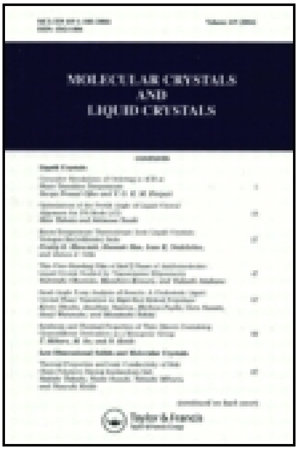

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

PHOTOISOMERISING EFFECTS IN NITROAZO FLEXOELECTRIC DIMERIC NEMATIC SYSTEMS

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Version of record first published: 24 Sep 2006

To cite this article: A. M. Remnant, S. P. Perkins & H. J. Coles (2001): PHOTOISOMERISING EFFECTS IN NITROAZO FLEXOELECTRIC DIMERIC NEMATIC SYSTEMS, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 366:1, 761-769

To link to this article: http://dx.doi.org/10.1080/10587250108024017

Mol. Cryst. and Liq. Cryst., 2001, Vol. 366, pp. 761-769
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Photoisomerising Effects in Nitroazo Flexoelectric Dimeric Nematic Systems

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The photoisomerisation of a flexoelectric chiral nematic bimesogen system dyed with an azo dye has been investigated. The host material has a pitch and field dependent tilt angle that are temperature independent. Upon illumination by ultra violet, the azo dye molecules undergo a shape change from their trans to cis isomer. The effect of the shape change of the dye on the mixture is to decrease the I-N* transition temperatures, to increase the response times and to decrease the transmitted optical intensity. For the same reduced temperatures, the tilt angles, pitch and threshold voltages for the transition from focal conic to homeotropic textures are unchanged. The macroscopic parameters observed suggest that the orientational order parameter of the system is reduced by UV illumination. The cis isomers do not appear to separate from the host material or significantly change the flexoelectric coefficient.

Keywords: flexoelectric; photoisomerising; bimesogen

INTRODUCTION

A molecule containing an azo unit will normally be converted from the trans to cis isomer when illuminated by UV light of 366 nm producing a reversible conformational change in the molecule. In this paper specially synthesised monomesogenic and asymmetric bimesogenic azo

dyes have been added to a highly chiral nematic flexoelectric system to investigate whether a shape change of the dye will produce a change in the macroscopic properties of the host.

EXPERIMENTAL

The host mixture is comprised of two nematic bimesogens[1] with the generic structure shown in figure 1a and differing methylene chain lengths, n. As the bimesogens have no chiral centre a chiral agent must be added to produce a highly twisted chiral nematic, flexoelectric phase. The chiral agents used in this study are CB15 and BDH1218 provided by Merck(UK)Ltd.

An azo dye, figure 1b, containing both a nitro azo unit and a mesogenic unit the same as the host has been synthesised. A further azo dye, denoted m=2 and shown in figure 1c, known to be photoisomerising[2] is also used for comparison.

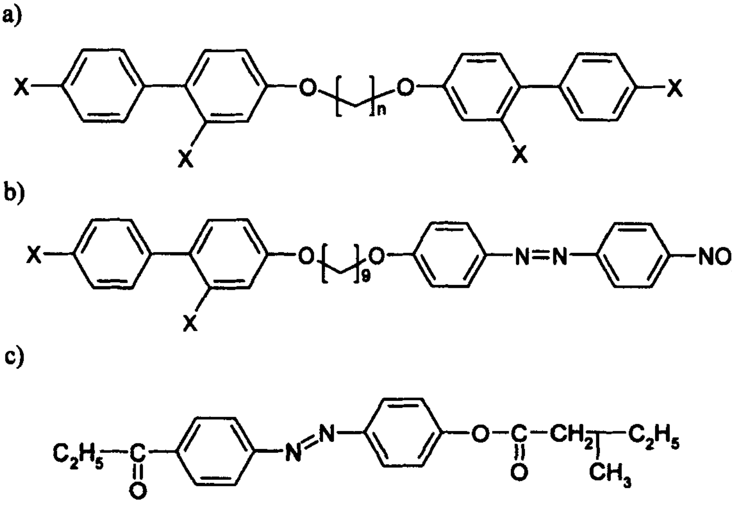

FIGURE 1 a) host bimesogen; b) nitro azo bimesogen; c) m=2 dye

The macroscopic electro-optic properties such as response time, tilt angle, pitch, helix unwinding voltage and the transmitted optical intensity can be used to characterise a chiral nematic flexoelectric liquid crystal. The pitch of the materials investigated has been found to be independent of temperature and presumably, therefore, of the order parameter.

