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# Physical properties of mixtures of low molar mass nematic liquid crystals with photochromic fulgide guest dyes

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This paper considers how a low concentration (< 2 per cent w/w) of a photochrome dissolved in a liquid crystal affects the physical properties of the host mesogen. A novel class of photochromes, the fulgide based dyes, have been used to give a new approach in this area of study. Unlike many other light active dyes, the fulgides exhibit only a relatively small shape change. Because of this, the influence of the changes in the physical properties of the guest (for example, the dipole moment) are readily studied. Both thiophene and furan fulgide doped liquid crystal systems were studied in the irradiated and non-irradiated states and as a function of concentration. The changes in phase transition temperature, refractive index and order parameter for these various states as compared to the pure host liquid crystal have been measured to investigate the way in which the dye alters the mesomorphic properties of the host, on a molecular level.

## 1. Introduction

Photochromism is the reversible change in absorption spectrum of molecules when exposed to (usually) ultra-violet or visible light. There are a wide variety of materials and mechanisms that constitute photochromic changes, such as *cis–trans* isomerism, bond cleavage, tautomerism and electron transfer. Although the mechanisms of photochromism itself are relatively well understood [1], interactions between photochromic materials and liquid crystal hosts are not nearly so well explained.

In terms of liquid crystal research, there are two main methods of introducing a photochromic material into a liquid crystal. The species may be either chemically attached to side chain liquid crystal polymers, or doped into liquid crystals (which may be either low molar mass or polymeric). In the case of photochromic liquid crystal copolymers, a high concentration of the chromophore may be included in the material. However, in common with other guest–host liquid crystalline systems the concentrations of chromophore are usually much lower in the case of low molar mass hosts. Several different photochromic species have been included in liquid crystalline systems, and in particular a great deal of work has been carried out on the azobenzene based dyes in liquid crystals [2–5]. Much of the work on low molar mass guest–host photochromic systems was carried out by Ikeda and co-workers [2], who showed that a reversible modulation of the dielectric constant was possible using the isomerisation of the azobenzene guest to modify the liquid crystalline order. More recently, the effect of azobenzene based guest materials, some of which were themselves liquid crystalline, in low molar mass nematic and smectic materials have been reported by Coles and Taylor [3]. In this work Raman scattering was used to probe the molecular reorientation induced by the photochromic reaction. Azobenzene containing groups

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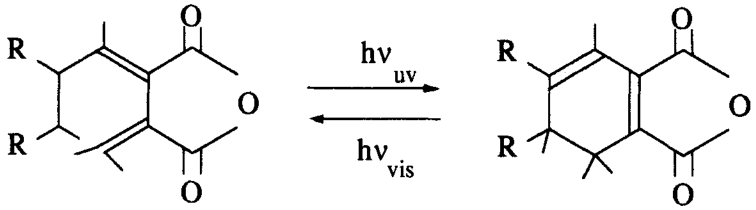


Figure 1. Photochromic ring-closure of fulgides.

were first included in liquid crystalline copolymers by Ringsdorf and Schmidt [4], and these materials were used by Eich and Wendorff [5] to demonstrate erasable holographic recording. In these materials, it was the *trans–cis* conformation change induced in the polymer on irradiation with UV light which led to a local change in the order and hence the optical properties of the liquid crystal. There has been less investigation into the effects of other species. There are, however, reports of the use of spiropyran materials in polymer liquid crystals [6]. These systems are also thermochromic as the reactions from the spiropyran to the merocyanine occur in both directions thermally.

In this paper, the investigation of a novel class of chromophores is reported. We have dissolved low concentrations of photochromic fulgide based dyes in a low molar mass nematic liquid crystal host. Fulgide based photochromes [7] have new and interesting properties with respect to other photochromic systems previously used in liquid crystal hosts. These include:

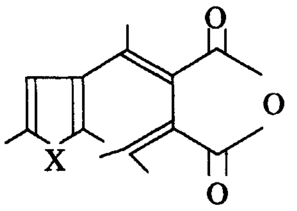
(1) High thermal stability of the UV excited isomer in the dark, giving greater control of the photochromic state of the system and reducing the dynamic effect of the equilibrium. In the case of both the azobenzene and spiropyran systems, the thermal back reaction is relatively rapid and measurements on the irradiated isomers are often carried out while the sample is still being irradiated. By using the fulgide dyes in which the irradiated state is thermally stable, it is possible to carry out measurements on the system in the absence of the irradiating source, thereby eliminating possible contributions to the effects observed due to temperature changes in the sample as it continues to absorb.

