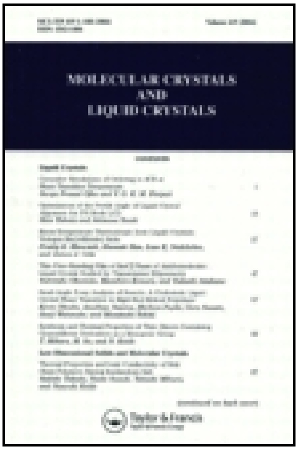

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Photo Sensitive Phase Behaviour of Mixtures of 4-cyano-4′-n-pentylbiphenyl and a Non-Mesogenic Chromophore methyl β-(1-naphthyl)propenoate

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Photo Sensitive Phase Behaviour of Mixtures of 4-cyano-4′-*n*-pentylbiphenyl and a Non-Mesogenic Chromophore methyl *β*-(1-naphthyl)propenoate

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The phase behaviour of mixtures of the liquid crystalline compound 4-cyano-4′-*n*-pentylbiphenyl and the photoactive chromophore methyl *β*-(1-naphthyl)propenoate is reported. Incorporation of the chromophore into the liquid crystal host leads to depressions of the nematic-isotropic transition temperature of up to 12 °C. Further photo-induced depressions of the nematic-isotropic transition temperatures of up to 4°C are recorded. These photo-induced shifts result from the optically pumped geometric $E \Rightarrow Z$ isomerisation of the chromophore to largely the Z isomer. Both isomers of the chromophore are non-mesogenic and the results demonstrate the wider range of chromophores, which undergo geometric isomerisation, that can be utilised for these light activated structural changes including isothermal photo-induced phase transitions.

Keywords: Liquid crystal mixtures, photo-induced phase transitions, photoactive liquid crystals.

INTRODUCTION

Photo-induced isothermal phase transitions may be generated in liquid crystalline materials through the addition of soluble photoactive molecular units.[1–9] These photoactive units or chromophores undergo photo-induced structural rearrangements which result in modified solvent-solute interactions and partial destabilisation of the liquid crystal phase. Photoactive units which exhibit geometric isomerisation are particularly suited to this purpose. Examples of the use of azobenzene units, either as mixtures of low molar mass liquid crystal compounds[3–9] or as components of a liquid crystal copolymer[10–14] have been presented in the literature. The trans or E isomers of azobenzenes when in the E configuration have an extended molecular form; in fact many such azobenzene based compounds exhibit liquid crystal phases.[15] The photo-induced geometric isomerisation from the extended E form to the twisted cis or Z form of substituted azobenzenes leads to significant changes in the molecular form, and not

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surprisingly this leads to marked depressions of the nematic-isotropic transition temperatures when these chromophores are mixed with conventional non photoactive liquid crystal compounds.[4–9] In this contribution we extend the use of photoactive compounds in the modification of the phase behaviour of liquid crystal compounds to non-mesogenic compounds in which neither of the two geometric isomers exhibit liquid crystal phases in their pure form. The positive results demonstrate the much broader range of chromophores which can be exploited for photo-induced control. Furthermore, the results highlight the subtleties that must be accounted for in any useful model of the phase behaviour of mixtures of mesogenic and non-mesogenic compounds.

MATERIALS

In the type of photoactive material investigated in this study, there are two essential components. The first component is a photo-responsive molecule which acts on the second component, a responsive liquid crystal matrix, to generate large scale molecular reorganisation with accompanying marked changes in the optical properties. In other words, the response of the mixture is much greater than that due to the photoactive molecules alone. Clearly, the matrix or solvent material must be inert to the incident light. In this study we have employed 4-cyano-4′-*n*-pentylbiphenyl (Figure 1a) as the liquid crystal host. This was obtained as K15 from Merck and used as supplied. It exhibits a nematic-isotropic transition at 35.3°C and a crystal-nematic transition at 23°C. The photoactive chromophore was methyl β-(1-naphthyl) propenoate[16] (Figure 1b) which we shall refer to as NAPHTH. It was prepared via the acid chloride of β-(1-naphthyl)propenoic acid which was made by the Doebner modification of the Knoevenagel reaction.[17,18] At room temperature it is a colourless liquid and within the

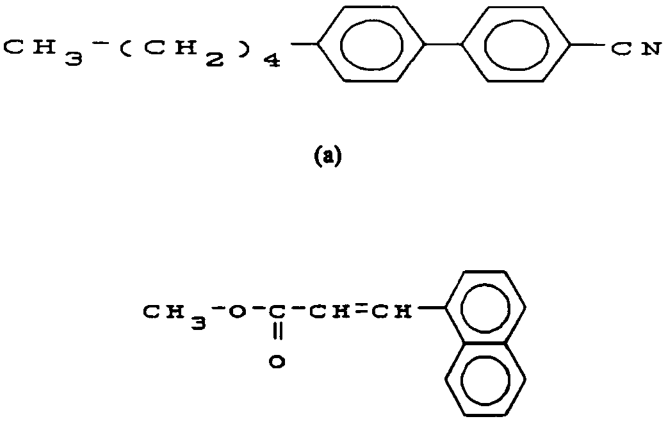

FIGURE 1 Chemical structure for the liquid crystal host material, (a), K15 and the chromophore unit, (b), NAPHTH.

