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A Reinvestigation of the Purported Induction of Preferred Conformations of Achiral Rigid Rod Solutes in Cholesteric Media

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Several achiral rigid rod solutes were dissolved in two different cholesteric liquid crystalline solvents, and pitch measurements were made by the Cano wedge, droplet and fingerprint methods. In the first two techniques, no effect of the achiral solutes on the pitch occurs at low concentration. Although some regimes of the samples prepared by the fingerprint technique show pitch shortening in the presence of some of the achiral solutes, the overall conclusion is that, contrary to previous reports, there appears to be no convincing evidence for the induction of preferred conformations in achiral solutes.

Keywords: Cholesteric, liquid crystal, chirality, pitch

INTRODUCTION

In previous work from this laboratory, it was reported that the achiral solutes 4,4‴-bis (2-butyloctyloxy)-*p*-quaterphenyl (BOOQP) and the polymer poly (hexylisocyanate) (PHI) with a M.W. of 35,000 adopted preferred conformations when dissolved in a cholesteric solvent consisting of *p*-methoxybenzylidene-*p*′-*n*-butylaniline (MBBA) doped with cholesteryl propionate (CP).[1,2] This conclusion was based on measurements of changes in the pitch of a cholesteric thin film in the so-called fingerprint texture. In this note, a reinvestigation of the behavior of achiral solutes in a cholesteric matrix was undertaken not only by the fingerprint technique, but also by two other well established methodologies for measuring pitch, namely the Cano wedge and droplet techniques.

EXPERIMENTAL

The measurements were performed on fifteen solute-solvent combinations. The structures of all compounds are given in Figure 1, and results are tabulated in Table I. The solvent systems employed were: (1) MBBA doped with either CP or CC at concentrations of 0.4 and 0.6 wt% respectively, or (2) K15 doped with ZLI 811 (also called S811) at a concentration of 0.5 wt%. The pitches of these cholesteric solvents at 20°C were as follows: CP/MBBA—27.5 μm, CC/MBBA—23.0 μm, ZLI 811/K 15–18 μm. In order to verify the measuring procedure, the helical twisting power (HTP) of ZLI 811 in K15

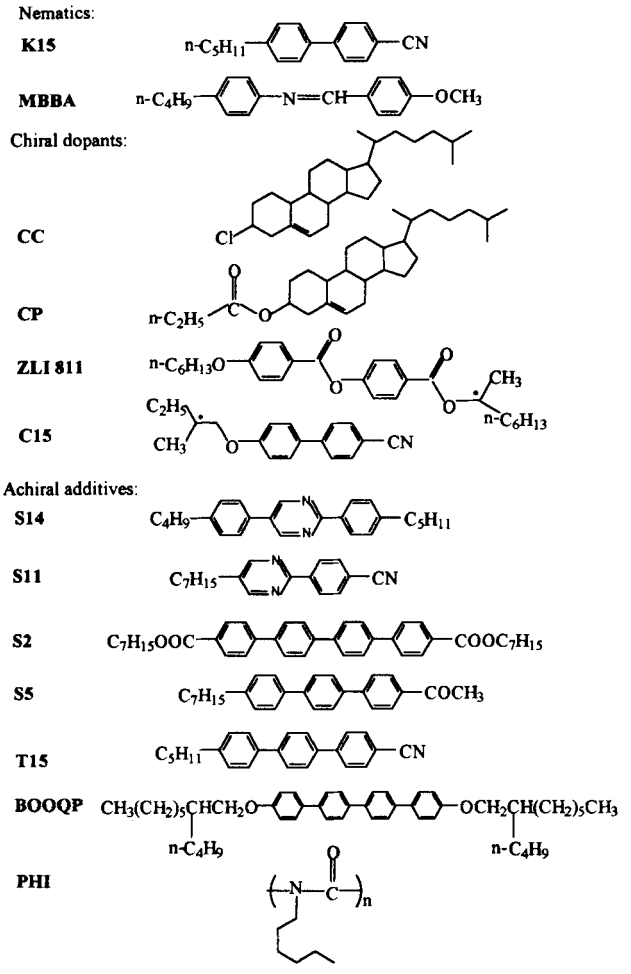

FIGURE 1 Structures of the nematics, chiral dopants, and achiral additives.

was determined by the three methods, in each case measuring the concentration-pitch dependence and evaluating HTP graphically as the slope of the inverse pitch vs concentration linear plot. The following values were obtained for HTP in units of (μm wt fraction)$^{-1}$: wedge 11.1; droplet 10.0; fingerprint 2.2. The values obtained by the wedge and droplet methods are consistent with those in the literature.[3,4] The fingerprint method value is five times lower, which agrees with the results of previous measurements,[3] that is, the apparent pitch in the fingerprint method is very sensitive to the boundary conditions.