(2) The photochromic reaction in the fulgide is based on ring closure, as shown in figure 1. The smaller steric changes in this reaction, as compared to the *trans–cis* isomerization in the azobenzenes, allows investigation of other photo-induced changes in the guest, such as modification of electron conjugation and dipoles. Here we report the initial studies of the physical properties of fulgide doped nematic liquid crystals in both the irradiated and non-irradiated states.

## 2. Experimental

### 2.1. *Materials*

The nematic liquid crystal host used in these studies was E7, a eutectic mixture of biphenyl based liquid crystals, which was provided by Merck Ltd (Poole, Dorset UK) and was used without further purification. This host was chosen in order to allow an acceptable solubility of the guest chromophore dyes. Nematogens in this class of mixtures were developed as hosts for the bulky anthraquinone dyes and so could also accept the large guest molecules used here.



(1) X = S
(2) X = O

Figure 2. Structures of the thiophene and furan fulgides.

Two fulgide based dyes, thiophene fulgide (**1**) and furan fulgide (**2**) were used as the guest materials (see figure 2). They undergo a ring-closure when exposed to ultra-violet light (of wavelength ~340 nm), the reverse reaction only occurring appreciably on exposure to visible light (of wavelength ~500 nm for the thiophene derivative and ~520 nm for the furan derivative). Three mixtures were used: E7 with thiophene fulgide to 1 percent concentration by weight (E7/T1); thiophene fulgide to 2 percent concentration (E7/T2) and furan fulgide to 1 percent concentration by weight (E7/F1).

The irradiation time which was necessary to produce the photostationary state (PSS) was found by measuring the absorption spectra of solutions of the photochrome as a function of UV irradiation time, as described below. The photostationary state which contains 100 percent of the ring-closed fulgide [8] occurs after sufficient UV irradiation of the system such that further irradiation gives no further change in the absorption spectra. The mechanisms of the photochromic changes [9] are not considered here because it is simply the end point of the isomerisation, the PSS, that is important in this work. A Philips Pye Unicam PU8800 UV/Vis Spectrophotometer was used to record the successive spectra of materials after various lengths of exposure to ultra-violet radiation of 4·4 mW cm$^{-2}$ at 366 nm. Although the intensity of exciting radiation is given, it is not in itself a critical factor. It is important only that for the UV exposure system used, the PSS is determined under those particular conditions. For example, a lower intensity could have been used for a longer exposure time and the photostationary state would still have been reached. One of the dye mixtures was used to fill planar aligned glass cells in which the thickness of the guest–host material was 7·5 $\mu$m. An initial absorption spectrum was taken of the unirradiated cell. The cell was then exposed to UV radiation for a known time and the absorption spectrum retaken. This process was repeated for cumulatively longer irradiation times until further exposure no longer changed the absorption spectrum. The UV exposure time required to achieve the maximum absorption was noted and used for each experiment where a 'ring-closed' sample was required. The photochromic behaviour of all the dye mixtures was investigated in this way. The cumulative spectra for E7/T2 are shown in figure 3, where the times given refer to UV exposure times. The mixtures with thiophene fulgide showed a peak absorption at around 530 nm, whilst that of furan fulgide showed a peak at 500 nm.