temperature range of this study it does not exhibit any liquid crystal phase. Geometric isomerisation occurs about the ethene bond. Mixtures of the liquid crystal matrix K15 and NAPHTH were prepared using, as a co-solvent, dichloromethane. Dilute solutions of these mixtures and of NAPHTH in dichloromethane were utilised for basic photochemical studies. Films were prepared by solvent casting onto a prepared substrate, for example microscope cover slips or quartz slides.

EXPERIMENTAL PROCEDURES

The phase behaviour of the basic materials and the mixtures was determined using differential scanning calorimetry (Perkin Elmer DSC-2 with a scan rate of 2.5°C min^{-1}) and polarised light microscopy (Carl-Zeiss Jenalab equipped with a Linkam TH600 thermal stage).

The composition of each chromophore containing sample, in terms of the fractions of E and Z isomers of NAPHTH, was evaluated using optical absorption spectroscopy in the range 250–600 nm (Perkin Elmer UV-VIS 330 Spectrophotometer) using either quartz cells, which contained the appropriate solution, or films prepared on glass cover slips. This approach utilised values of the extinction coefficients for the two isomeric forms of NAPHTH which had been obtained using a combination of optical absorption spectroscopy and High Performance Liquid Chromatography (HPLC) analysis.[16, 19] In this procedure the absorbances at two wavelengths are employed to eliminate any errors that might arise from an estimation of the total chromophore content from the feedstock quantities. The absorbances at 290 nm and 340 nm, in the $\pi \Rightarrow \pi^*$ absorption band of the chromophore, were chosen since it is at these wavelengths that the absorption spectra show the greatest sensitivity to compositional changes. The fraction x of the Z isomer can be obtained using the expression:

$$x = \frac{\varepsilon_{E_{\lambda_1}} - Y\varepsilon_{Z_{\lambda_2}}}{Y(\varepsilon_{Z_{\lambda_2}} - \varepsilon_{E_{\lambda_2}}) - (\varepsilon_{Z_{\lambda_1}} - \varepsilon_{E_{\lambda_1}})} \tag{1}$$

where

$$Y = \frac{A_{\lambda_1}}{A_{\lambda_2}} \tag{2}$$

and A is the measured absorbance and ε is the molar absorption coefficient with the subscripts E and Z relating to the isomer type and $\lambda_{1,2}$ referring to the two measurement wavelengths. In this procedure the minimal effects of the solvent and solution vessel are accounted for in the double beam spectrophotometer employed for absorption measurements. In this work, all absorption spectra presented were obtained from solution samples. Cast films of the mixtures were found to have similar spectra to the solutions, however the strongly scattering liquid crystal textures limited the quality of the spectra which could be obtained from liquid crystal films.

In order to photo-induce significant shifts in the isomer populations, it is necessary to use a light beam with a narrow spread of wavelengths. The configuration shown in Figure 2 was utilised to perform these selective irradiation experiments. The 150 W Xe arc lamp coupled with the monochromator (working range: 190–700 nm) allows

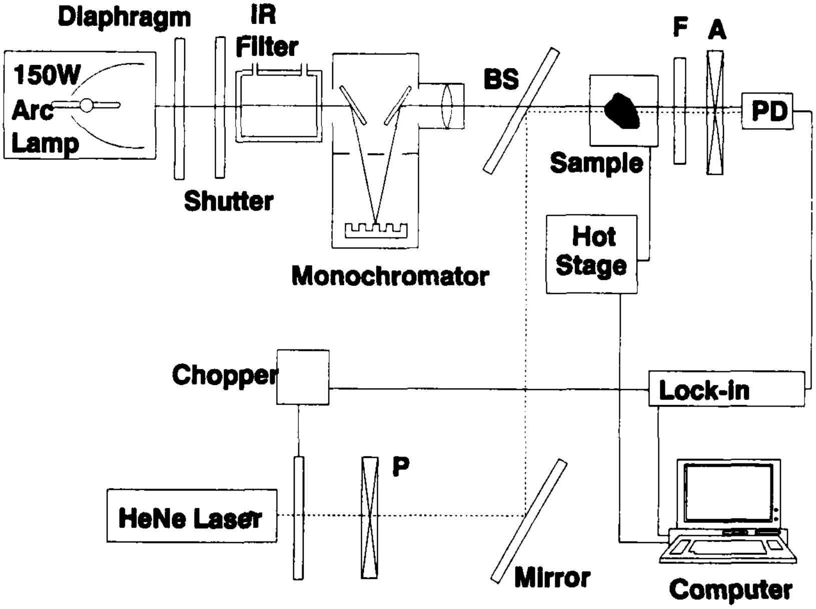

FIGURE 2 Experimental set up used for in-situ irradiation experiments of K15 + NAPHTH films. BS-Beam Splitter, P-Polariser, A-Analyser, PD-Photodiode and F-Bandpass filter (centred on 632.8 nm).

