Orientation and solvatochromism of dichroic dye molecules in liquid crystals.

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The orientation and solvatochromism of some dye molecules in a liquid crystal have been investigated. Interactions with the host and the structure of the dye molecule affect the macroscopic alignment of dichroic dye molecules in a liquid crystal. It was observed that some dye molecules show a large bathochromic shift of their absorption maxima in the liquid crystal host relative to the situation in isotropic solvents. It is suggested that this is due to the occurrence of a much weaker reaction field in the anisotropic, rigid host. These dye molecules show little or no apparent order in the anisotropic host despite the observation of a reduction in the electro optic switching time when the dye is present. The highest degree of macroscopic alignment was observed for a merocyanine compound, which showed the smallest solvatochromic shift in the liquid crystal host. These results are discussed in terms of the steric, dipolar and hydrogen bond interactions between the guest and the host.

INTRODUCTION.
Ever since the pioneering work of Heilmeier and Zanont [1], there has been considerable interest in doping nematic liquid crystals (LCs) with dichroic dyes. The effect observed, termed the guest-host effect, is

thought to be primarily due to the steric interactions between the dye and the LC, i.e. van der Waals interactions.

This effect revealed some interesting features that are of interest in the use of LCs in displays. In particular, the alignment of the dipole moment of the dye with the director of the LC offers the prospect of a coloured liquid crystal display (LCD) that can be switched to a transparent state in an on-off fashion with an external electric field [1-4]. Additionally, it has been observed that the electro-optic response time of nematic LCs can be improved by dye dopants with large dipole moments, which is also of great interest in display applications [5]. This observation suggests that in addition to steric interactions one has to consider the role of dipolar interactions in the guest-host effect for these molecules.

However, in spite of the attractive features of the guest-host effect there are still some questions that need to be addressed before it can be fully and successfully exploited in display applications. One problem is to find a guest material with a high solubility in the host material. Another requirement is that the guest material is stable in terms of colour and photochemically inert. Within this context anthraquinone compounds have been extensively investigated [6,7]. Another family of compounds, which have been found to have excellent solubility, are the azo chromophores [8-10]. However, this class of material absorbs mainly in the blue and UV part of the electromagnetic spectrum, which is a serious limitation for their usage in a potential full colour LCD.

Another slightly different problem relates to the structure of the dye dopant. In order to obtain success in display applications it is necessary to obtain a high contrast ratio of the transparent versus reflecting/absorbing states. In this context it is of utmost importance for the transition dipole moment of the dye to align well with the director of the LC. This in turn is dependent upon the structural properties of the dye, i.e. it is important for the dipole moment to have a close alignment with the long axis of the dye molecule. Long linear molecules are therefore preferred before flat bi-axial structures, as there can be a large deviation between the transition dipole moment of the dye and its molecular axis in this case. Within this context a structural criteria has been defined as a guide, and this is that the length to breadth (l/b) ratio should be large. A class of compounds where this condition is met is the linear polyenes [7-11]. Those dyes are also termed pleochroic dyes.

Prior studies have shown that azo-compounds can align well with the director of the LC resulting in relatively high order parameters [8,10]. This is also the case for some anthraquinone compounds

although the order parameters in these cases are generally less than for the azo compounds because of the smaller l/b ratio of the anthraquinone systems. For the same reason naphtalene compounds have shown relatively low order parameters since these are biaxial flat ring structures with an even lower l/b ratio [12].

