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Accurate Measurement of the Helical Twisting Power of Chiral Dopants

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We report on an accurate measurement of the helical twisting power (HTP) of chiral dopants. In the usual Cano-wedge method, the wedge angle is determined from the separation of laser beams reflected from the windows of the test cell. Here we propose to use an optical fiber based spectrometer to accurately measure the call thickness instead. Knowing the cell thickness at the positions of the disclination lines allows evaluation of the HTP. We show that this extension of the Cano-wedge method greatly increases the accuracy with which the HTP is determined.

We have applied this technique to determine the HTP of ZLI811 in a variety of hosts with negative dielectric anisotropy.

INTRODUCTION

When chiral molecules are admixed into a nematic host, chirality is imparted to the entire system. An interesting, and not yet fully understood question is, from both theoretical and experimental point of view, what is the handedness and the pitch of the resultant helical structure? [1] From the device development point of view, it is essential to know how the natural pitch, p_0, of the mixture is related to the concentration of the chiral dopant. In the low concentration limit, p_0 is inversely proportional to the dopant concentration[2]. HTP is the reciprocal of the constant of proportionality.

There are several methods of measuring the pitch reported in the literature, each useful in a particular range of the pitch to be measured. The Bragg reflection method [3] is useful for characterizing short pitch materials, where the central wavelength of selective reflection, $\lambda_0=np_0$ (n being the mean index of

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refraction), falls in the visible spectrum. The droplet, fingerprint and Cano wedge methods are more useful for materials with longer pitch [4–6].

In the Cano wedge method, the chiral mixture is filled into a wedge shaped cell where the windows have been treated to produce homogenous alignment at the boundaries. Due to this homogeneous alignment, periodic compression and dilation of the helical structure of the cholesteric occurs, and disclination lines form in the cell perpendicular to the gradient of the cell thickness. The pitch can be determined from measurements of the wedge angle and the distance between the disclination lines. The wedge angle is usually determined by measuring the angular separation between reflections of a laser beam from the two windows of the unfilled cell. A considerably more accurate evaluation of the HTP could be carried out if the exact thickness of the cell was known as a function of position. Using an optical fiber based spectrometer, the variation of cell thickness with position can be measured with relative ease.

In the case of strong anchoring (a valid assumption for all of the cells we used) and linear dependence of cell thickness on position, the separation between adjacent disclination lines should be uniform throughout the cell. We found, however, that this was not the case. In most cells, a monotonic variation in the line spacing was observed. We show that this can be accounted for by a small deviation of the thickness from the linear dependence on position. This slight curvature of the "wedge", similar to that reported by Gerritsma et al. [7], consistently appeared, despite special care exercised in avoiding it. In these cases, the usual method of assuming a perfectly wedge-shaped cell and measuring the wedge angle using reflected light, can only give a less accurate result.

EXPERIMENTAL

Wedge shaped cells were fabricated using 3 mm thick glass plates (Glass-tek Industries); thick glass was used in order to minimize flexing of the substrates. The cell windows were 25 mm wide and 37 mm long. Mylar foils (DuPont) were used as spacers; a single spacer was used at the thick edge of the wedge, and no spacer was used at the thin edge. The substrates were coated with polyimide (PI2555, HD Microsystems) film and unidirectionally buffed. This surface treatment is known to give strong planar anchoring of the director. The assembled cell was pressed between two brass blocks, and a two component epoxy adhesive was applied at the edges of the cell, leaving only three small gaps for filling. Once the cells were assembled, the thickness variation with position was measured. To measure the cell thickness, we used a PC2000 Miniature Fiber Optics Spectrometer (Ocean Optics). A beam of white light was focused to an approxi-

mately 150 μm diameter spot where it was incident on the cell. The transmission spectrum in the range of 400–830 nm was measured, and the wavelengths where the extrema occurred were used to calculate the cell thickness. A computer controlled translation stage moved the cell in 1 mm steps and the thickness was evaluated at every step. Observing the interference fringes in the unfilled cells we found that the cell thickness remained constant to within 0.5 μm with position in the direction parallel to the thin edge of the wedge; the variation of cell thickness with position in the direction perpendicular to the thin edge of the wedge is shown in Fig. 1.