The response time[3] depends upon the undisturbed helix pitch, p, the effective viscosity, γ, and the mean elastic constant, K. The elastic constant depends on the square of the order parameter[4] so the response time, at a fixed temperature below the I-N* transition, should increase due to a reduction in order. However the viscosity will reduce with increasing temperature following an approximate Arrhenius dependency.

$$\tau = \frac{p^2\gamma}{\pi^2 K} \qquad (1) \qquad \tau = f\left(S^{-2}\right)$$

The tilt angle, θ, depends upon the applied field, E, the mean flexoelectric coefficient, $\bar{e}$, the pitch and the elastic constant[3]. The elastic constant and flexoelectric coefficient both depend on the square of the order parameter so the tilt angle is independent of S.

$$\tan\theta = \frac{E\bar{e}p}{2\pi K} \qquad (2) \qquad \theta = f\left(S^{0}\right)$$

The electric field, E_c, required for complete unwinding of the helix depends on the elastic constant, the pitch and the dielectric anisotropy $\Delta\varepsilon$. Both the elastic constant and the dielectric anisotropy depend on S^2 so again the unwinding voltage is independent of the order parameter.

$$E_c = \left(\frac{4\pi K_{22}}{\Delta\varepsilon}\right)^{\frac{1}{2}} \frac{\pi^2}{2p} \qquad (3) \qquad E_c = f\left(S^{0}\right)$$

The transmitted intensity depends upon the angle between the polariser extinction axis and the optic axis, Ψ, and the optical anisotropy, Δn. The optical anisotropy is proportional to the order parameter so the intensity should decrease if the order is reduced.

$$I = I_0 \sin^2(2\psi)\sin^2\left[\frac{\pi d}{\lambda}\Delta n\right] \qquad (4) \qquad I = f(S)$$

CHARACTERISATION

The flexoelectric properties of tilt angle, response time and critical fields for texture changes have been measured. The phase sequence and transition temperatures of the mixtures were determined by optical microscopy. To investigate the flexoelectric properties a square wave driving voltage was applied to 5μm cells with ITO transparent electrodes and an anti-parallel rubbed polyimide alignment. The uniformly lying helix texture[5] was obtained by unidirectional shearing of the sample while a voltage just above that required to produce the focal conic texture was applied. The tilt angles were determined by crossed polariser optical microscopy. The pitch was measured using a spectrometer, as the wavelength at which the maximum intensity was absorbed by the sample in the grandjean texture. The optical response time was measured as the time taken for a 10 to 90% change in the transmitted intensity through the cell. The critical fields for the transition from the grandjean texture to focal conic and from focal conic to homeotropic were determined by measuring the transmitted light intensity. The samples were illuminated by ultra violet light of 300 - 400 nm and up to 430 mWcm^{-2} from a mercury lamp fitted to a side arm assembly to the microscope.

RESULTS

A chiral nematic flexoelectric mixture, made up of 50% of the n = 7 to 50% of the n = 11 chain length bimesogen plus 20% by weight ratio of the chiral agent CB15, was used as the host material. The chiral nematic phase ranges from -3°C to 44°C. The tilt angle of the host (20° for 6V/μm) is linearly proportional to the applied field, while being independent of temperature for a fixed voltage. The response times (of the order of 1-2 ms) of the mixture decreases with increased voltage and temperature. The pitch (800 nm) of the material is independent of temperature, as is the voltage for complete unwinding of the helix (~10 V/μm).

The azo bimesogenic dye was added to the flexoelectric host in concentrations of 5, 10 and 20% by weight to the chiral nematic host. The I–N* transition temperatures were changed by up to 10% for the 20% mixture. The response times are slightly increased, by up to 20%

for 20% dye addition while the tilt angles are slightly decreased, by up to 15% for 20% dye addition.