The biphenyl based liquid crystals that constitute the E7 nematic are known to absorb light readily in the ultra-violet spectral region. However, in the work presented here, this did not cause a problem when irradiating the guest–host mixtures, due to the nature of these photochromic changes. For many chromophores, there is a dynamic equilibrium between the two states which needs constant UV irradiation to be maintained. Absorption of UV by the host mesogen would cause the equilibrium to shift towards the ground state species, reducing the fraction of isomers contributing to the photostationary state, and reducing the effect on physical properties. With the

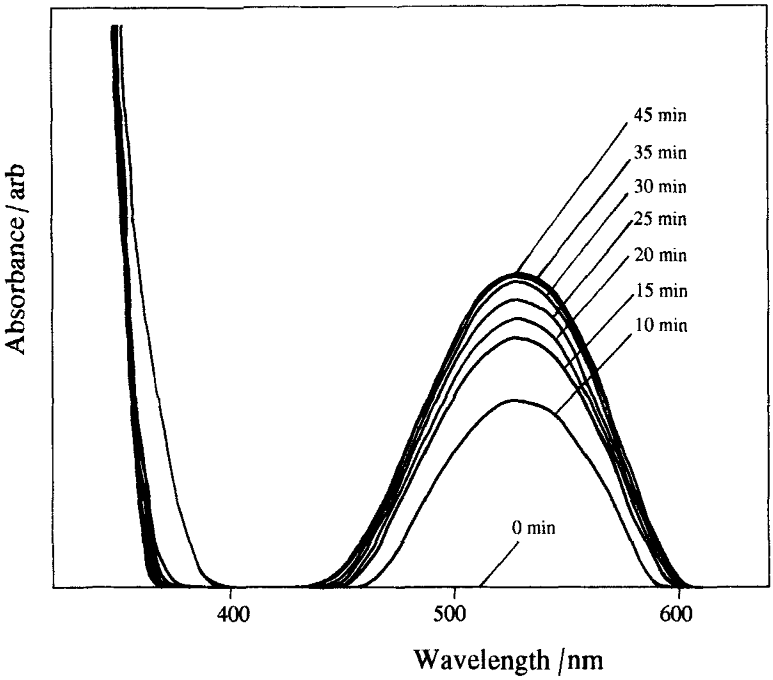


Figure 3. Absorption spectra for E7/T2 with increasing UV irradiation times (given in minutes) at 366 nm. The photostationary state for this system is clearly achieved after ~ 35 min of exposure. The absorption edge shown at ~ 360 nm is due to the glass of the cells used.

fulgide based dyes the effect is fortunately different. As the fulgides are largely stable in the dark, once in the ring-closed form there is a very small probability of relaxation to the ring-opened form. Thus, UV quenching by the E7 host was compensated for by using a relatively longer exposure time than would have been necessary for the photochrome in a normal solvent, giving a photostationary state rich in the ring-closed isomer (100 percent).

Measurements on the ring-closed samples were carried out in the absence of irradiating light as (*a*) it was unnecessary to irradiate the samples continuously once the photostationary state had been reached as the thermal back reaction was so slow, and (*b*) it was advantageous to remove the exciting radiation to ensure that any effects which were observed were due to the photochromic changes alone and not a combination of these with temperature changes caused by the absorption.

### 2.2. *Phase transition temperatures*

The phase transitions of the pure liquid crystal and of the dye mixtures were investigated using an Olympus CH-2 polarizing microscope and a Linkam TMS91 Controller and Silver Block Hot Stage. The cells were heated at a rate of 0·1°C min$^{-1}$. The hot stage used a platinum resistance thermometer and measured the temperature to an accuracy of ±0·1°C. The sample cells were made from two clean microscope cover slips and were used without an alignment layer. The thin cover slips gave a good thermal contact between the sample and the heating block. A red filter was placed over the white light source when observing the UV irradiated mixtures to avoid ring-opening of the dyes.

As the materials exhibit a biphasic region, there is no unique phase transition temperature. In order to characterize the transition, both the onset of new phase (at $T_{\mathrm{N/N+I}}$) and the complete disappearance of the previous phase (at $T_{\mathrm{N+I/I}}$) were noted, giving a transition range ($\Delta T = T_{\mathrm{N+I/I}} - T_{\mathrm{N/N+I}}$). The limits of this range were measured to an accuracy of ±0·2°C, the accuracy limits being primarily related to the uncertainty in determining the start and end of the phase transition.