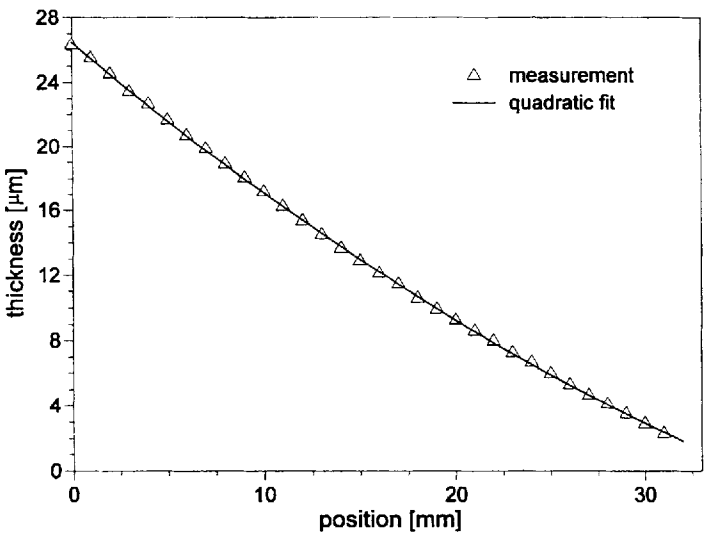

FIGURE 1 Thickness of cell vs. position measured from thick edge. The solid line is a quadratic fit

Chiral nematic mixtures were made by admixing the chiral dopant ZLI811 in concentrations of 1–3wt% with several commercially available nematics having negative dielectric anisotropy. All materials were obtained from Merck Inc. The cells were capillary filled with the liquid crystal-chiral dopant mixtures. Because of the rigidity imparted by the epoxy and because thick substrates were used, we are confident that the cell thickness did not change when the cell was filled. After filling, once the texture of the liquid crystal equilibrated, the position of each disclination line was determined under a polarizing microscope. We point out that this latter measurement can be carried out in an alternate way under certain circumstances. The test cell, placed between crossed sheet polarizers, can be scanned using a flat-bed scanner equipped with a transparency adapter. If the dis-

clination line separation is large enough, and the thickness-birefringence-pitch combination results in a sufficiently high contrast of the scanned image then the position of the disclination lines can be evaluated quickly and accurately from the scanned image.

All the measurements were carried out at room temperature.

RESULTS AND DISCUSSION

After the thickness variation and the positions of the disclination lines were carefully measured, we calculated the thickness of the cell at the position of each disclination line. As we show below, this data allows the calculation of the pitch of the cholesteric mixture.

Theory

We first consider the energetics of the director configuration in the cell. Due to the thickness variation and the strong planar anchoring, the helical structure of the liquid crystal will be periodically dilated and compressed as function of position along the wedge direction.

The twist term in the Frank free energy density is

$$f_t = \frac{1}{2} K_2 (\mathrm{n}(\nabla \times \mathrm{n}) + q_0)^2$$

where K_2 is the twist elastic constant, **n** is the director, and $q_0=2\pi/p_0$. We choose a coordinate system where x is along the thickness gradient and the long edge of the cell, and z is the direction perpendicular to the cell walls. Since the wedge angle is small, we ignore here the difference in directions of the normals, as well as the elastic contribution to the free energy associated with this.

Assuming a uniformly varying twist angle, $\varphi(z) = zm\pi/d$, where $m(x)$ is the number of half turns, $d(x)$ is the sample thickness, the director field can be written as $\mathbf{n}(z) = [\cos\varphi(x,z), \sin \varphi(x,z),0]$. Strong anchoring implies that $m(x)$ can only take on integer values. The sample is thus divided into domains corresponding to integer values of half-turns, separated by disclination walls where the number of half-turns jumps by 1. After substitution, the free energy becomes

$$f_t = \frac{1}{2} K_2 \left(\frac{m2\pi}{2d} - q_0 \right)^2$$

Using the notation, p = 2d/m we can further write

$$f_t = 2\pi^2 K_2 \left(\frac{1}{p} - \frac{1}{p_0}\right)^2$$

We next number the disclination lines sequentially with the index n, starting with n = 0 at the first disclination line at the thick end of the cell. If the number of half turns on the thicker side of this line is m_o, then $m = m_o - n$. We denote the cell thickness at the n^{th} disclination with d_n, and the corresponding pitch on the thick side of the n^{th} disclination line is $p_n = 2d_n / m = 2d_n /(m_o - n)$.

