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Search for optical biaxiality in discotic liquid crystals

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Abstract. Using a high-finesses Fabry–Perot structure, we examine the behaviour of discotic liquid crystals for possible biaxiality. This is done by confining the discotic liquid crystals in the Fabry–Perot cavity and examining the mode structure in presence and absence of an applied electric field. It is concluded that at least in the discotic liquid crystal that we have examined, there is no evidence of biaxiality.

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The molecular shape is important for the occurrence of liquid crystals [1]. Although discotic liquid crystals, composed of disc shaped molecules, have been known from some time [2], there are relatively few physical studies of these materials. The structure of the recently synthesized dumb-bell shaped molecules, essentially made up of two discs linked by a bridging group, have led to the suggestion that these materials might be biaxial nematics. Although there are reports in the literature [3] about the existence or doubts of biaxiality in these materials as yet there have been no systematic studies to explore their optical properties. In this paper we examine this question using well oriented samples of elongated plate like molecules, and compare these results with studies on other similar but more symmetrical discotic liquid crystals. From these comparative studies, we conclude that the optical biaxiality is not detectable in the liquid crystal phase formed by the dumb-bell shaped molecules that we have examined.

Results and discussion

In order to examine the optical properties of a material, it is generally necessary to obtain well-aligned samples. Since the techniques for aligning discotic liquid crystals is not well known, we have used that straight forward approach of attempting to align the discotic liquid crystals using existing alignment techniques for rod like molecules that exhibit nematic phases. Previous work on the materials that we have chosen to examine, has shown that it is fairly easy to obtain an oriented sample in which the optic axis lies normal to the polymer coated glass plates even when untreated surfaces are used. It was our hope that if biaxiality exist, then the molecular asymmetry could be used in conjunction with the rubbed polymer surfaces to orient the sample in which the index ellipsoid [4] could be oriented in a fixed relation to the rubbing axis. For this study we have chosen two molecules which have quite different molecular shapes. In one case (a), the molecule is composed of two disc-like structures which are linked by an alkyl chain, producing an overall dumb-bell shape (Fig. 1a). In other case (b), the molecule is symmetric and resembles a disc (Fig. 1b). In the first case the molecules may be like elongated plates, with the plate axis containing the aromatic rings. In the second case, the molecules are essentially disk and for reasons of symmetry can only be uniaxial nematics. While the rubbed polymer surfaces was excepted to orient the dumb-bell axis along the rubbing axis, the experimental results discussed below show any evidence of this; instead, it suggests that the dum-bell axis must be oriented either randomly or in such a way that the optical properties are identical with respect to rotation of the sample about its surface normal. In other words, the sample in the discotic phase appears optically isotropic when the light propagation vector is normal to the cell surface, indicating that the sample is uniaxial and that the optic axis lies parallel to the surface normal even when rubbed polymer surfaces are used to produce mono-domain samples. Identical results were obtained for the simple disc-shaped molecules shown in Fig. 1b.

The detail examination of the optical properties of discotic liquid crystals were carried out using a high-finesse Fabry-Perot cavity. The Fabry-Perot cavity is formed by placing two mirrors face to face. These structures resembles a typical liquid crystal cell in which the two inner surfaces have been coated with dielectric mirrors. At normal incidence if the light falling on the structure is

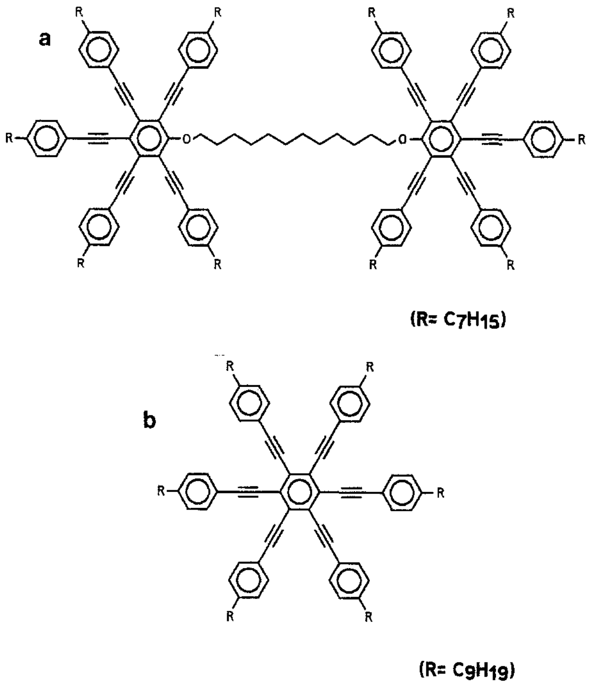

Fig. 1a, b. Chemical structures of the discotic liquid crystals used in this study