In this report we have investigated the macroscopic alignment and solvatochromism of some new guest systems in a nematic LC mixture. These are a tetracyanoquino-dimethane (TCNQ) adduct, dimethyl-morpholino-methyl piperidino-dicyanoquinodimethane (MORPIP) and three zwitterionic merocyanine compounds. These were found to have excellent solubility into the LC mixture. The orientation of these guest systems was studied by means of a combination of absorption and luminescence spectroscopy. The results are discussed in view of their structural characteristics and interaction with the LC host.
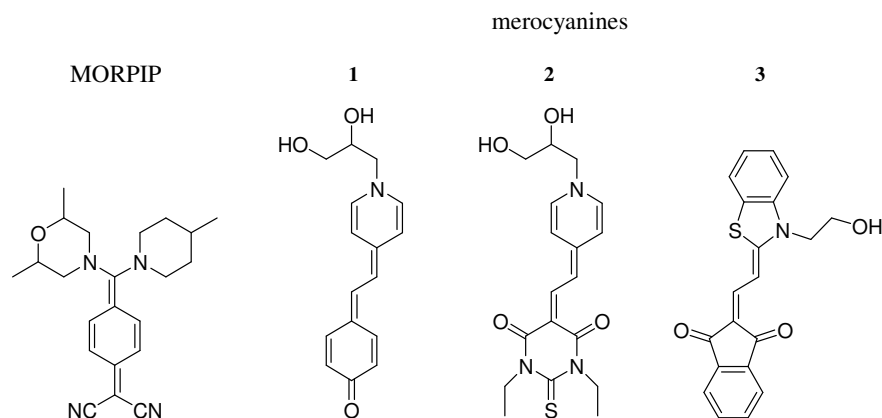
merocyanines

MORPIP   1   2   3

FIGURE 1. The chemical structures of the dye dopants.

MATERIAL AND METHODS.
Merocyanine compounds **1**, **2** and **3** were synthesised according to [13] and MORPIP were synthesised according to [14]. The structures of the compounds are shown in figure 1. LCs were doped with guest material at a maximum doping level of 5% w/w and stirred ~24 hours before filling into a 10 μm aligned cell (EHC Ltd). The LC was the nematic mixture BL001 (Merck), which consists of 51% K15 (5CB; 4-pentyl1-4'-cyanobiphenyl), 25% K21 (4-heptyl-4'—cyanobiphenyl), 16% M24 (4-octyloxy-4'-cyanobiphenyl), and 8% T15 (4-pentyl-4'-cyanoterphenyl).

Absorption was measured on a Perkin Elmer Lambda 19 spectrophotometer and luminescence was measured using a Jobin Yvon Horiba Fluoromax 3 both equipped with Glan-Thompson polarisers.

From the absorption experiments the order parameter S was obtained through the equation [15]

$$S(\lambda_{max}) = \frac{A_{II}(\lambda) - A_{\perp}(\lambda)}{A_{II}(\lambda) + 2 \cdot A_{\perp}(\lambda)} \qquad (1)$$

where $A_{II}(\lambda)$ is the wavelength maximum in the absorption spectrum measured with the polarisation vector of the probe light parallel to the alignment direction of the cell, and consequently $A_{\perp}(\lambda)$ is measured with the cell tilted at 90° relative to the parallel measurement. The order parameter S is a measure of the average orientation of the molecular transition dipoles of the dye relative to the director of the LC, which lies along the rubbing direction of the cell.

From the luminescence experiments the luminescence anisotropy can be obtained through the equation [16],

$$r(\lambda_{max}) = \frac{F_{II}(\lambda) - G \cdot F_{\perp}(\lambda)}{F_{II}(\lambda) + 2 \cdot G \cdot F_{\perp}(\lambda)} \qquad (2)$$

where $F_{II}(\lambda)$ is the luminescence spectrum obtained for parallel polarisation of the excitation and luminescence radiation. Similarly, $F_{\perp}(\lambda)$ is the luminescence spectrum with perpendicular polarisation of the luminescence relative the excitation light. G is an instrumental correction factor. The cell is mounted in the spectrometer with the rubbing direction vertical, i.e., in parallel fashion with the polarisation of the $F_{II}(\lambda)$ component.

Dipole moments were calculated with a semi-empirical approach using the MOPAC software package.