narrow band (11.9 nm) irradiation of the selected sample. The sample is contained within a specially designed variable temperature stage (controllable from −30 to 200°C at variable ramp rates of 1 to 50°C min^{-1}). The transition of the sample, from a liquid crystalline phase to an isotropic fluid, was detected using optical methods analogous to polarising optical microscopy techniques: when a sample which is liquid crystalline is inserted between two crossed polarisers, a fraction of the transmitted laser light is detected at the photodiode; when the sample exhibited an isotropic phase no light is transmitted. A helium-neon laser was used as a probe light which was modulated using an optical chopper and the signal recovered using phase sensitive lock-in techniques. The latter procedure ensured that the laser beam intensity could be distinguished from the high level of ambient light from the arc lamp. A computer system was used to both record the intensity of the transmitted light through the sample under investigation as a function of both time and temperature and to control an optical shutter on the primary UV light beam to allow controlled exposure times of irradiation.

RESULTS

Photochemistry in Solution

Figure 3a shows the optical absorption spectrum obtained for the as prepared NAPHTH dissolved in dichloromethane. This curve is essentially the same as that

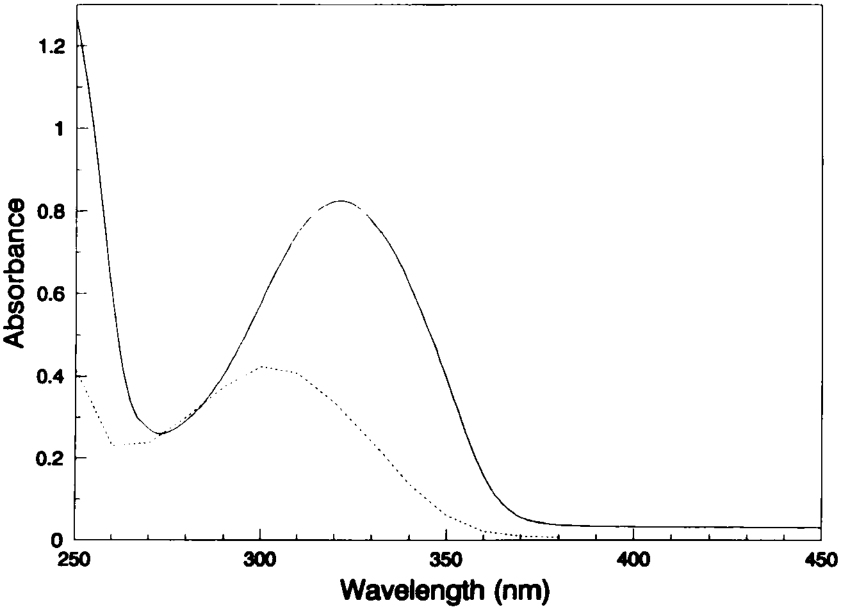

FIGURE 3 Optical absorption spectra, taken in dichloromethane solution, for (a) the initial 0% Z NAPHTH (——), (b) the photostationary state comprising 80% Z NAPHTH (•••) and (c) 100% Z NAPHTH (---) [16].

obtained by Barley[19] for the *E* isomer, for which the composition had been verified by HPLC analysis of the as prepared chromophore in a solution of methanol.[19] The absorption band at 320 nm is due to the $\pi \Rightarrow \pi^*$ transition. Irradiation using a narrow band of light centred on the high wavelength side of this absorption band causes $E \Rightarrow Z$ isomerisation of the NAPHTH chromophore. This occurs because at those wavelengths the absorption peak is due principally to the *E* isomer and hence only the *E* isomer is excited. When the chromophore returns to the ground state, both the *E* and *Z* isomers are equally probable. However, since only the *E* isomer will be subsequently excited, this leads to an optical pumping process in which the *E* isomer population is steadily transformed into the *Z* isomer. If there is some overlap of the absorptions of the *E* and *Z* isomers, the resultant isomer composition will be in proportion to the ratio of the absorbances at the wavelength of the incident light. Figure 3b shows the resulting absorption curve for the photostationary state achieved using irradiation at 340 nm. A comparison of this absorption curve with that reported by Proctor *et al.* [16] for the *Z* isomer (Figure 3c), showed that in the final solution the chromophore was not entirely in the *Z* isomeric form, but still comprised some approximately 20% *E* isomer. As the curve for 100% *Z* isomer in Figure 3c shows, the peak absorption for the $\pi \Rightarrow \pi^*$ absorption bands for the *E* and *Z* isomers are separated by 20 nm. It is the closeness of these bands that determines that 100 percent conversion $E \Rightarrow Z$ is not possible.

