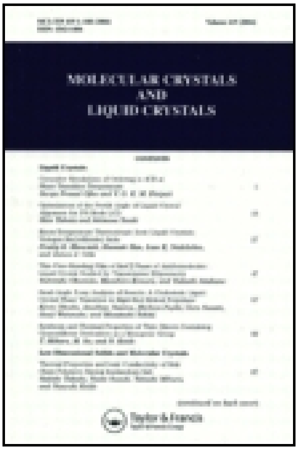

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Effect of Boundary Conditions on the Pitch and Helical Twisting Power of Chiral Solutes in Nematic Liquid Crystals

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Effect of Boundary Conditions on the Pitch and Helical Twisting Power of Chiral Solutes in Nematic Liquid Crystals

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The methods of determining the pitch of cholesteric (chiral nematic) liquid crystals require specific boundary conditions in order to visualize the rotation of the optic axes. As a consequence of these boundaries, pitch perturbations may occur. In this work, it is demonstrated that the fingerprint method, which requires homeotropic boundaries, leads to systematically larger pitch values than the Cano wedge or droplet methods. Further, the values of pitch determined by the fingerprint method are particularly sensitive to the nature of the wall anchoring.

Keywords: cholesteric, nematic, pitch, helical twisting power

INTRODUCTION

When a chiral compound is dissolved in a nematic liquid crystal, there occurs a remarkable coupling of the local disymmetry of the molecule with the macroscopic orientational ordering of the solvent phase.[1-5] This coupling results in a cholesteric liquid crystal characterized by both its handedness and its pitch. In the limit of low concentration, the pitch P of the cholesteric helix is inversely proportional to the concentration C of chiral solute ($P^{-1} = \beta C$).[6,7] The proportionality constant β is referred to as the "helical twisting power" (HTP) of the solute, and a number of studies have attempted to correlate HTP with size and shape related parameters.[8-12]

There are several methods of measuring pitch reported in the literature: the reflection method,[13,14] primarily appropriate when the wavelength of maximum reflection ($\lambda = \bar{n}P$, where $\bar{n}$ is the average refractive index) is in the visible region of the spectrum; the droplet method,[15] the Cano wedge method,[16] and the fingerprint method.[12,17] The latter three methods are primarily useful when the pitch is in the range 10–100 μm.

Cladis and Kleman[17] noted a small discrepancy between the pitch measured by the fingerprint method and the Cano wedge method, with the latter pitch being shorter than the former. They attributed this dependence to distortions in the helix associated with the thickness of the sample, and the tendency of the liquid to distort to adapt to the boundaries. However, there has not been a detailed study of the influence of the boundary conditions and wall anchoring on the values obtained for the pitch from these various methodologies, and it is therefore difficult to correlate values of HTP obtained by the different methods.

In this paper, we measure the pitch of a variety of chiral nematic liquid crystals by three different methods and systematically vary the degree of wall anchoring. We demonstrate that quite large distortions in the pitch can be caused by strong homeotropic anchoring, and that determinations by the fingerprint method can vary markedly depending on the nature of the surfaces confining the sample. The discrepancy in pitch values between the fingerprint, Cano wedge and droplet methods in several cholesteric liquid crystals are shown to be relatively independent of thickness of sample (or size of droplet), whereas they are strongly dependent on wall treatment.

EXPERIMENTAL

The cholesteric (chiral nematic) liquid crystal mixtures were prepared by adding chiral dopants to thermotropic nematics. The materials, all of which are commercially available, are listed in Table I.

The so-called "fingerprint texture" of cholesterics is one in which the helix axis is parallel to the glass walls, and the molecular optic axis is precessing with a helical periodicity. When viewed between crossed polars, one observes a series of black and light regions as the director proceeds from registry alternatively perpendicular and parallel to the observation direction.[17] A large number of fingerprints are measured and their sizes averaged to obtain the pitch (two fingerprints = 360° rotation of the optic axis).

In order to obtain homeotropic alignment, glass slides are treated by coating them with: a) 0.5% lecithin from egg yolk (Fluka #61755) in $CHCl_3$: b) 0.5% lecithin from soybean (Sigma Chemical #P3644); c) 0.5% of a 50% by weight *N*-octadecyldimethyl-3-trimethoxysilylpropylammonium chloride (DMOAP) solution in methanol (Petrarch) in aqueous solution. The coatings are rinsed with solvent or water and dried at 80°C in a nitrogen atmosphere for one hour.