### 2.3. *Abbé refractometer*

An Abbé refractometer was used to measure the parallel and perpendicular refractive indices ($n_{\parallel}$ and $n_{\perp}$) of the samples. This apparatus contains sample material between two prisms and measures two critical angles of the birefringent sample which are then converted into refractive index values. Measurements are obtained to an accuracy of ±0·002. Temperature variation of the Abbé refractometer was achieved by passing a heated fluid around the prisms using a circulating bath. A Pt100 platinum resistance thermometer was used to measure the temperature of the liquid crystal. The bath had good thermal insulation and, provided the system was allowed to come to equilibrium at a set temperature, the temperature could be determined to ±0·2°C. As homeotropic alignment of the sample was used, the measured refractive indices are simply equivalent to $n_{\parallel}$ and $n_{\perp}$ of the nematic phase. Measurements were taken using a helium–neon laser at 632·8 nm which is outside the absorption bands of the ring-closed photochromic dyes (see figure 3); again this meant that the dyes were not ring-opened during measurements.

### 2.4. *Order parameter*

Order parameter gives an indication of how well correlated molecules are with respect to one another. Thus, this property is a good measure of the disruption caused to the liquid crystal by adding the dyes. Order parameter values were obtained from the refractive index versus temperature data by using the Haller method of analysis [10]. This method postulates the form of the temperature dependence of the order parameter, $S$. When compared with the statistical description of $S$ (see equation (1)) the unknown parameters are determined and $S$ calculated.

$$S = \left(1 - \frac{T}{T^*}\right)^{\beta} = \left(\frac{n_{\parallel}^2 - n_{\perp}^2}{\bar{n}^2 - 1}\right)\left(\frac{\bar{\alpha}}{\Delta\alpha}\right), \qquad (1)$$

where $\bar{n}^2 = \frac{1}{3}(n_{\parallel}^2 + 2n_{\perp}^2)$, $\alpha$ is the polarizability, and $\bar{\alpha} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$ and $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$. $T^*$ represents the temperature at which $S$ would fall to zero if the curve was not interrupted by a transition. A three parameter fitting program using single valued decomposition was used to find values for $T^*$, $\beta$ and $(\bar{\alpha}/\Delta\alpha)$ by fitting the variation of refractive index with temperature through the nematic phase until the onset of the isotropic phase transition (i.e. up to $T_{\mathrm{N/N+I}}$). The fitting program initially holds $T^*$ constant while fitting $\beta$ and $(\bar{\alpha}/\Delta\alpha)$. Subsequent fits are made with $T^*$ throughout the range $T_{\mathrm{N/N+I}}$ to ($T_{\mathrm{N/N+I}}$ + 5 K) at 0·1 K intervals. The program also determines a goodness of fit value, Chi-squared ($\chi^2$) for each fit made. The fit parameters with the minimum associated $\chi^2$ value were the ones used (this was assumed to be the global minimum of the function). The values of $T^*$ and $\beta$ were then substituted into the left-hand side of equation (1) and used to calculate the $S(T)$ curve. Order parameter variation for the biphasic region (between $T_{\mathrm{N/N+I}}$ and $T_{\mathrm{N+I/I}}$) does not follow the Haller model and data from this region were not included in the fit.

Table 1. Phase transition behaviour of E7 and fulgide-doped E7 mixtures. The transition range ($\Delta T = T_{\mathrm{N+I/I}} - T_{\mathrm{N/N+I}}$) is defined as the difference between the onset of new phase (at $T_{\mathrm{N/N+I}}$) and the complete disappearance of the previous phase (at $T_{\mathrm{N+I/I}}$).

| | | | UV exposed (denoted by *) | |
|---|---|---|---|---|
| Mixture | Heating/°C | Cooling/°C | Heating/°C | Cooling/°C |
| E7 | 59·3–61·5 | 57·7–60·5 | — | — |
| ΔT | 2·4 | 2·8 | — | — |
| E7/T1 | 56·4–57·8 | 54·0–57·1 | 56·8–58·2 | 54·6–57·6 |
| ΔT | 1·4 | 3·1 | 1·4 | 3·0 |
| E7/T2 | 52·4–56·4 | 50·4–55·1 | 53·6–56·7 | 52·4–55·7 |
| ΔT | 4·0 | 4·7 | 3·1 | 3·3 |
| E7/F1 | 55·9–58·7 | 54·3–57·6 | 56·0–58·8 | 54·4–57·8 |
| ΔT | 2·8 | 3·3 | 2·8 | 3·4 |