The $E \Rightarrow Z$ isomerisation is a reversible process, and irradiation of a solution containing the chromophore in the form of 80% *Z* isomer in the region 270–290 nm results in some conversion to the *E* isomer. Figure 4 shows the results of the reversal

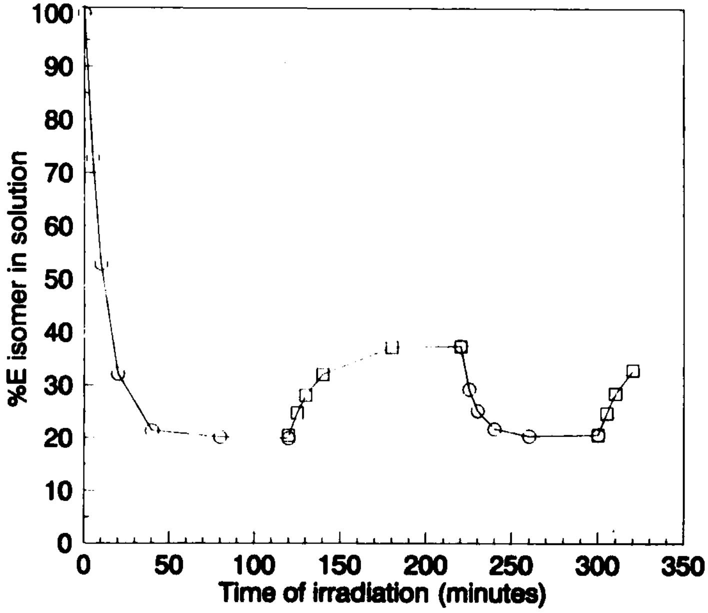

FIGURE 4 Decay and rise of the change in percentage *E* isomer of NAPHTH in dichloromethane solution as a result of irradiation at 340 nm (○) and 290 nm (□).

cycle possible. Initially the solution contains 100% of the *E* isomer. Irradiation at 340 nm results in a photostationary state with the solution containing ~ 80% of the *Z* form. On irradiation at 300nm this transforms to a second photostationary state consisting of ~ 40% of the *E* isomer. In effect, after the initial irradiation, the NAPHTH chromophore can be cycled between two photostationary states with compositions of 40%*E*/60%*Z* and 20%*E*/80%*Z*. Figure 4 shows the kinetics of the optical pumping between these two photostationary states. These results clearly show the reversibility of the process. The limited extent of the reversibility is due to the overlapping nature of the $\pi \Rightarrow \pi^*$ absorption bands of the *E* and *Z* isomers.

Thermally induced isomerisation $Z \Rightarrow E$ was not observed in the NAPHTH chromophore in solutions, or in mixtures of K15 and NAPHTH. This has also been found to be the case by Proctor *et al.*[16] who found that at high temperatures the chromophore decomposed.

An important aspect of the design of photoactive materials is the window of wavelengths available for photo-stimulation. Figure 5a shows the absorption spectrum for K15, which exhibits a strong absorbance centred at 270 nm which overlaps the absorption spectrum of the NAPHTH chromophore (Figure 5b). Although the absorption band of the K15 molecule overlaps with that of the NAPHTH chromophore it was found that $E \Rightarrow Z$ isomerisation was still possible, since at the selected irradiation wavelength, chosen to be 340 nm, the absorption of K15 is minimal. It is the overlap between the absorption spectra of the host and the photoactive units which precludes the possibility of the reverse $Z \Rightarrow E$ isomerisation. Figure 5c shows the absorption

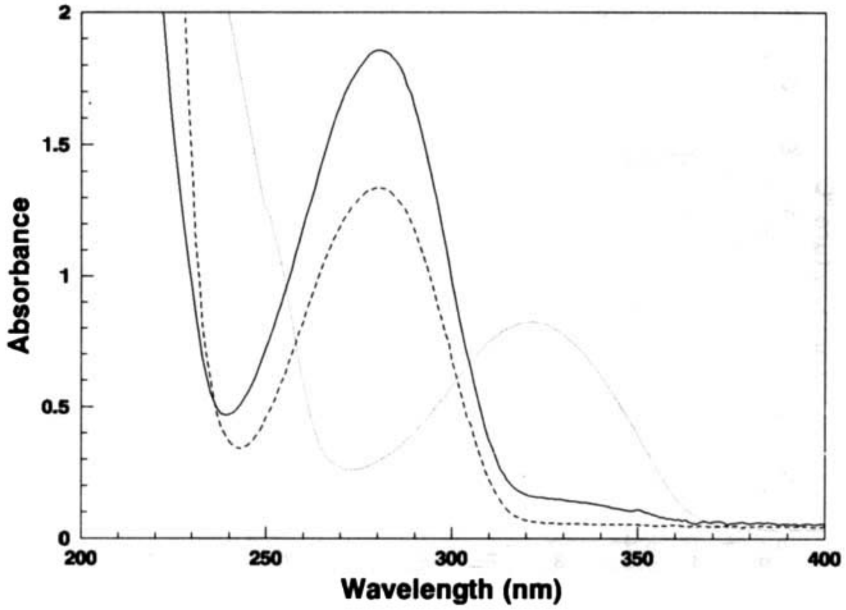

FIGURE 5 Optical absorption spectra for (a) K15 (---), (b) *E* isomer of NAPHTH (•••) and (c) a mixture of K15 (99%) and the *E* isomer of NAPHTH (1%) (——).