Another method of obtaining homeotropic alignment, employed by Cladis and Kleman,[17] is to add a small amount of toluene to the liquid crystal, converting it to an isotropic phase. As the toluene is allowed to evaporate, the fingerprint texture develops spontaneously. The texture is however, not as good as is obtained utilizing either lecithin or DMOAP. The alignment with either DMOAP or <u>fresh</u> preparations of egg yolk or soybean lecithin is particularly good, indicative of the strong wall anchoring. It should be cautioned, however, that aged samples of lecithin which have not been stored at low temperature do not give good alignment.

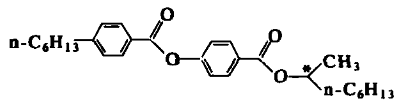
In the Cano wedge method, cholesteric liquid crystals are confined to a wedge-shaped space, and show a series of stripes (disclination lines) under the polarizing microscope. The pitch can be calculated knowing the wedge angle and distance between disclinations. This periodic structure can be achieved when the slides are

TABLE I

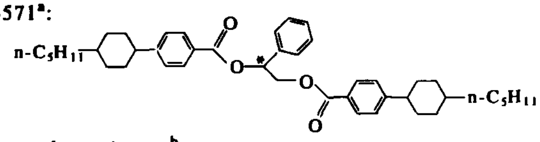
Structures of the chiral dopants and nematic liquid crystals used

Chiral dopants:

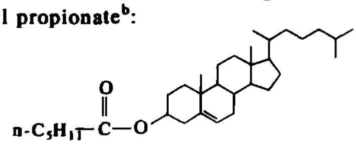
ZLI-811[a]:



ZLI-4571[a]:

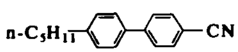


Cholesteryl propionate[b]:

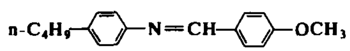


Nematics:

K15[c]:



MBBA[d]:



Chemicals were commercially available from:

a: E. Merck; b: Eastman Kodak; c: BDH; d: Aldrich Chemical Co.

treated to promote homogeneous alignment by coating them with 1% polyvinyl alcohol (MW 30,000–50,000) in aqueous solution and drying at 110°C for an hour. The wedge angle is about 0.4°.

In the droplet method, the cholesteric liquid crystal is suspended in glycerol in which it is virtually insoluble. A series of droplets of the cholesteric are formed with a fairly wide size distribution from 80 to 200 μm. The director adopts a tangential orientation to the interface induced by surface tension. Since the helical axes are aligned along the radical disclination, an optical pattern of a series of rings can be observed in polarized microscopy, and the pitch measured in a manner completely analogous to the fingerprint method.

RESULTS AND DISCUSSION

In the cholesteric liquid crystal mixture ZLI-811/K15, the pitch values were determined by the fingerprint method utilizing the various boundary conditions described above. Figure 1 is a plot of reciprocal pitch vs. concentration as determined by these methods. All of the agents which promote homeotropic alignment give much larger pitch values than that which is observed on an untreated slide. On the untreated slide, toluene evaporation from the isotropic sample yields spontaneous

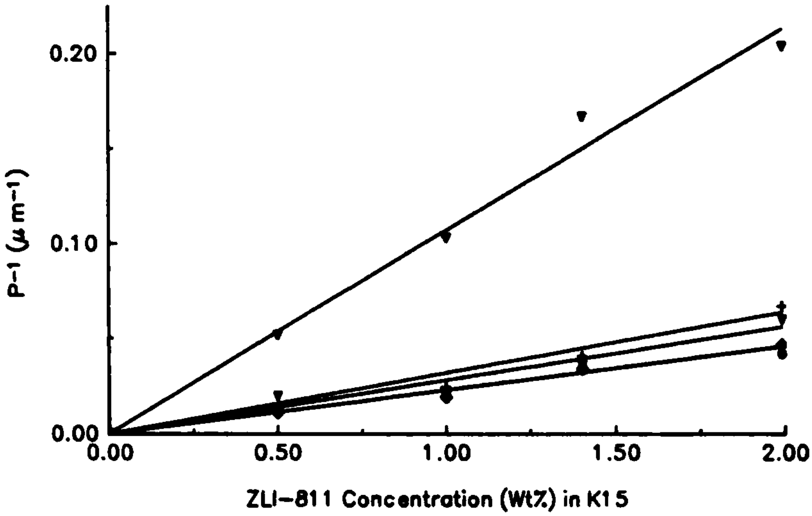


FIGURE 1 The discrepancy among the measurements made by the fingerprint method utilizing different boundary conditions for the chiral additive ZLI-811 dissolved in nematic K15: a. slides treated with DMOAP (●); b. slides treated with egg lecithin (♦); c. slides treated with soybean lecithin (+); d. slides treated with DMOAP, and toluene allowed to evaporate from the isotropic phase (▽); e. untreated slides, and toluene allowed to evaporate from the isotropic phase (▼).

