22(4) 22(1)

TABLE VI (continued)

Structure	Order parameter	Absorption (λ nm)	References (Liquid crystal mixtures)
	0.55 0.55	600 585	33(3) 11(8)
	—	—	3
	—	—	3
	—	—	3
	—	—	3
	—	—	3
	—	—	3
	0.70	437	27(7)
	0.69	446	27(7)
	0.68	430	27(7)
	0.71	415	11(8)
	—	370	18
	—	355	18
	0.66 0.57	— —	21(7) 21(26)
Carotene	0.69 0.59	— —	21(27) 21(26)

λ_{max} for each, where that information is available. Table VII lists the liquid crystal hosts that were used.

The results of the work on guest-host systems, particularly those useful as display devices, can be summarized as follows.

The important parameter in evaluating the usefulness of a guest dye in a liquid crystal host is the order parameter. It is very dependent upon the host used and is quite random with respect to the molecular structure of the host. The order parameter is also dependent upon the dye structure, being, in general, greater as the length to breadth ratio of the molecule increases. Other criterion affecting the display properties of the dye are its solubility, spectral properties and stability. There seems to have been very little systematic evaluation of dye solubility in spite of the fact that all of the other measurements are dependent on adequate solubility in the liquid crystal host.

TABLE VII

Liquid crystal mixtures

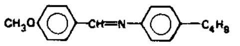
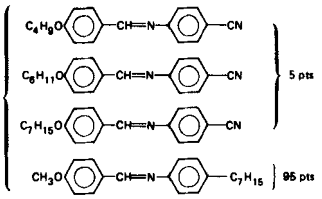
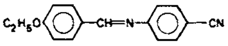
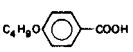
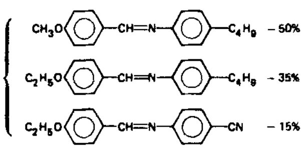
Structure	References
1. 	19, 20, 5, 14, 30, 24, 18
2. 	9
3. 	7, 3
4. Cholesteryl laurate/cholesteryl chloride compensated	24, 22, 23
5. Merck Mixture W.I.	5
6. 	8, 1
7. 	27, 28, 29, 30, 33

TABLE VII (continued)

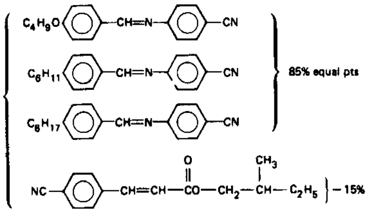
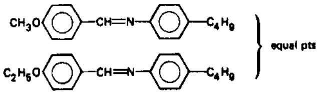
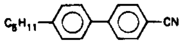
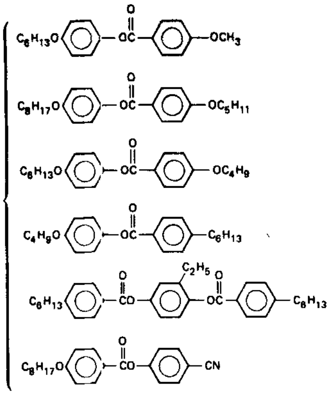
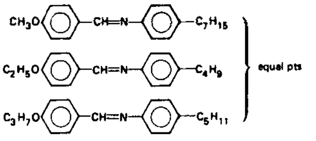
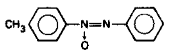
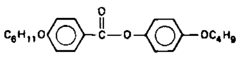
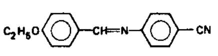
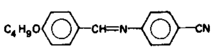
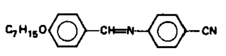
Structure	References
8.  Optically active	11, 30
9. 	30, 33
10. Hoffman-La Roche 101 Ester Mixture	30
11. Hoffman-La Roche 200 Schiff Base Mixture	30
12. B.D.H. E-7 Alkylcyanobiphenyls and terphenyls mixture	30, 2
13. B.D.H. E-9	2
14. B.D.H. E-7 + 15% CB-15	13
15. B.D.H. E-3	25
16. B.D.H. E-8	25, 31
17. 	26
18. 	17

TABLE VII (continued)

19.		16, 15
20.		18
21.	Merck IV Mixture	18
22.		18
23.		18
24.		18
25.		18
26.	Merck ZLI · 612	21
27.	Merck N-9	21
28.	Cholesteryl chloride/cholesteryl nonanoate compensated	4
29.	$CH_3(CH_2)_3CH{=}CH{-}CH{=}CH{-}COOH$ (trans, trans)	6

The spectral properties of the dye coincide in general with conventional solution spectroscopy except of course where two transitions of opposite polarizations overlap and then they can be separated and studied individually.[19] For dyes with equal order parameters or dichroic ratios, the extinction coefficient will of course be an important factor when evaluating usefulness in a display system. Unfortunately, the great majority of the workers in this field simply express the dye concentration as a weight percent dissolved in the host. Some of the anthraquinones[2] and the cholesteric azo dyes[33] do however have their molar extinction coefficients tabulated. The bulk of the dyes for which the order parameter has been obtained are of two classes, either the merocyanines or the azo dyes, and the long wavelength band for each of these types have an extinction coefficient of about 20,000 to 50,000.[35] Thus the limiting factor in the intensity of the color obtained from a particular dye has been generally proportional to the solubility of the dye in the liquid crystal host.

The stabilities of the dyes, particularly photostability in the presence of a field, is of particular concern in display applications, and ranges from very poor for some of the long polyazo dyes to very good for dyes based on the anthraquinone structure.

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16. Japan Kokai, **75**, 73, 887 (1975).
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