RESULTS AND DISCUSSION.
All the guest compounds investigated in this study were found to dissolve very easily in the LC host. None of the guest-host mixtures showed any sign of un-dissolved or suspended dye particles in the mixture at the loading ratios used in this study (~5% w/w for the merocyanines and about 1% for MORPIP). In general there are several factors, which govern the solubility of dichroic dyes in LCs. These include the shape and symmetry of the dye molecule, the presence and nature of substituents and side groups, and temperature [7,9,10]. The first relates to the length of the dye molecule. It has previously been observed that long azo dyes are more difficult to dissolve than the shorter ones [10]. In view of this one might expect MORPIP to have the highest solubility since it is the shortest of the four compounds studied

here. However, MORPIP has relatively bulky side groups, which outweigh the length effect relative to the merocyanine compounds **1**-**3**.
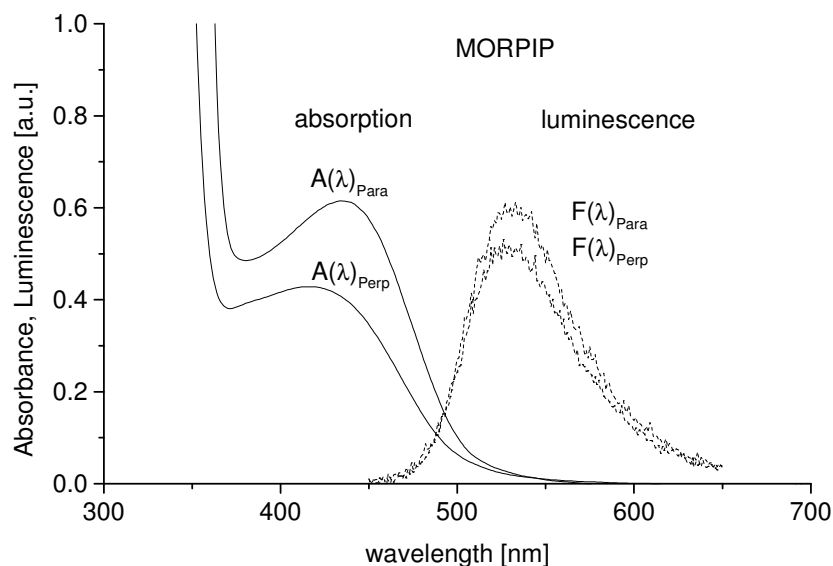

FIGURE 2. Polarised absorption and luminescence spectra (for excitation at 440 nm) of MORPIP in the liquid crystal host.

The spectra of the dyes in the LC host showed varying degrees of solvatochromism relative to the isotropic solvents methanol (MeOH) and acetonitrile (MeCN). These are polar solvents with solvent density parameters of 0.308 and 0.305 respectively [14]. The data are listed in table 1. The shape of the absorption band of MORPIP was identical to that reported previously [17], i.e. a broad featureless profile devoid of any vibronic structures. The merocyanines **1** and **3** have similar spectral profiles in both the isotropic solvents and the LC. However, the main absorption band of merocyanine **2**, which is also featureless in the isotopic solvents, splits into two components in the LC.

The solvatochromism of high dipole adducts of TCNQ in various dielectric media have been investigated by Szablewski et al [18]. In principle, polar media posses a high reaction field and in this environment a zwitterionic charge separation and stabilisation will occur relative to the gas phase, where the reaction field is zero. A consequence of this is that the dipole moment will increase and there is a solvatochromic shift of the absorption band. For molecules where the charge separation in the ground state is less than that at the cyanine

limit for polyenes, or the equivalent of equal charge redistribution between donor and acceptor moieties for other types of molecule, this results in a bathochromic shift. For molecules where the charge separation in the ground state is larger than that at the cyanine limit, or its equivalent, there is a hypsochromic shift, i.e. anomalous solvatochromism. We anticipated that the dipolar dye systems investigated here would behave in the latter manner.

Dye	λ [nm] MeCN	λ [nm] MeOH	λ [nm] LC
MORPIP	400	400	450
Merocyanine 1	-	400	470
Merocyanine 2	500	480	420, 520
Merocyanine 3	505	510	520

TABLE 1. Absorption maxima of the dyes in various media, merocyanine **1** was not soluble in MeCN. The error in the measured values is approximately ± 2 nm.