The free energy density on the thick side of the n^{th} disclination line is therefore

$$f_{tn} = 2\pi^2 K_2 \left(\frac{1}{p_n} - \frac{1}{p_0}\right)^2$$

while on the thin side of the same line it is

$$f_{tn+1} = 2\pi^2 K_2 \left(\frac{1}{p_{n+1}} - \frac{1}{p_0}\right)^2.$$

Since in equilibrium the disclination line does not move, the free energy density on the two sides of the line must be the same. This means that

$$\frac{1}{p_n} - \frac{1}{p_0} = -\frac{1}{p_{n+1}} + \frac{1}{p_0}$$

Substitution for p_n gives

$$d_n = -n\frac{p_0}{2} + (m_o - \frac{1}{2})\frac{p_o}{2} \qquad (1)$$

Eq. (1). implies that plotting the thickness of the cell d_n at the disclination lines versus the disclination line number n should give a straight line, with slope $p_0/2$

It is interesting to consider the disclination line spacing. The cell thickness change from one disclination line to the next is $\Delta d_n = d_{n+1} - d_n = - p_0/2$. If the cell thickness varies linearly with position, that is, $d_n = bx_n + c$, then the separation between the disclination lines is a constant, given by

$$\Delta x_n = \frac{\Delta d_n}{b} = -\frac{p_0}{2b}. \qquad (2)$$

Therefore in a cell in which the thickness variation is strictly linear, the disclination lines should be equidistant. This is the situation usually discussed in the literature (e.g. [8]). We found, however, that despite the special care taken in constructing our cells, in most cases there was a considerable deviation from the linear thickness dependence. In all cases, a quadratic expression of the form $d_n = ax^2_n + bx_n + c$ gave excellent fit to the measured data. In this case, the disclination line separation is given approximately by

$$\Delta x_n = \frac{\Delta d_n}{2ax + b} = -\frac{p_0}{4ax + 2b} \tag{3}$$

We present data from a representative cell which is typical and serves well to illustrate the point of this paper.

Fig. 1 shows the variation of cell thickness with position. The solid line is a quadratic fit given by $d = 7.62\times10^{-3}$-*+$x^2 - 1.013x + 26.47$.

Fig. 2 shows the texture of the cell between crossed polarizers. The image was processed to emphasize the disclination lines. Clearly the disclination lines are not equidistant; there is a monotonic increase in line separation as the cell gets thinner.

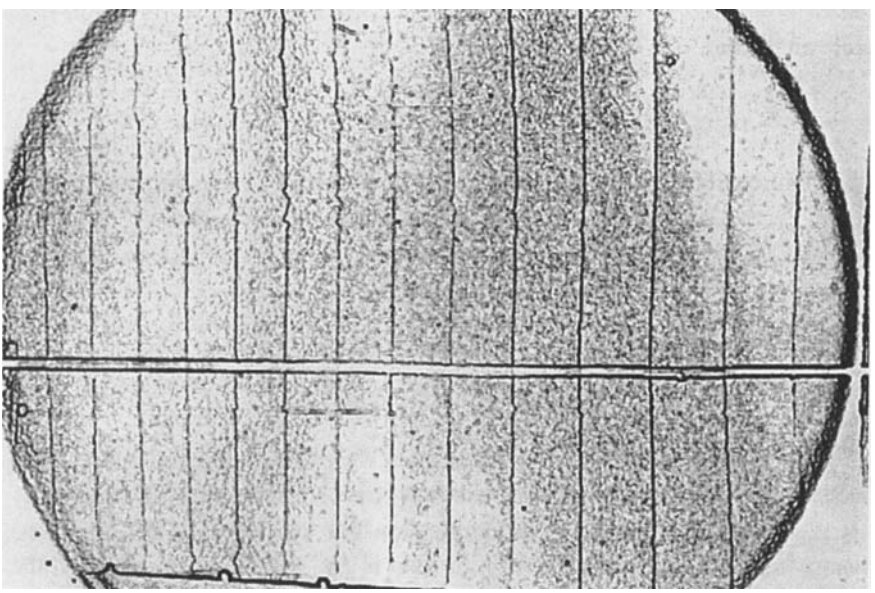

FIGURE 2 Image the cell viewed between crossed polarizers (processed image). The horizontal line is not a defect, but a mark indicating the line along which the measurement was carried out

It is useful to consider the role of anchoring strength. The effect of weak anchoring on the formation and position of the disclination lines in the Cano wedged cell was analyzed by Warenghem [9]. He showed that in the case of sufficiently weak anchoring and below a critical thickness, the disclination lines do not form at all. Above the critical thickness the disclination lines appear in pairs, and finally the line separation becomes uniform as the thickness increases. The critical thickness can be estimated as $d_C = K_2/W_0$, where W_0 is the anchoring

strength. Using approximate values of $K_2 \sim 10^{-11}$J/m and $W_0 \sim 10^{-5}$-10^{-4}J/m^2 for strong anchoring, we estimate d_c to be ~1–0.1 μm. Since our sample thickness is never less than 2 μm, we assume that "strong anchoring" conditions prevail.