polychromatic, then the transmission through such a structure allows narrow bands of light to pass through. The transmitted wavelength depends on the refractive index of the material in the cavity and the cavity length. Thus, for an isotropic fluid with refractive index of n, the peak transmission would be determined by the cavity resonances observed when $m\lambda_m = 2nd$, where m is an integer, d is the cavity length and λ_m is the resonant wavelengths with mode number m. In the case of an uniaxial material, there are only two principal values of the refractive index. If the sample is aligned such that the optic axis lies normal to the glass plates, then the two orthogonal eigen-polarization have the same eigen-values for the Fabry–Perot cavity and only one set of resonances is observed. If, however, the light propagates at an oblique angle to the sample, then the two eigen-values of the cavity are no longer the same and the sample exhibits two sets of resonances,one with the eigen-vector corresponding to polarization parallel to the plane containing the sample normal and the propagation vector, and the other with the polarization perpendicular to it. Similarly, two sets of resonances would also be observed if the optical axis is tilted with respect to the propagation direction by using an applied electric field. This shows that if the sample were uniaxial, then by applying an electric field, one of the cavity modes should remain the same while the other changes. This behavior has previously been examined for the rod-like nematics [5]. The manner in which the eigenvalues change with the applied electric field would depend on the details of how the liquid crystal molecules are distorted in the bulk of the sample and therefore depend on the magnitude of the dielectric anisotropy, and the values of the elastic constants [6]. However, for the uniaxial materials with the optic axis initially perpendicular to the glass plates, if the optical axis can be tilted by 90 degrees in the limit of high electric field then the two sets of the cavity modes would correspond to the ordinary and the extra-ordinary refractive indices of the discotic liquid crystals. Thus, the two sets of resonances can be used to measure the sample birefringence if the sample thickness is known exactly because these modes would be given by $2n_o d = m\lambda_m^o$ and $2n_e d = m\lambda_m^e$ in the limit of high electric field, where n_o and n_e are the ordinary and the extra-ordinary indices.

For biaxial material, the three principal values of the index can be determined if the sample can be oriented in two different geometries. For one orientation of the index ellipsoid, one can obtain the two values, say n_x *and* n_y. For the other orientation, typically perpendicular to the first, it is possible to get two more values of the index, say n_x and n_z. The tiling of the optical index ellipsoid is accomplished by applying a high values of the electric field so that molecules gets reoriented by 90 degrees. Thus all three principal values to be determined by examining the two sets of cavity resonances in the absence and in the presence of an applied electric field.

In our studies, we have chosen a geometry, in which the disc shaped liquid-crystal molecules lie parallel to the mirror planes. This is achieved by coating the surface with a thin coating of poly(butylene terepthalate) alignment polymer [7]. In order to break the surface symmetry to provide a preferential orientation of the discs for the dumb-bell shaped molecules, the surfaces were rubbed so as to attempt orientation of the dumb-bell axis of the molecules. It was determined that applying an electric field normal to the disc plane, caused the discs to align such that the disc planes became parallel to the direction of the applied electric field. Thus, by combination of an applied electric field and a uniformly aligned sample, it should be possible to obtain all three principal values of the refractive index, if the surface distortions can be neglected.

The materials that we have chosen for our study are shown in Fig. 1. Both materials, the dodecyl bridged radial pentayne twin diether (a) and the centrosymmetric radial hexayne (b), were synthesized and characterized by spectroscopic and elemental analysis according to the procedure published elsewhere [8–10]. The following data were obtained by polarizing microscope/differential scanning calorimetry in °C or ΔH in kJ/mol using Mettler FP 82 hot stage and Mettler TA 3000/DSC 30 S calorimetry system; the heating and cooling rates were 5 degrees/min (Cr: Crystalline, $\mathrm{N_D}$: nematic-discotic, Iso: isotropic liquid)

(a) 1.12-Bis[pentakis(4-heptylphenylethynylphenyloxy] dodecane [9]

$$\mathrm{C_{174}H_{214}O_2},\ \text{M.W.}2337.2,\ \mathrm{Cr}\frac{75.5/76.3}{\Delta H = 57}\mathrm{N_D}\frac{84.7/85.1}{\Delta H = 0.5}\mathrm{Iso}$$