As can be seen from the solvatochromic data in table 1, MORPIP and merocyanine **1** show large bathochromic shifts in the LC relative to the isotropic solvents. These shifts are larger than those observed for azo compounds, which are typically around 20 nm in Ethanol [8]. The shift observed for the azo dyes is in the direction anticipated if the LC acts as a more polar solvent than the isotropic solvents. Thus we would have expected a hypsochromic shift for MORPIP and merocyanine **1**. Two factors, which may contribute to this anomalous result, are the existence of specific dye-host interactions and the response of the LC to the dye. Isotropic solvents can easily rearrange themselves around a solute in configurations that result in a high reaction field. In the LC, on the other hand, the structure of the host is somewhat rigid so that solvent reorganisation around a solute is less likely to occur, particularly if steric interactions are dominant. While this would be expected to lower the reaction field a high degree of alignment of the dye with the host could counter this effect. The situation will be more complicated if there are specific interactions between the dye and the host that affect the alignment of the dye and the LC molecules. Table 2 contains the dipole moments of the dyes used in this study. The dipole moment of MORPIP is 15 ± 1 Debye in a range of solvents [17] and merocyanine **1** has a calculated dipole moment of 14.3 Debye. These are somewhat larger than the dipole moments of azo dyes and could be the origin of the unexpected spectral shift observed for these two dyes. In addition there is the possibility of hydrogen bonding between the dyes and the LC forming complexes

with well-defined geometry. These factors are considered further below in the light of the measured order parameters.
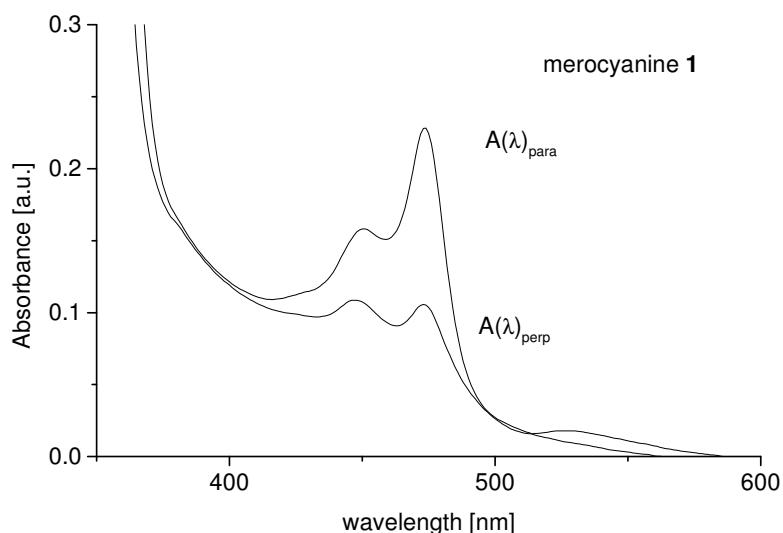

FIGURE 3. Absorption spectra of merocyanine **1** in the liquid crystal host.

Merocyanine **2** shows a complicated behaviour when dissolved in the LC as the single absorption profile observed in the isotropic solvents splits into two bands of almost equal oscillator strength. At present there is no clear-cut explanation for this effect but it could be due to a tautomeric reaction with two states in equilibrium.

Dye	$\bar{\mu}$ [Debye]	$S(\lambda_{max})$	$r(\lambda_{max})$
MORPIP	15 ± 1[a]	0.12	0.14
Merocyanine 1	14.3[b]	0.26	-
Merocyanine 2	10.9[b]	0	0
Merocyanine 3	3.6[b]	0.46	0.27

TABLE 2. The dipole moments were obtained a) experimentally and b) theoretically. Absorption order parameter and luminescence anisotropy are calculated using equations 1 and 2. Merocyanine **1** did not exhibit any detectable luminescence.

The absorption spectra of merocyanine **3** show the smallest variation in different media. Its behaviour is closer to that of the azo dyes with a small bathochromic shift of only 10-15 nm relative the isotropic solvents. This suggests that the ground state charge transfer is less than that at the cyanine limit and its interaction with the host is

predominantly steric. This conclusion is supported by calculated dipole moment of only 3.6 Debye.