## 3. Results and discussion

### 3.1. *Phase transitions*

Table 1 shows the temperature ranges of the nematic to isotropic phase transition, both on heating and cooling, with and without UV irradiation. Addition alone of the photochromic dyes had the effect of lowering the temperature of the start of the biphasic region (lower $T_{\mathrm{N/N+I}}$) as well as in general increasing the width of the phase transition (increased $\Delta T$). This is an effect which would be expected in any guest–host system. However, on heating the E7/TI mixture $\Delta T$ is greatly reduced. While it is not clear why this should be so, we return to the point later when discussing the order parameter results. With E7/T1 there was a slight but not significant change in $T_{\mathrm{N/N+I}}$ after UV exposure. The E7/T2 mixture shows the lowest onset of transition and the widest biphasic region as compared to the other dye mixtures. This is consistent with this guest–host mixture having the largest concentration of dye. The UV irradiated mixture E7/T2 (E7/T2*) showed the phase transition occurring at a higher temperature and had a narrower biphasic region. We speculate that E7/T2* is slightly more stable in the ring closed state and has less of an impurity effect on the mixture. This fits with the more planar structure of the ring-closed state of the thiophene fulgide (see figures 1 and 2).

### 3.2. *Refractive index*

Graphs 1, 2 and 3 in figure 4 show the variation of refractive index with temperature on heating through the transition of the three unirradiated photochromic mixtures as compared to the pure nematic material E7. The errors in the measurements are contained within the size of the symbols. On all of these graphs can be seen the effect of the biphasic region (indicated by the shaded areas) by the persistence of two refractive index values even after the curve has levelled off to its isotropic value. Within the errors of the experiment, all the mixtures plateau to the same refractive index values within the biphasic region. The persistence of $n_{\parallel}$ into the biphasic region mirrors the width of that region as measured using polarizing microscopy (see table 1). The refractive indices of all the UV irradiated mixtures were unchanged from those of the ring-opened mixtures and are therefore not shown. The ring-closed mixture E7/F1* showed a slight upward shift in refractive index values as compared to E7/F1, but this was not a marked change and was within the errors of the experiment.