spectrum for a mixture of K15 and NAPHTH. To test the hypothesis that irradiation at a wavelength of 340 nm does not affect the liquid crystal matrix, K15, a film of K15 was prepared and irradiated for 180 min. Both the optical absorption spectra and resultant nematic-isotropic transition temperatures of films of 100% K15 cast from un-irradiated and irradiated solutions, were found to be the same. However, irradiation at 300 nm, rather than inducing $Z \Rightarrow E$ conversion of the NAPHTH chromophore, caused a degradation in the spectra for the K15 component.

Phase Behaviour of K15/E-NAPHTH Mixtures

Mixtures of NAPHTH and K15 were prepared with concentration in the range of 0% to 50% w/w NAPHTH. For the mixtures containing 0% to 20% NAPHTH, optical microscopy on cast films showed a nematic phase in the liquid crystal region. As the concentration of NAPHTH was increased from 0% the nematic to isotropic transition temperature of the mixture, T_{NI}, decreased and broadened. The broadening of the transition was attributable to the presence of a biphasic region which was observed by optical microscopy: Upon heating (and cooling) a temperature region existed where both isotropic and nematic phases were observed to coexist (indicated in Figure 6 by two points for T_{NI}). Such a biphasic region is expected from a two component mixture.[22] No phase separation was observed in the nematic phase even for mixtures of K15 containing up to 20% NAPHTH.

DSC analyses of the mixtures were performed at heating and cooling rates of 2.5°C min^{-1}. Prior to the heating scans on the DSC instrument the sample was

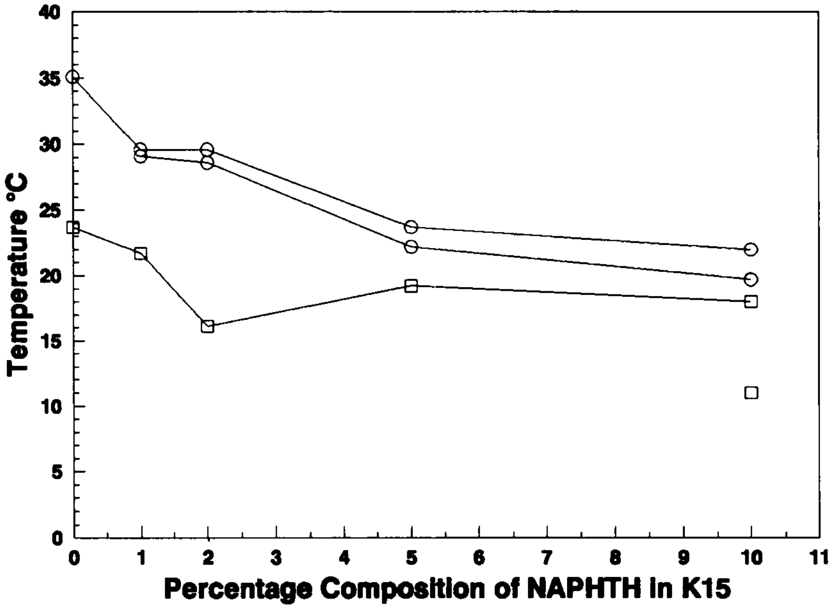

FIGURE 6 Phase diagram for NAPHTH and K15 mixtures (T_{NI}, ○ and T_{KN}, □). The data points were obtained from the DSC measurements.

quenched in liquid nitrogen for ~ 10 seconds to ensure that the sample was in the crystalline phase. The phase diagram based on the results obtained from DSC is shown in Figure 6. For T_{NI} the transition temperature was observed to decrease with increasing content of NAPHTH whilst the T_{KN} transition temperature decreased to a lesser extent. The enthalpies for both transitions were observed to decrease with increasing content of NAPHTH in the mixture. Such trends are expected since we are adding a non-mesogenic solute to the K15. The effect of adding this non-mesogenic solute on the T_{NI} transition decreases as the concentration of NAPHTH increases. This would suggest some degree of phase separation although no such segregation could be observed in the polarising optical microscope. The possibility of specific interactions between the K15 and NAPHTH molecules can be excluded since there were no significant differences in the optical absorption spectra recorded for samples of NAPHTH in either a solution of dichloromethane or K15.

