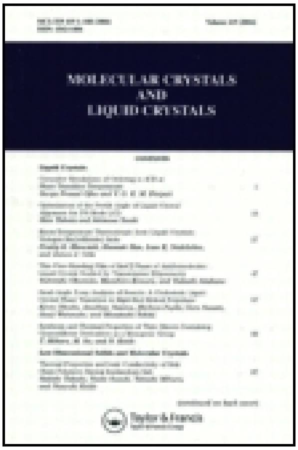

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CHOLESTERIC PITCH AND BLUE PHASES IN A CHIRAL-RACEMIC MIXTURE

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ABSTRACT

The cholesteric and "blue" phases (BP) of a mixture of the chiral and racemic forms of the same compound were studied as a function of composition and temperature. It was found that the clearing point and the cholesteric-S_A transition temperature was independent of composition. The pitch of the cholesteric at a given temperature was inversely proportional to the fraction of chiral material, as was the lattice parameter of BPII. The lattice parameter of BPI did not follow the above rule. No second-order BPI-BPIIb transition was seen.

It is concluded that this mixture is thermodynamically ideal(6,7) in that the intermolecular interactions between two molecules are independent of their relative chirality. Thus, this system comes close to the theorist's ideal of one in which only the chirality is varied.

I. INTRODUCTION

It is a common observation that the "blue" phases (BP) exist only for cholesteric materials of pitch < 5000Å. Further, as the pitch is increased by the addition of a nematogen, it is found that BPII (the higher-temperature BP) is supplanted by BPI, which at the larger pitches is the only BP(1). There have been several theories concerning the nature of the BP's, some of which make predictions about the phase diagram as a function of chirality(2,3). However, it is difficult to connect these theories with existing data on mixtures because the addition of a nematogen to the cholesterogen changes the mixture's elastic constants and thermodynamic properties, and induces phase separation and compositional segregation. In this paper we report on an investigation of a chiral-racemic mixture. This mixture is found to exhibit minimal phase separation. Evidence will be presented that the system's thermodynamic properties don't change as the chirality is altered by addition of the racemic mixture.

II. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

The compound used was terepthaloyloxy-bis-4-(2'-methylbutyl) benzoate, prepared in both (—) and racemic forms. The materials were synthesized from either S(−)-2-methylbutan-1-ol (Fluka) or a racemic mixture of 2-methylbutan-1-ol by standard methods which retained the optically active center or totally racemized the system. The final products were purified by column chromatography on silica gel (80-200 mesh, 3x30cm.) and repeated crystallization from ethanol until their transition temperatures were constant. Their purity was checked by thin-layer chromatography and HPLC, and the structures elucidated by IR spectroscopy. Even though the two products were made by different methods, their transition temperatures (iso-(BP or nematic), (cholesteric or nematic)-S_A, and S_A to S_C) agree with each other to within two degrees.

Samples were made between clean glass slides and coverslips. ACM-72, followed by rubbing was sometimes used to secure (100) orientation of BPII, so that its symmetry could be confirmed as sc$^{(4)}$. The sample was kept in a Mettler FP5/52 hotstage.

The microscope was set up for both transmission and reflection modes, both with crossed polarizers. Switching between modes was accomplished by turning off the light source used for the undesired mode. The light for the reflection mode was provided by a monochromator whose output slit was imaged by the microscope onto the sample, thus providing a gradient of wavelength across the field of view. The reflection mode was used for measurements of the reflection wavelengths of cholesteric and "blue" phases, whereas the identification of phases and detection of phase transitions was done in transmission mode. The boundary between one-phase regions was taken to be the temperature at which two phases coexisted in equilibrium. The width of this region was generally very small. Since the cholesteric phase grew, shrank, and nucleated very slowly, the BP-chol. boundary had to be found by a slightly different method than the other coexistence lines. The cholesteric phase was nucleated in the BP by cooling the sample to a temperature a degree below the BP region. Then, the sample was brought up to a trial temperature in the region of the BP-chol. boundary and watched for at least ten minutes. Any growth or shrinkage of the cholesteric was taken as a sign that the trial temperature was too low or too high, respectively. The temperature was changed in the appropriate direction, and the process repeated. The BP-cholesteric transition was taken to be the center of the region over which no change in the size of the cholesteric region could be seen.