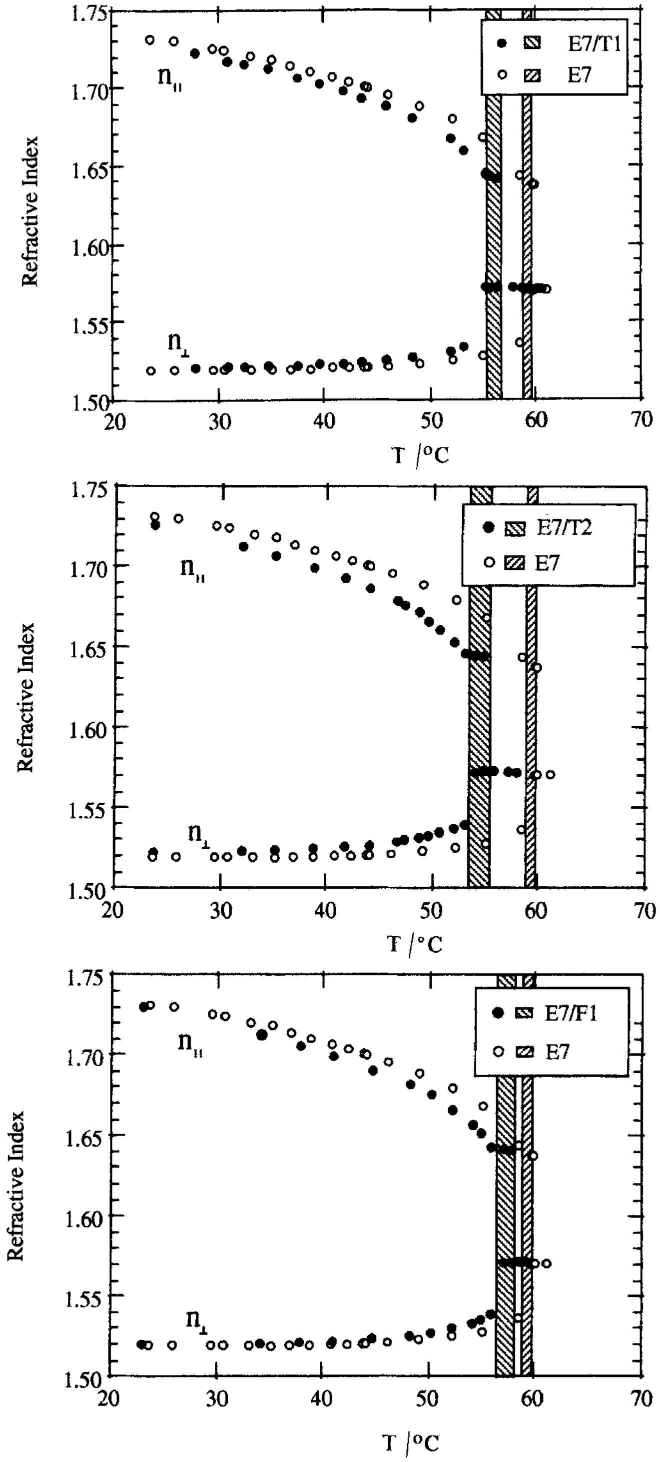


Figure 4. Refractive index variation with temperature for E7 and unirradiated E7/T1 (Graph 1), E7 and E7/T2 (Graph 2) and E7 and E7/F1 (Graph 3). The shaded areas represent the biphasic regions. Data for the irradiated materials are not shown as there was no difference between the measurements of these and the non-irradiated materials.

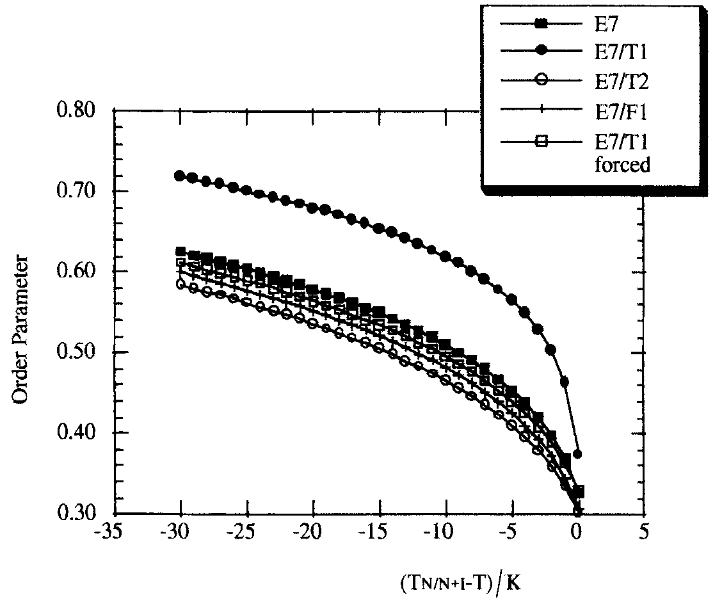


Figure 5. Order parameter variation with reduced temperature for E7 and the non-irradiated fulgide doped E7 mixtures. Again, data are not shown for the irradiated samples as these coincide with the data of the non-irradiated materials. The figure shows two curves for E7/T1, the best fit and a forced fit.

### 3.3. *Order parameter*

The variation of the order parameters of the three photochromic mixtures and E7 are shown in figure 5, where the reduced temperature used is with reference to the onset of the biphasic region ($T_{N/N+I}$). For the systems analysed, a typical error on the order parameter value was $\pm 0{\cdot}02$. The fit parameters calculated by the fitting program, $T^*$ and $\beta$, and their goodness of fit to the data set, $\chi^2$, are shown in table 2.