The absorption order parameters and the luminescence anisotropies for the four dyes are listed in table 2. The results show that MORPIP has an apparently poor orientation in the anisotropic host. Merocyanine **1** was not luminescent. The absorption order parameter is slightly larger than that of MORPIP but the degree of alignment with the LC is still apparently poor. In principle this could be due to the formation of nano-scale aggregates of the dye molecules in the LC host. Such aggregates would not be visible and would be randomly oriented resulting in a low order parameter. However, the formation of aggregates with zero net dipole is inconsistent with the decrease in electro-optic response time observed upon doping with MORPIP. Following the discussion of the solvatochromism above it is more likely that specific dye-LC interactions account for both the unexpected bathochromic shift and the low order parameters. In this regard we note the hydrogen bonding can affect the electronic properties of the dye dopant due to charge re-distribution and hence affect the permanent dipole moment. This could in turn explain the low absorption order parameters and luminescence anisotropies.
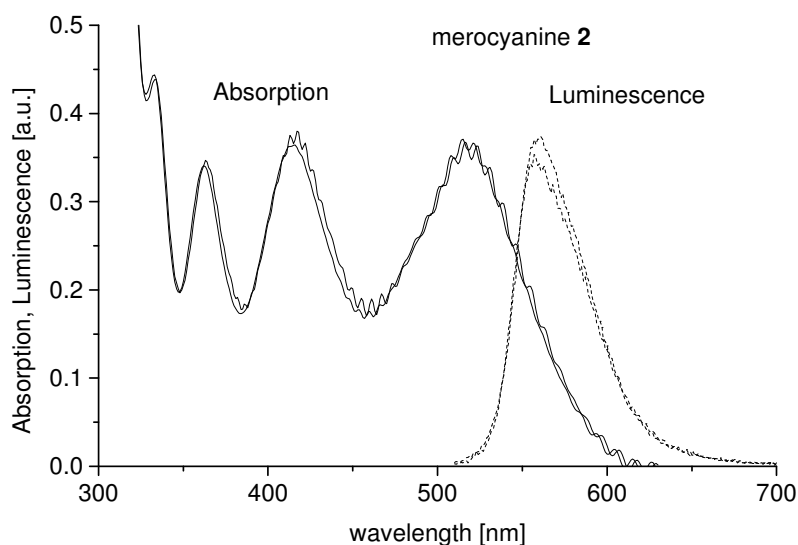

FIGURE 4. Absorption and luminescence spectra (for excitation at 440 nm) of merocyanine **2** in the liquid crystal host. The two overlapping lines in the absorption and luminescence are spectra detected for the two different polarisations. They are as can be seen of the same intensity.

Merocyanine **2** showed zero absorption order parameter and luminescence anisotropy, suggesting a completely random orientation of dye molecules in the anisotropic host. This is a surprising result since the molecular geometry is similar to that of the other merocyanines studied, both of which have measurable order parameters. The absorption profile in the LC indicates the existence of at least two molecular species, possibly a dynamic equilibrium of tautomeric forms as previously suggested. This could help to explain the apparent absence of orientational order for this dye. However, an alternative explanation is suggested below.
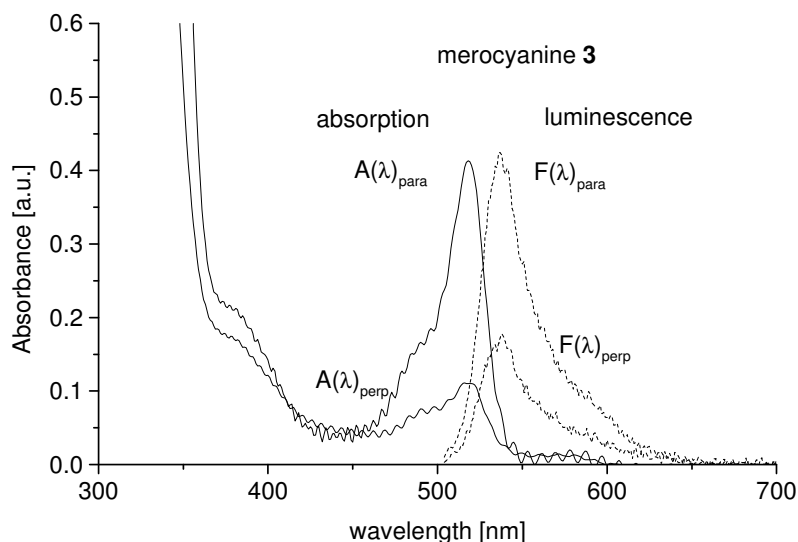