Photo-Induced Phase Transitions

Films, 5–10 μm in thickness, of the mixtures were placed in the hot stage of the experimental setup shown in Figure 2. The samples were heated through their nematic ⇒ isotropic transition (at 2.0°C min^{-1}) and the intensity of the transmitted laser light was recorded by the computer system. Figure 7 shows a typical response recorded for a mixture of 1% NAPHTH in 99% K15. In this manner the transition temperature T_{NI} of the sample was measured and such values were comparable to the values

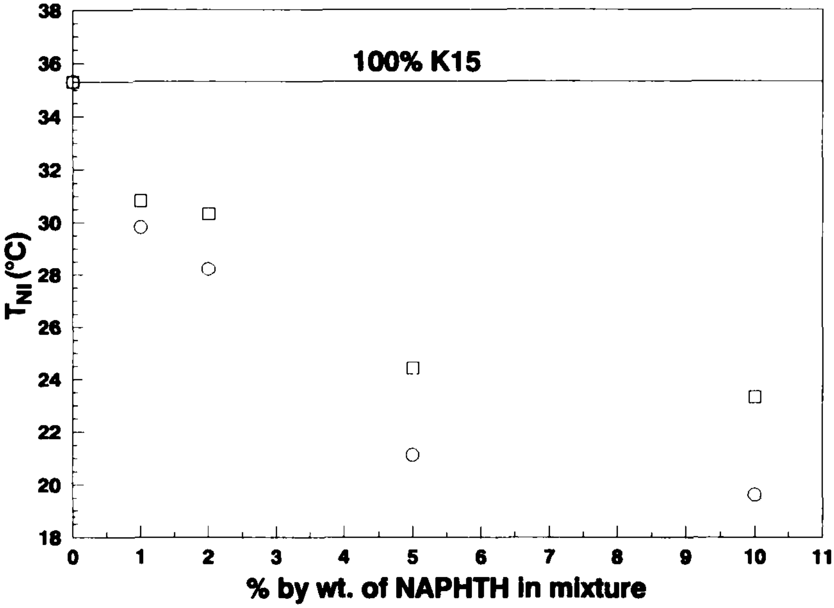

FIGURE 7 The reversible phase transition for a 1% NAPHTH/99% K15 mixture as measured in the experimental set up of Figure 2. The sample, in the form of a thin film was heated at a rate of 2.0°C/min.

observed by DSC. Films were held at a temperature $T = T_{NI} - 4\,^{\circ}\mathrm{C}$ and then irradiated at 340 nm. The precise temperature of irradiation was found not to be a critical factor. The irradiation was allowed to continue for a total of 40 minutes, to ensure a maximum $E \Rightarrow Z$ conversion. In this situation the resultant mixture comprised K15 and ~ 80% Z/20% E isomer ratio of NAPHTH. The films were then cooled, with the irradiating beam still incident on the film in order to maintain the photostationary state. The films were then heated at a controlled rate ($2.0\,^{\circ}\mathrm{C\,min}^{-1}$) to determine T^{*}_{NI}, the depressed transition temperature. Once the new transition temperature had been measured the films were rapidly cooled and dissolved in dichloromethane and an optical absorption spectrum of the solution was taken. These spectra confirmed that the maximum amount of $E \Rightarrow Z$ conversion had taken place (giving ~ 80% Z) upon irradiation of each film. The experiment was repeated for each doped mixture and the resulting phase transition temperatures are plotted as a function of the composition of NAPHTH in Figure 8. For the 80% K15/20% NAPHTH mixture the nematic-isotropic transition temperature was depressed from ~ 2°C to a value below − 30°C, and it could not be evaluated using the experimental configuration described. The fact that these photo-induced phase transition depressions did indeed arise from $E \Rightarrow Z$ conversion was confirmed by examination of the optical absorption spectra taken for samples of the K15/NAPHTH mixtures before and after irradiation. The thermal stability of the Z isomer of NAPHTH allowed a mixture with K15 to be prepared using a sample of the Z isomer which had been prepared by irradiation of a solution NAPHTH in dichloromethane. Such a mixture showed a similar depression in the phase transition temperature to that recorded for a K15/NAPHTH mixture irradiated directly.