Wavelengths of Bragg reflections were measured by using the microscope in reflection mode, and finding the wavelength at which the brightest, most uniform platelets reflected the most light. Since this test was done using the eye for a detector, the wavelength range was limited. Fortunately, the BP usually exhibited two reflections, related by a wavelength ratio of $\sqrt{2}$, so it was possible to use the second reflection when the lowest-order one went into the infra-red range. When both wavelengths could be measured, their ratio was $\sqrt{2}$ to within the measurement error (2%). In all cases where it is known that the second reflection was used, the measured wavelength has been multiplied by $\sqrt{2}$ to convert it to an equivalent wavelength for the first reflection. For the cholesteric phase, and BP platelets showing well-defined Darwin bands, the wavelength was taken to be that of the band's center. Pitches too long to be measured optically were measured using a Cano wedge of 2 cm. radius and a filar micrometer. The index of refraction of the sample was found by comparing the Bragg wavelength of a sample with its layer spacing as found using the wedge. Wedge-derived values of pitch have been converted to Bragg wavelengths using the measured index of 1.45.

III. PHASES

The phase diagram for this system is shown in Fig. 1.
Since there was some irreproducibility (amounting to 1-2°C) in the transition temperature due to chemical degradation in the oven and differences of sample placement, all temperatures are plotted as differences from the clearing point. The actual clearing points averaged 160.95°C, with no systematic trends with composition. The two-phase regions were always much narrower than the one-phase areas, and they could not be reliably mapped. Thus, Fig. 1 shows only boundaries between single-phase regions, with the inevitable topology of peritectic and eutectic points suppressed.

The "fog" phase appeared as a bluish or greenish-gray cloud with optical rotation but no discernible structure. These properties are in agreement with those previously reported for the "fog" phase$^{(5)}$, hence the labeling on the phase diagram. The phase labeled "BPII" often came out of the isotropic or fog in the form of rounded squares displaying the longest wavelength for that phase. The square platelets showed a Bragg reflection along the observation axis provided their reflection wavelength was in the visible range. The appearance of this phase changes continuously with composition and wavelength over the whole region labeled "BPII". Again, the above properties are consistent with those previously reported for BPII$^{(4)}$, hence the label. Finally, BPI is identified as the phase to which BPII transformed on cooling, if it didn't turn cholesteric. Typical "cross-hatch" patterns are seen at the II-I transition. BPIIb$^{(1)}$ is not shown on this diagram because no break in the wavelength-temperature curves were seen except at the I-II transition. This point will be discussed more fully below.

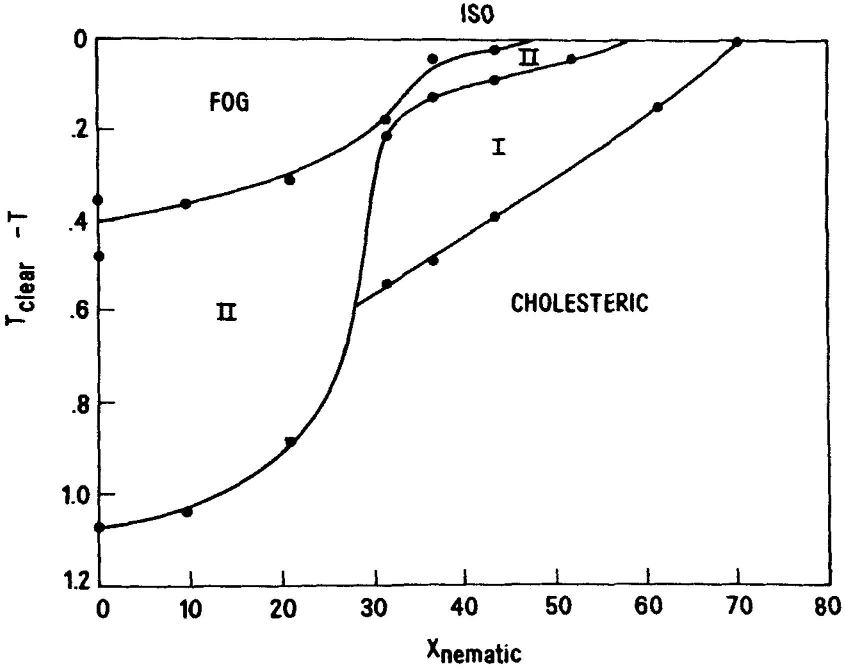

Fig. 1. Phase diagram for the chiral-racemic mixture. Ordinate is T-(clearing point). Abscissa is mol. fraction of chiral material.