Fig. 3. shows the graph of the thickness of the cell at the disclination lines versus the disclination line number. This dependence is linear, in good agreement with Eq. 1. The slope is $-p_o/2$. We find that m_o=15, and the director makes only one half turn after the last disclination line (right side of image in Fig. 2) in good agreement with theory since here the cell is approximately 2 μm thick and the half pitch is $p_o/2 = 1.73$ μm.

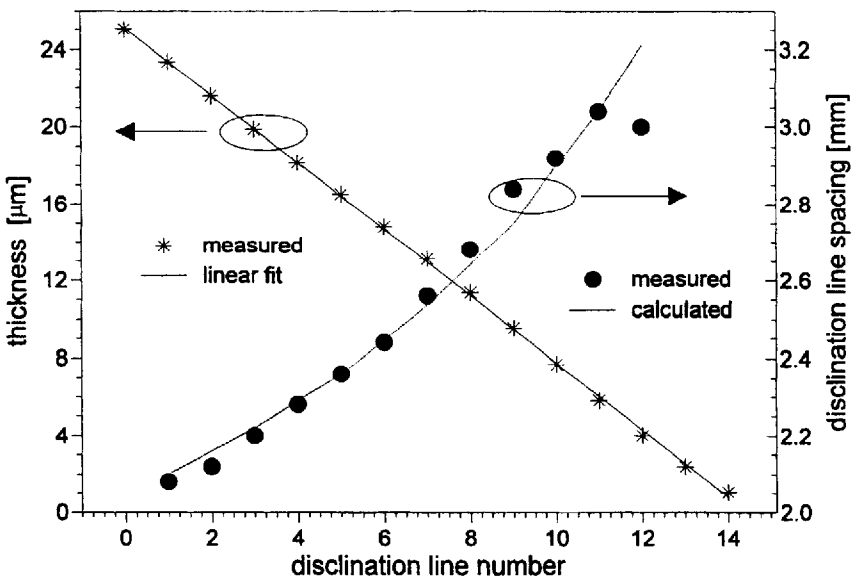

FIGURE 3 Disclanation line spacing (solid dots) and cell thickness (asterisks) versus disclination line number. The dotted line is line spacing from Eq. 3. The solid line is from Eq. 1.: the slope gives negative half pitch

The disclination line spacing is also plotted in Fig 3. The solid line is from Eq. 3; the agreement with experiment indicates the validity of this approach.

We found that using our extended Cano method, the pitch determined from different cells varied by less than ±1%.

Our cell geometry, with approximately 30 μm thickness at the thick edge and the length of 3 cm gives a wedge angle of 1mrad. Attempts to determine the wedge angle using the laser beam reflection method indicated that at angles such as ours the accuracy of this method is severely limited by interference between

reflections from individual substrates and by the divergence of the beam. We estimated that the accuracy of the wedge angle determined with this method was not better than 20% which is considerably worse than the accuracy of the direct measurement of the thickness variation.

Using the Cano wedge method, extended with the cell thickness measurement as described above, the HTP of the chiral dopant ZLI811 was determined in four different nematic hosts with negative dielectric anisotropy. The results are shown in Table I. The available literature data is also indicated.

TABLE I

Host	HTP [μm^{-1}]
ZLI2806	8.41 (8.5 @ 20°C [8])
ZLI4788–000	12.44
MLC6609	10.47
MLC2038	12.78

CONCLUSION

We have used the Cano wedge method to measure the helical twisting power of chiral dopants in nematic hosts. We demonstrated that precise knowledge of the thickness of the cell as function of position considerably increases the accuracy of the method. An optical fiber based spectrometer, with a measuring beam diameter of 150 μm, was used to determine the cell thickness. A small deviation from the linear dependence of thickness on position can result in a variation in the disclination line separation. The agreement between the experimental data and our simple model shows that the strong anchoring limit is a valid assumption and the non-uniformity of the disclination line spacing is due to the deviation from the linear dependence of cell thickness with position. Careful measurements of cell thickness allows determination of the pitch of the sample and the helical twisting power of the chiral dopant with better than ±1% accuracy.

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