TABLE II

Absolute helical twisting power (HTP) of the solute ZLI-811 in the nematic liquid crystal K15 as determined utilizing differing boundary conditions

Conditions	HTP
Slides treated with DMOAP	2.3
Slides treated with egg lecithin	2.3
Slides treated with soybean lecithin	3.2
Untreated slides,toluene evaporation	11.0
Slides treated with DMOAP, toluene evaporation	2.8

homeotropy, but the texture achieved is very poor. It is possible to measure the pitch from certain regions of the sample, but the texture is non-uniform.

The slope of each line gives the HTPs which are summarized in Table II. Slides treated with DMOAP and egg or soybean lecithin give the largest observed pitch values, and hence the lowest HTPs. These wall treatments are known to produce excellent homeotropic alignment, and the net effect is to cause a pitch perturbation favoring the untwisted state. As compared to untreated slides, DMOAP and egg or soybean lecithin treatments decrease the HTP almost five times.

TABLE III

Absolute helical twisting powers of chiral solutes obtained by the Fingerprint (F), Cano Wedge (W) and Droplet (D) methods

Chiral Solute	Nematic Solvent	HTP as determined by various methods F	W	D	Literature
CP	MBBA	2.0	8.6	8.2	9[17], 8.4[18]
ZLI811	K15	2.3	12.0	10.7	11.1*[19]
ZLI4571	K15	8.4	35.7	36.2	37.7*[20]

* The solvent in these experiments was E7, a ternary mixture whose major component is K15.

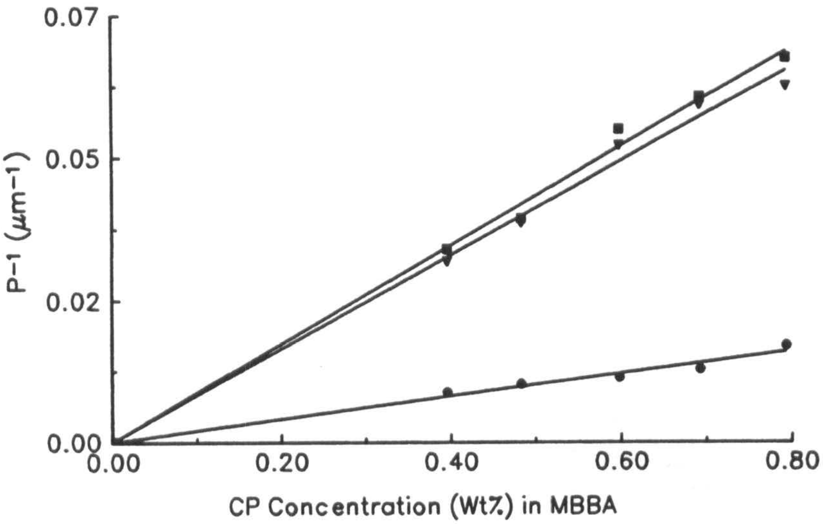


FIGURE 2 Comparison among the fingerprint (●), Cano wedge (■) and droplet method (▼) for the chiral additive CP dissolved in nematic MBBA.

The purpose of adding toluene to the sample is to induce the isotropic transition. Slow evaporation of the toluene causes the cholesteric fingerprint texture to develop. If the sample is simply placed on an untreated slide directly in the cholesteric phase, only a very poor texture is achieved and it is impossible to obtain reproducible pitch measurements. The pitch determined on an untreated slide utilizing toluene evaporation is approximately 5 times shorter than that observed when DMOAP is used at the boundary. A combination of toluene evaporation and DMOAP wall treatment leads to a pitch value that is about 20% shorter than that typical of the DMOAP wall treatment.