(b) Hexakis(4-nonylphenylethynyl)benzene

$$\mathrm{C108H138},\ \text{M.W. } 1766.2,\ \mathrm{Cr}\frac{70.4/71.7}{\Delta H = 82.7}\mathrm{N_D}\frac{87.3/88.3}{\Delta H = 0.1}\mathrm{Iso.}$$

For both liquid crystals, we find that when the material is confined between two rubbed surfaces, the structure is optically isotropic when viewed perpendicular to the cell surfaces. This immediately suggests that two of the three principal indices are the same and therefore the material is uniaxial. Thus such a cell when viewed between cross polarizers, appears black with no visible variation in intensity as angle that the rubbing axis makes with the polarizer axis is changed. If the material were biaxial, one would expect a variation in intensity as the optic plane is rotated with respect to the polarizers.

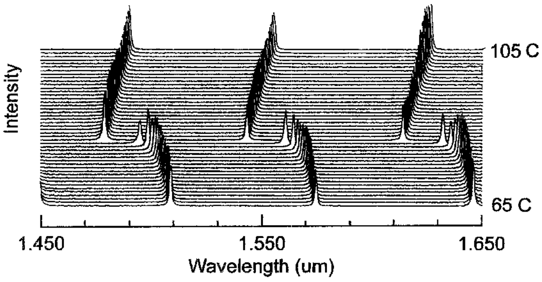

Fig. 2. Fabry–Perot resonances for an oriented, unidirectionally rubbed, sample of discotic liquid crystal (a) as a function of temperature. At fixed temperature, only one resonance is observed, indicating the lack of optical biaxiality. The sample thickness is about 10 μm

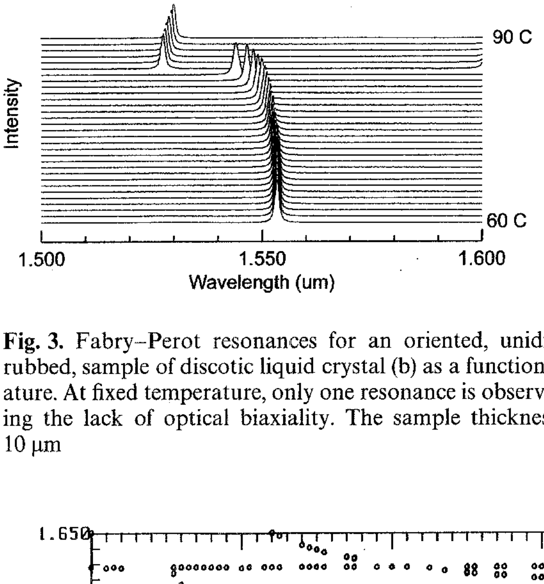

Fig. 3. Fabry–Perot resonances for an oriented, unidirectionally rubbed, sample of discotic liquid crystal (b) as a function of temperature. At fixed temperature, only one resonance is observed, indicating the lack of optical biaxiality. The sample thickness is about 10 μm

In the absence of an electric field, identical results are obtained whether the samples are prepared with surfaces that have been rubbed or not rubbed, suggesting that the rubbing process has practically no effect on the observed optical properties. In both cases the optic axis is perpendicular to the glass plates as is the director. However, these two samples behave differently when subjected to an applied electric field. For fields above the Frederick's threshold voltage, a birefringent but un-oriented sample is observed for the un-rubbed sample, while an oriented birefringent sample is observed in the case of the rubbed sample. The birefringence arises because the optic axis is no longer along the propagation direction, but at an angle with respect to the surface plane. For the un-oriented birefringent samples, while this angle is fixed with respect to the propagation direction, it is degenerated in the sample plane giving rise to schlieren texture with ± 1 and ± 1/2 defects. For the oriented birefringent samples the angle is fixed with respect to the propagation direction as well as the rubbing axis. The behavior is essentially the same for both materials (a) and (b). In the oriented birefringent samples, in the presence of an applied electric field, the discs reorient such that the disc planes lie along the direction of the electric fields as well as the rubbing axis. However, this is only possible if the anchoring at the surface is weak, or if the anisotropic surface force produced by rubbing the surface is somehow transmitted to the bulk. We are currently examining this behavior in more detail.