The irradiated mixtures showed no change in order parameter as compared to the unirradiated mixtures. At $T_{N/N+I}$, E7/T2 and E7/F1 have order parameters very similar to E7 (0·33), whilst that of E7/T1 is slightly higher (0·37). The decreased stability for E7/T2 as indicated by the lowest $T_{N/N+I}$ from the phase transitions results, is verified by this mixture having the lowest order parameter values throughout its nematic range. It should, however, be mentioned that the conclusions drawn from the phase transition measurements and order parameter data for both the mixture E7/T2 and its UV irradiated counterpart E7/T2* appear to be slightly incompatible. Recall that the biphasic region for E7/T2* was narrower than that of E7/T2 and that the $T_{N/N+I}$ of the ring-closed mixture was slightly higher by a corresponding amount.

Table 2. Fit parameters used in order parameter calculations for the various mixtures and E7.

| Mixtures | T*/K | $\beta$ | $\chi^2$ | Initial start temperature/K |
|---|---|---|---|---|
| E7 | 332·95 | 0·20 | 0·30 | 331·85 |
| E7/T1 | 326·75 | 0·14 | 5·44 | 326·55 |
| E7/T2 | 328·15 | 0·23 | 0·81 | 326·35 |
| E7/F1 | 330·45 | 0·21 | 0·06 | 329·15 |
| Forced E7/T1 | 328·15 | 0·21 | 25·25 | 326·55 |

However, the refractive index and associated order parameter data for the two states of E7/T2 showed no discernible differences. We assume that in this case the measurements of phase transition temperatures were more sensitive to what must be very small changes on irradiation than the order parameter measurements were. This effect was not observed in either of the lower concentration mixtures.

Another point to note from the data is that the E7/T1 mixture has a much increased order parameter value as compared to the pure E7, an effect which is especially marked on the approach to the $T_{N/N+I}$ phase transition where the E7/T1 curve is much steeper. From the fitting parameters for E7/T1, given in table 2, it can be seen that (i)$T^*$ is much closer to $T_{N/N+I}$, and (ii) $\beta$ is much lower in this case than it is for the other mixtures. In addition, the $\chi^2$ value indicates that the curve obtained does not form as good a fit to the data in this case. This is consistent with the phenomena noted for the phase transition behaviour of this material. As we previously noted for E7/T1, the properties of the biphasic region are different on heating and cooling; a thermal hysteresis is observed. It is therefore reasonable to assume that parameters such as $T^*$ and $\beta$ are also dependent on the direction of heating (this effect has certainly been observed for other pretransitional effects in more strongly 'monotropic' systems such as cholesteryl nonanoate [11]). Consequently, we expect that the Haller model does not fit the behaviour of the system on the approach to the transition as well as it does for the other, more reversible systems. The $\chi^2$ value for E7/T1 shows this to be the case, as it is an order of magnitude worse than for the rest of the materials. It can be seen from table 2 and figure 5 that if the E7/T1 mixture is forced to have a $\beta$ value in line with the other mixtures (0·21), the goodness of fit is of course far worse ($\chi^2 = 25{\cdot}25$) as we are no longer at the global minimum, but a more reasonable value of $T^*$ is obtained. The overall curve is also closer to what would be expected for a mixture with a low concentration of the fulgide dye. In short, the model used starts to break down for this particular mixture due to its unusual phase transition behaviour and our fitting program confirms this to be so.

## 4. Conclusion

The main conclusion which may be drawn from this work is that the ring closure of the fulgide chromophores on UV irradiation has little effect on the structure and ordering of the nematic phase. Whilst this result may appear to be of limited use, it is essential to the understanding of these and associated photochromic systems. It indicates that the photo-induced steric changes can take place without affecting the liquid crystal. The systems retain their original physical properties whilst changing their optical transmission properties. This is quite different from the effects reported for azobenzene dyed liquid crystals [2–5]. Further work is currently underway to evaluate more complex fulgide systems in which the photo-reaction changes properties of the dye in addition to the optical transmission. The work reported here forms a vital platform for the correct evaluation of the more complex systems. As has been noted, there are some slight effects seen as functions of dye type and concentration but, whilst these are interesting in themselves, they either do not vary with UV exposure or there are no systematic changes in the physical properties of the various mixtures upon exposure.

To complete this work on achiral photochromic mesogens, there will be a paper to follow on the elastic constant behaviour of the systems considered here, again in both the irradiated and unirradiated states. This will allow a more complete picture of these systems to be made.

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