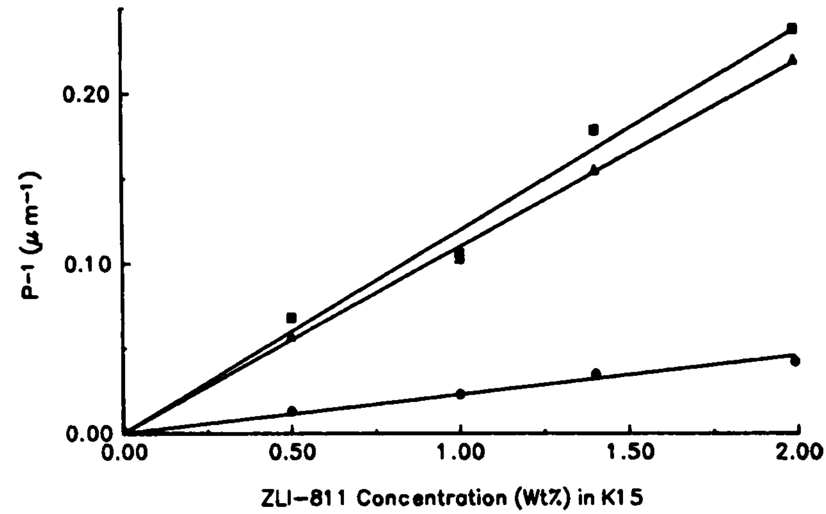


FIGURE 3 Comparison among the fingerprint (●), Cano wedge (■) and droplet method (▲) for the chiral additive ZLI-811 dissolved in nematic K15.

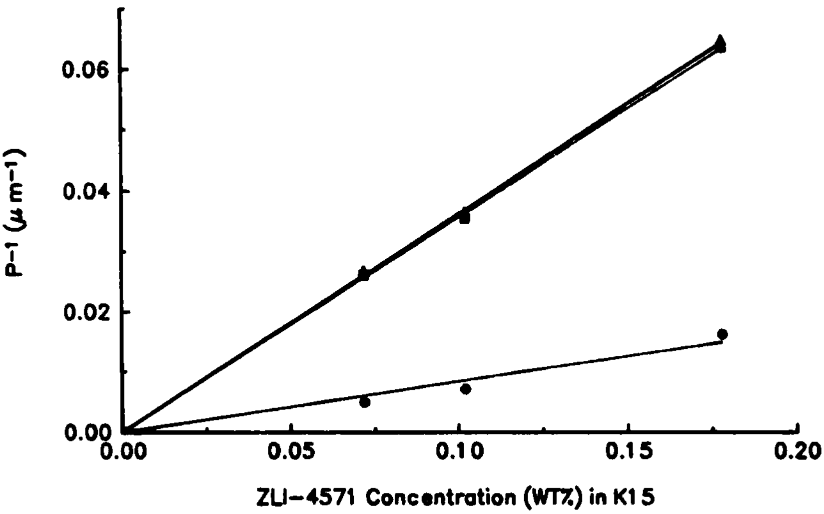


FIGURE 4 Comparison among the fingerprint (●), Cano wedge (■) and droplet method (▲) for the chiral additive ZLI-4571 dissolved in nematic K15.

To confirm the generality of this strong dependence of pitch on wall anchoring and on method of measurement, a number of chiral solutes with varying HTPs were examined. ZLI-4571 was chosen because it has an extremely large HTP in K15. A system that has been widely studied and for which a great deal of data are available is cholesteryl propionate (CP) in the nematic MBBA. Table III presents a comparison of the HTPs of these solutes as measured by a variety of methods.

The HTPs of cholesterics determined by the fingerprint method in Table III utilize DMOAP at the boundary. Results obtained by the Cano wedge and droplet methods are consistent with those in the literature determined by the same methods. For all the systems studied, the fingerprint method values are lower than those obtained by either the Cano wedge or droplet method. These latter two methods agree within about 10%. The detailed dependencies of pitch on concentration for all the systems are presented in Figures 2–4, and within the range of concentrations for which these methodologies are appropriate, there appears to be no dependence of the HTP ratios between the methods on concentration of chiral solute. In these measurements, thicknesses of samples were varied from 6 to 30 μm for the fingerprint method, while the angle was changed from 0.2–0.4° for the Cano wedge method. No thickness dependence was observed within these ranges.

CONCLUSION

In the fingerprint method, wall anchoring and alignment can have an extremely large effect on the determined values of the pitch. The fingerprint method is an extremely convenient one, but it is essential to compare the pitch with values determined by other methodologies if one is interested in a value approximating the macroscopic unperturbed pitch. The Cano wedge and droplet methods also show some (smaller) deviations from one another. Indeed all three methods obviously place constraints on the director field at the boundaries which must be considered in comparing results.

Acknowledgment

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