Using such a rubbed oriented sample in a Fabry–Perot configuration, it allows one to obtain the three values of the principle indices, as discussed above, and allows quantitative determination of the values of the indices. Careful measurements show that in the absence of an applied electric field, only one set of resonances are obtained. This set corresponds to a single value of index but several resonant wavelengths corresponding to different mode numbers. The results for liquid crystals (a) and (b) are shown in Figs. 2 and 3, respectively. Both figures

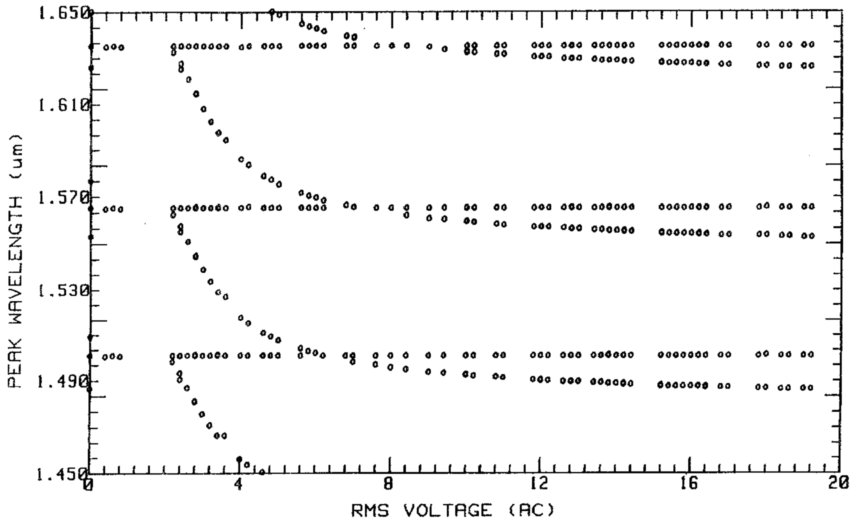

Fig. 4. Peak positions for the resonances for an oriented sample (a) as a function of applied electric field at 77 °C. The data are obtained with randomly chosen value of the field, and hence the curve is discontinuous. Notice that one of the peak resonances does not change with field, indicating uniaxial behaviour. The sample thickness is about 10 μm

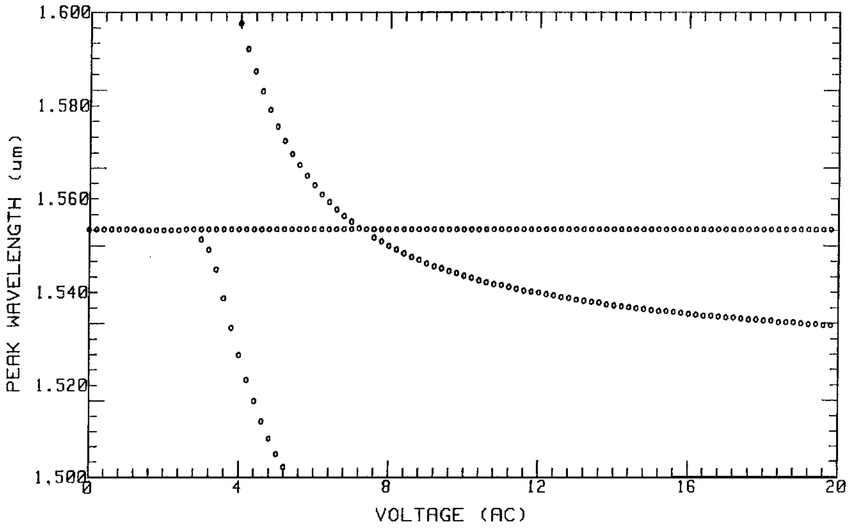

Fig. 5. Peak positions for the resonances for an oriented sample (b) as a function of applied electric field at 77 °C. Notice that one of the peak resonances does not change with field, indicating uniaxial behaviour. The sample thickness is about 10 μm

reveal peak shifts with changes in the sample temperature, but no splitting of the resonances, suggesting that the material remains uniaxial at all temperatures at which the material exhibits liquid crystallinity. Except for the phase transition temperatures, the behavior is virtually identical. We conclude that the absence of two sets of resonances indicates that both the materials are uniaxial. The evidence for uniaxiality is further verified by applying an electric field across the sample and determining the peak values of the resonances. The results are depicted in Fig. 4 at a fixed temperature. If the material were biaxial, then above the threshold voltage, both the resonances would show a shift with the magnitude of the applied field. Notice that in Figs. 4 and 5 corresponding to compound (a) and (b), one of the resonances remains fixed with changes in the applied electric field providing further evidence that the material is uniaxial. From the lack of shift in one of the resonance modes, we can estimate that the biaxiality is less then 1 part in 10^4.

In conclusion, we have shown that for the material that we have examined, there is no evidence for optical biaxiality, although the chemical structure of the molecule suggests that in principle, biaxial behavior may be possible.

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