The dyed mixtures were illuminated by 31 mWcm^{-2} of ultra violet radiation. Measurement of the transmitted optical intensity show that the I to N* transition temperature of the 5% mixture was reduced from 43°C to 41°C by UV illumination. Figure 2 shows that the magnitude of the tilt angle was unaffected by the UV illumination. The magnitude of the response time, as a function of reduced temperature, figure 3, is increased by the UV illumination. The voltage required to completely unwind the helix from the focal conic texture to the homeotropic texture was unchanged as a function of reduced temperature as shown in figure 4.

For temperatures below 41°C, optical micrographs show that there is no change in the texture of the mixture, upon UV illumination, and no biphasic separation of the bent cis dye from the host material. For temperatures between 41 and 43°C, the texture changes from ULH before illumination, to isotropic after illumination. However figure 5 shows that for the sample held at 38° C the effect of UV illumination is to reversibly reduce the magnitude of the transmitted light.

To confirm the results for the 5% bimesogen dye the mixtures of 10% and 20% bimesogen were also investigated. Mixtures containing a different azo dye, m=2, and mixtures using the chiral agent in place of CB15 showed similar results on UV illumination. The mixture with BDH1218 as the chiral agent had a shorter pitch of 510nm. The pitch could be measured with a spectrometer on the microscope while being illuminated by UV. As a function of reduced temperature the pitch does not change significantly with UV illumination as shown in figure 6.

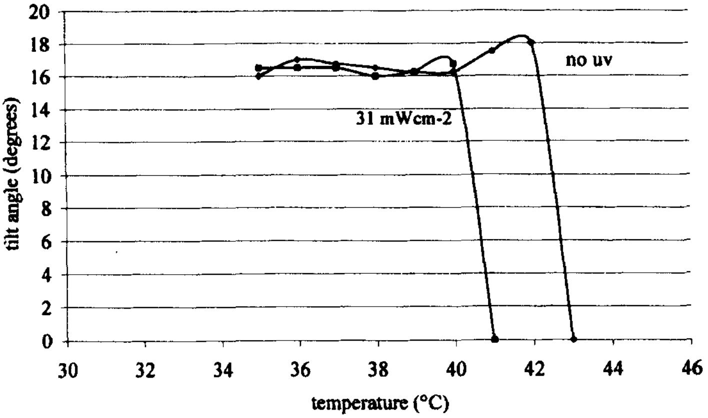

FIGURE 2 Tilt angle against temperature for the 5% azo bimesogen dyed mixture with and without UV illumination, measured at 32 Hz, 6.5 V/μm.

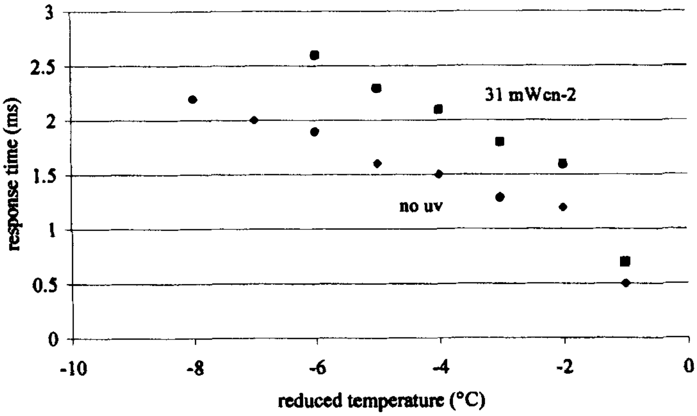

FIGURE 3 Response time against reduced temperature for the 5% azo bimesogen dyed mixture with and without UV illumination, measured at 32 Hz, 6.5 V/μm.