FIGURE 5. Absorption and luminescence spectra (for excitation at 440 nm) of merocyanine **3** in the liquid crystal host.

Merocyanine **3** has the highest order of the four dye systems studied here. The degree of alignment shows greater similarity to that of azo dyes than the other dyes we have studied. This lends further support to the view that steric interactions predominate for this dye.

In the light of the apparent total lack of order for merocyanine **2** a more radical interpretation follows from the use of the absorption order parameter to calculate an average orientation angle $\tilde{\theta}$ from the relation [15],

$$S(\lambda_{max}) = \frac{1}{2}\left(3 \cdot \left\langle \cos^2 \tilde{\theta} \right\rangle - 1\right) \qquad (3)$$

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Then rather than assuming a random distribution for the angle between the transition dipole moment and the LC director we could assume that specific interactions, dipolar interactions and hydrogen bonding, lead to the formation of complexes with a narrow range of angles between the transition dipole and the director. On this basis we find values for this angle of 80°, 45° and 54.7° for MORPIP and merocyanines **1** and **2** respectively. Similarly an angle α between the polarisation of the excitation light and the luminescence can be calculated from the equation [16],

$$r(\lambda_{max}) = \frac{1}{5}(3 \cdot \cos^2 \alpha - 1) \qquad (4)$$

The values of α are 71° and 54.7° for MORPIP and merocyanine **2** respectively. The existence of complexes with a fixed geometry would also explain the reduction in electro-optic response observed for MORPIP. In order to test this hypothesis and the other possibilities considered above measurements on a number of dipolar TCNQ adducts and merocyanine dyes are in hand.

It is also possible that the formation of hydrogen bonds could also influence the behaviour of merocyanie **3.** However, the data available suggests that the properties of the guest-host system incorporating this dye are adequately described by steric interactions between the dye and the LC. Of the four compounds investigated here merocyanine **1** is most likely to form intra molecular hydrogen bonds, followed by merocyanine **2** and **3** and MORPIP. However, MORPIP has probably the largest tendency to from aggregates via dipole-dipole interactions, followed by merocyanines **1,2** and **3** in that order.

CONCLUSIONS
Merocyanine **3** displays a high orientational order in the LC host coupled with a small solvatochromic shift, both comparable to those observed with azo dyes. It has a modest theoretical dipole moment so that steric interaction between guest and host, mediated by van der Waals forces, is probably the dominating solvent-solute interaction. In contrast merocyanine **1** and MORPIP have apparently poor orientational order coupled with large solvatochromic shifts in the opposite direction to that anticipated. A possible explanation for these differences is the occurrence of specific dye-LC interaction due to either the high dipole moments of the dyes or hydrogen bonding or a combination of both factors. Griffiths et al [8] have examined the impact of intra-molecular hydrogen bonds in various azo compounds and found that such bonds generally result in lower order parameters.

However, the situation with respect to intermolecular hydrogen bonds (interactions with the host) is less clear. Hydrogen bonds will affect the electron density distribution in the dye molecule and hence its dipole moment. Both these effects could result in low order parameters. A reduction in dipole moment will also affect the reaction field, which could explain the observed spectral shifts. A more radical explanation would be that these specific interactions lead to the production of complexes with rather well defined angles between the transition dipole of the complex and the orientation of the complex in the LC host. Further experiments are being undertaken to explore these possibilities further.

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