IV. WAVELENGTH VS. TEMPERATURE AND COMPOSITION

The wavelength vs. temperature curves for various compositions are plotted in Figs. 2 and 3. The temperature origins of all curves have been adjusted for a clearing point of 160.95° as explained above. Fig. 2a shows the data for the cholesteric, and Fig. 2b for the BP's.

In Fig. 3 the same data is plotted, with all wavelengths multiplied by the chiral fraction.

This scaling should bring all the curves together if there is such a thing as a "chirality" which is proportional to the chiral fraction. It is clear that to within experimental error, the cholesteric pitch is indeed inversely proportional to the chiral fraction. Note the sharp increase in the pitch at lower temperatures due to the incipient Ch-S_A transition.

The data for BPII also show scaling except for the small BPII region in the 47.9% chiral sample. However, if one multiplies the data for this sample by $\sqrt{2}$,

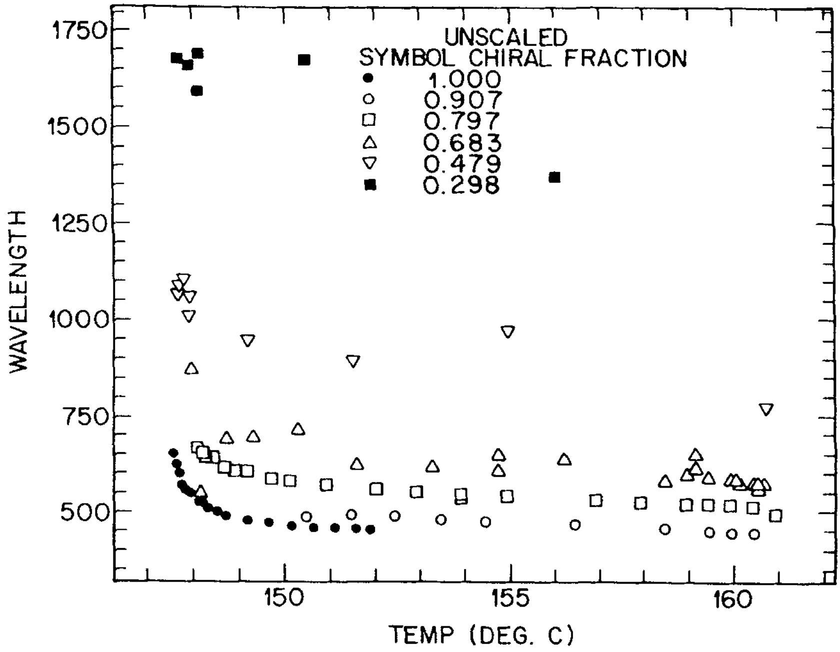

Fig. 2a. Bragg wavelength for the cholesteric phase as a function of temperature for various compositions. The numeric labels denote the fraction of chiral compound.

the numbers become consistent with those for the other compositions. The reflection which yielded these data are thus identified as the (110) reflection.

The scaling hypothesis appears to break down for BPI. Note that the ratio of the scaled wavelengths for the two compositions for which there is data in the BPI range is temperature-dependent. Thus, one cannot ascribe the difference in the scaled wavelength to a difference in the indexes of the reflections. Since the BPI wavelengths were comparable to or less than those for BPII, it may be surmised that the BPI was observed in the (200) reflection.

V. CONCLUSIONS

The independence of the clearing and Ch-S_A temperatures on composition

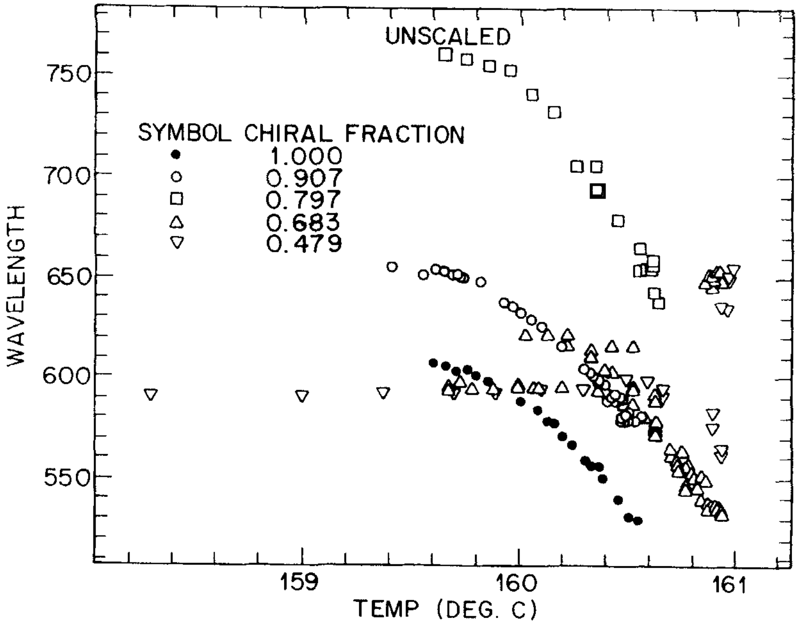

Fig. 2b. Bragg wavelength as a function of temperature for BPI and BPII at various compositions.