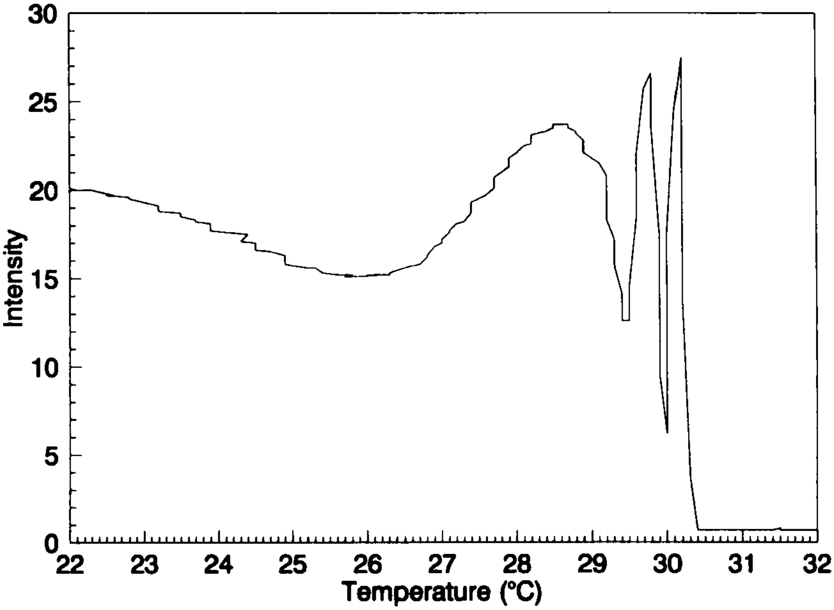

FIGURE 8 A plot showing the T_{NI} (□) values for the K15/*E* NAPHTH mixtures compared with the T_{NI} (○) of those mixtures after selective irradiation at 340 nm for 40 minutes. Essentially these are a mixture of K15/20% *E* NAPHTH + 80% *Z* NAPHTH.

A question that arises with regards to the isomerisation processes of the chromophore unit is, whether the liquid crystal matrix has any affect upon the rates of isomerisation? Since in solution photoisomerisation studies of the chromophores the solute molecules are much smaller than the liquid crystal matrix molecules (K15) and that the liquid crystal mixtures are much higher in chromophore concentration, one might expect that the interaction of the solute K15 molecules would be greater than the dichloromethane molecules. The result is that one would expect the rate of isomerisation to be slower in the case of the K15 mixtures. However, it was found that the rates for isomerisation in both solvents occurred on approximately the same time scale.

MOLECULAR MODELS

In order to provide some appreciation of the nature of the two geometric isomers of NAPHTH, we have used semi-empirical molecular orbital procedures[20] to examine the low energy conformations of the *E* and *Z* isomers. In particular we have used the PM3 semi-empirical Hamiltonian within MOPAC version 6.0. Complete optimisations were performed on structures generated using QUANTA[21] in which the groups about the ethene bond were arranged initially in the cis or trans forms with remainder of the molecule in a planar form. No constraints were imposed. Figure 9 shows space-filling models of the optimised structures. The *E* isomer is planar and extended.

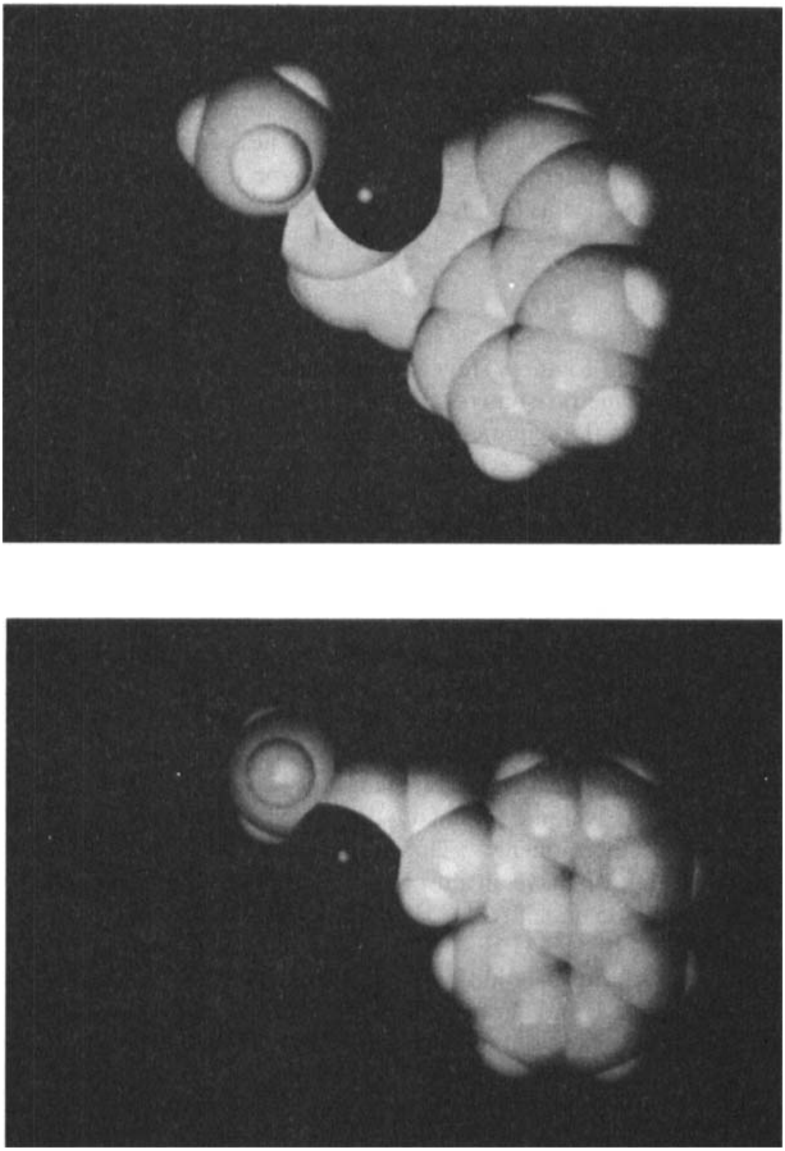

FIGURE 9 Molecular conformations of the *E* and *Z* isomers of NAPHTH based upon low energy structures obtained using semi-empirical quantum mechanical calculations as described in the text. See color plate I.