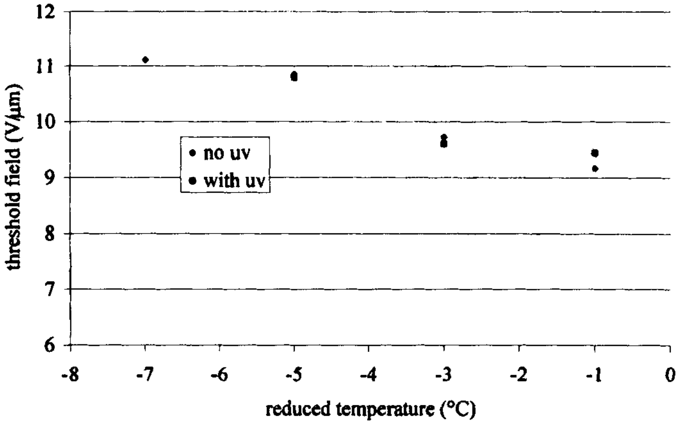

FIGURE 4 Threshold voltages from focal conic to homeotropic, with and without UV illumination, measured at 33 Hz.

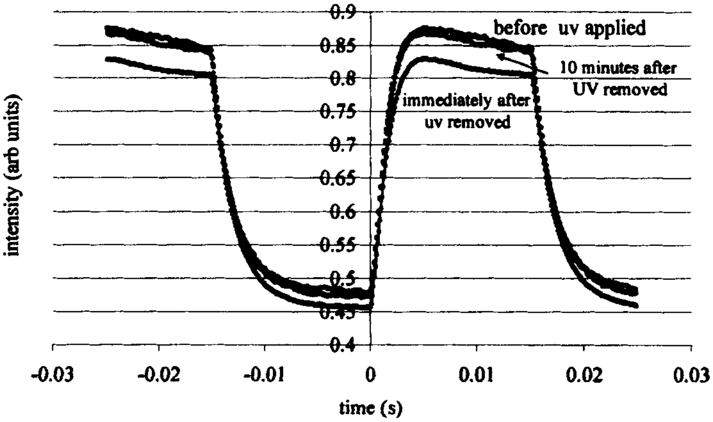

FIGURE 5 Optical transmission through the 5% bimesogen sample held at 38°C before, immediately after and 10 minutes after UV illumination, measured at 33 Hz, 8 V/μm.

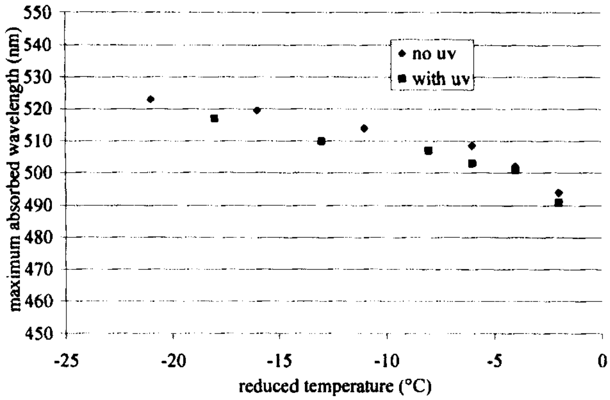

FIGURE 6 Maximum absorbed wavelength against reduced temperature for the 50%7, 50%11+5%BDH1218+5%azo bimesogen mixture.

CONCLUSIONS

The addition of both azo dyes to the host did not significantly effect the flexoelectric characteristics. Illumination of the samples by ultra violet reduced the I-N* transition temperatures, increased the response times and decreased the transmitted intensity. As a function of reduced temperature the tilt angles, the pitch and the focal conic to homeotropic threshold voltages of the mixtures were unaffected by UV illumination.

Lowering of the I-N* transition temperatures indicate that the bent cis isomers disrupt the order in the flexoelectric host. The response time is approximately inversely proportional to the order parameter so reducing the order by UV illumination correlates to the increase in response time observed. Similarly the optical transmission will decrease with decreasing order, on UV illumination, cf. equation 4. The tilt angle, for a given field, and the threshold field for helix unwinding are, at the same reduced temperature, independent of the UV illumination. Thus given equations 2 and 3, they are independent of the order parameter.

It is clear that the shape change of the dye molecule disturbs the order parameter of the host but does not appear to change the flexoelectric coefficient of the material. This is in contrast to the thermochromic materials studied in [6] where the trans-cis isomerisation of an azo dye additive altered markedly the flexoelectric properties. Since the thermochromic properties are a manifestation of the helix pitch altering rapidly, on approaching a smectic phase, whereas in our system the pitch is virtually independent of temperature we conclude that the UV illumination produces isothermal changes in the order parameter alone and not molecular shape changes that might be expected to alter the flexoelectric properties.

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