The experimental procedure for the fingerprint method has been previously described.[1] The alignment of the liquid crystals on the glass surface is extremely important in obtaining consistent results. Treatment of the glass slides to achieve the

TABLE I

Determination of the helical twisting power of some achiral and chiral solutes in nematic solvents

Solvent	Solute	Maximum Conc. Wt%	Number of Samples	HTP[a] (μm. wt fraction)$^{-1}$
K15	ZLI 811	0.50	5	-11.10^{b} -10.0^{c} -2.20^{d}
K15-ZLI 811	CP	0.25	4	-6.50^{c} -0.90^{d}
K15-ZLI 811	S2	0.13	4	$0^{b,c}$
K15-ZLI 811	S5	0.17	3	$0^{b,c}$
K15-ZLI 811	S11	30.00	6	$+0.063^{b}$
K15-ZLI 811	S14	0.52	5	$0^{b,c}$
K15-ZLI 811	T15	2.90	4	$0^{b,c}$
MBBA	CP	2.70	3	-9.10^{b}
MBBA	CC	3.10	4	-7.30^{b}
MBBA-CP	BOOQP	0.50	4	$0^{b,c}$
MBBA-CC	PHI	0.50	5	$0^{b,c}$
MBBA-CP	C15	0.50	3	-1.5^{c}

[a] The values of HTP are designated by the method of determination as follows: [b] wedge, [c] droplet and [d] fingerprint.

required homeotropic alignment is accomplished by the following protocol: (1) Use acetone to rinse the slides and dry them in air. (2) Dip a clean dry slide into a solution of 0.5% by volume of a 50% by weight N-octadecyldimethyl-3-trimethoxysilylpropylammonium chloride (DMOAP) solution in methanol (Petrarch) at pH = 6, and agitate for five minutes. (3) Rinse the slides with distilled water. (4) Use nitrogen gas to blow off the liquid drops on the surface of the slides. (5) Dry at 110°C in a nitrogen atmosphere for one hour. (6) Store in a desiccator.

The droplet method involves a suspension of the liquid crystal in an immiscible liquid (glycerol).[5] Slight variations were made in the traditional Cano wedge technique[3,4,6] by using 1/8″ thick glass plates coated with Nylon-6 which seems to afford a more homogenous planar texture.

RESULTS AND DISCUSSION

As seen in Table I, there appears to be no effect of such solutes at very low concentrations when the studies are performed by the Cano wedge technique and by the droplet technique. The fingerprint technique also appears to show no effect when the data are collected over the entire sample *without any attempt to select regimes in which pitch is shortened.* There *are* however, some regimes in the samples in which the fingeprint distance appears to shorten. In the previous work,[1,2] which was part of the dissertation research of Shang,[7] *unbeknownst to the other authors,* a protocol was adopted in which the *minimum* pitch values observed in samples were measured. These minimun pitch values correlated with concentration. However in light of the complete absence of any effect in either the wedge or droplet methods, it must be concluded that, within the

experimental error of all three methodologies, there is no convincing evidence of pitch contraction.

Note that solute S11 is very soluble in K15-ZLI 811, so that any non-linearity in the inverse pitch-concentration relationship caused by induced conformational effects might have been expected to be observable. Instead pitch simply increases as K15-ZLI 811 is diluted with S11.

There is also an error in the paper by Green, Weng, Shang, and Labes[2] regarding pitch contraction caused by PHI in CP-MBBA and CC-MBBA. No pitch contraction can be observed by either the wedge or droplet methods. Further, it was *assumed* that CP forms a left-handed cholesteric in MBBA and CC forms a right-handed cholesteric. This is incorrect--both compounds form left-handed cholesteric phases when interacting with MBBA. The handedness of the phases was determined by two methods: (1) by the color shift method, that is from the direction in which color stripes between disclination lines in a wedge change upon rotation of the lower polarizer of the microscope,[4] and (2) by measuring the pitch changes of the medium caused by doping with known chiral dopants with opposite handedness, such as R 811 and S 811. These results are also consistent with a previous determination of the handedness of these phases by Adams *et al.*[8]

One is left with the question of what causes the domains observed in the fingerprint method which show pitch shortening. Since the fingerprint texture is obviously very sensitive to perturbations, one possible explanation is that the compounds in question are very insoluble and frequently crystallize out in small amounts at defects and at surfaces causing local pitch perturbations. To test whether this assumption might have validity, some experiments were done aimed at detection of any possible surface effect when CP-MBBA is doped with BOOQP. This system was chosen because it exhibited the most marked regimes of fingerprint shortening.[1] In these experiments, the achiral dopant was not dissolved in the CP-MBBA matrix, but was deposited onto the surface of slides already treated with the homeotropic aligning reagent DMOAP prior to preparing the sandwich cell for fingerprint texture observation. The slides were dipped momentarily into a 3 wt% solution of BOOQP in toluene and then dried in a nitrogen stream. This procedure resulted in noticeable shortening of the fingerprint distances measured immediately after sample preparation. For example, a pitch of 135 μm in a reference sample was shortened to 115 μm in this manner. However the shortening of the pitch was not uniform. It varied from region to region, and after 12 hours relaxation, the difference had decreased substantially. These data add credence to the conclusion that a surface interaction due to the presence of poorly soluble achiral solutes in chiral matrices might account for the apparent pitch contraction observed by the fingerprint method.

CONCLUSION

It is apparent from this reinvestigation that there is as yet no convincing evidence for induced conformational effects when achiral solutes are dissolved in cholesteric solvents.

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