The dipole moment calculated within MOPAC was 2.36D and was more or less parallel to the long axis of the molecule. In contrast the *Z* isomer is a more globular shaped molecule. Steric interactions twist the propenoate unit out of the plane of the naphthyl unit. The dipole moment is 1.68D and lies at an angle to the plane of the naphthyl unit and is more or less parallel to the short axis of the naphthyl unit. These proposed forms of the low energy conformations of the *E* and *Z* isomers illustrate that, although both isomers are non-mesogenic, there is considerable difference in the shape of the molecular envelope and in the direction of dipolar coupling between the chromophore and the K15 molecules. In essence, the *E* isomer approaches the extended shape of a mesogen in which the dipole moment lies along the long axis of the chromophore. The *Z* isomer is much closer in shape to a spherical molecule and moreover the dipole moment is orthogonal to the "extended" axis of the chromophore.

DISCUSSION

The results presented in Figure 8 show conclusively that photo-induced shifts in the populations of the geometric isomers of a non-mesogenic photoactive solute can lead to significant changes in the nematic-isotropic transition temperature of the mesomorphic solvent. The depressions, which arise as a result of the shift in the isomer population from $E \Rightarrow Z$, are modest compared with those recorded for a similar K15 based system, in which the *E* isomer of the solute (4-butyl-4'methoxyazobenzene) was itself mesogenic.[9]

Theories of the phase behaviour of mixtures of mesomorphic solvents and non-mesogenic solutes have shown that where the solvent and solute have similar molecular volumes, the depression in the nematic-isotropic transition temperature is linear with composition.[22,23] It is possible that, for the results reported here, the departures from linearity at high chromophore doping levels may be related to some limited phase separation. However in the models developed by Humphries *et al.*[22,23] there are no anisotropic interactions between the solute and the solvent. However, it is clear from nmr studies that for many liquid crystal mixtures, the non-mesogenic solute is ordered with respect to its environment.[24] This is the case even when the solute is not mesogenic, although it will have an anisotropic molecular shape. Figure 8 shows that, the addition of the *E* isomer of NAPHTH to K15 leads to depressions of up to 12°C for a mixture containing 10% NAPHTH. The photo-induced population shift from the *E* to *Z* isomer results in an additional depression of ~4°C. In other words the differences between the *E* and *Z* isomers of NAPHTH are modest compared with the differences between K15 and the *E* isomer of NAPHTH. In a simplistic approach we can relate the magnitude of the phase depression to the molecular shape of the chromophore, and in particular how nearly it approaches that of a spherical molecule with no anisotropic interactions. In the case of the *E* isomer of NAPHTH the dipole moment lies parallel to the long axis of the molecule and hence the two classic contributions of repulsion and attraction reinforce. In contrast, the dipole moment of the *Z* isomer forms an angle of ~ 90° to the "long axis" of the molecule and hence these two components are in competition. We could ascribe a degree of mesogenicity to a photoactive chromophore based on the scalar product of a geometric anisotropy vector and the dipole moment. It is the subtleties of the variation in this product which result in the photo-induced phase depressions. We have observed similar small shifts in a liquid crystal polymer system in which an analogue of NAPHTH was incorporated by chemical attachment into a side-chain liquid crystal polymer system.[25] In the case of K15 and 4-butyl-4'methoxyazobenzene,[9] both the change in the geometric shape and in the dipole moment are large and hence much larger phase shifts are observed, with depressions of 25–30°C recorded for equivalent chromophore concentrations.

In this particular guest-host system, the phase transition shifts are not fully photoreversible, simply because the K15 host absorbs strongly in the wavelength region which would induce significant *Z* to *E* isomerisation. Clearly, the design of photoactive materials is dependent upon potential end uses, as to whether photo-reversibility is required.

SUMMARY

We have shown that non-mesogenic chromophores, which can undergo photo-induced geometric isomerisation, can induce useful shifts in the nematic-isotropic transition temperatures of a mesomorphic host solvent. It is of significance in the design of such materials that substantial proportions of NAPHTH can be dissolved into K15 without major phase separation. In this system the addition of the *E* isomer of the chromophore results in large shifts in the nematic-isotropic transition temperatures. Photo-induced conversion of the *E* isomer to the *Z* isomer leads to a further depression of up to 4°C. This system exhibits thermal stability of the photo-induced changes. These photo-induced changes to the phase behaviour highlight the subtlety of the interactions between the solute and solvent in mixtures of mesomorphic and non-mesogenic molecular units.

Acknowledgements

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