indicate that the mixing between (++),(−−), and (+−) forms of the compound used is thermodynamically ideal. In other words the interaction potentials between the various forms of the molecule are identical to each other. This conclusion is supported by the success of the pitch scaling law in the cholesteric phase. Let us assume that the inverse pitch is a linear combination of the numbers of (++), (+−), and (−−) near-neighbor molecular pairs. Clearly, the (++) and (−−) pairs have equal and opposite contributions, and the (+−) pairs don't add anything to the total. Let the sample be made of x moles of (−) material in $1-x$ moles of racemate, which is in turn half (+) and half (−)*. Thus, there are $1+x/2$ moles of (−) and $1-x/2$ moles of (+). If random mixing is assumed, then the inverse pitch which is proportional to the difference between the numbers of (−−) and (++) pairs will thus be proportional to $\frac{1}{4}((1+x)^2-(1-x)^2)$ or x. Thus, the inverse pitch is proportional to the chiral fraction if and only if the twist elastic constant is composition-independent - a tacit assumption of the above calculation, as well as a logical consequence of the equality of molecular interactions between (++) and

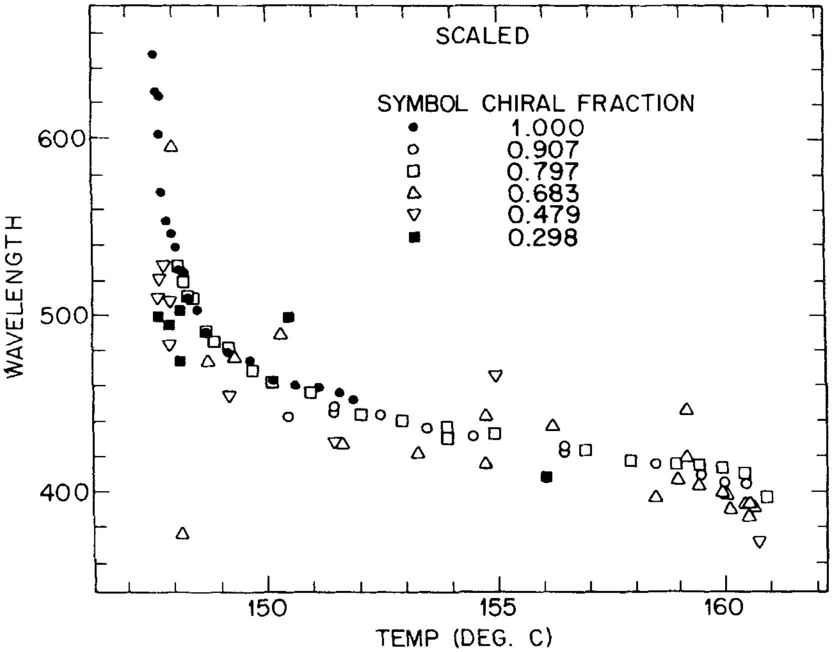

Fig. 3a. Same as Fig. 2a, but with the wavelengths multiplied by the chiral fraction.

(+−) pairs. This system is therefore an ideal one for investigating the influence of chirality on the BP, since all other properties of the system are constant across the phase diagram, and phase separation is not observed.

That scaling works for BPII shows that the ratio of the lattice parameter to the cholesteric pitch is independent of chirality, although it does depend on temperature. However, the BPI lattice parameter is not so simply related to the pitch, indicating that the units of which BPI is made may not be as rigidly defined as those which make up BPII.

None of the BPII wavelength vs. temperature curves show any breaks in slope suggestive of a BPIIb$^{(1)}$ phase. In particular, the compositions for which BPI does not appear also have long BPII ranges over which a second-order transition should be obvious. Thus it is shown that BPIIb is not present in every system.

The phase diagram in Fig. 1 could be considered the "true" temperature-

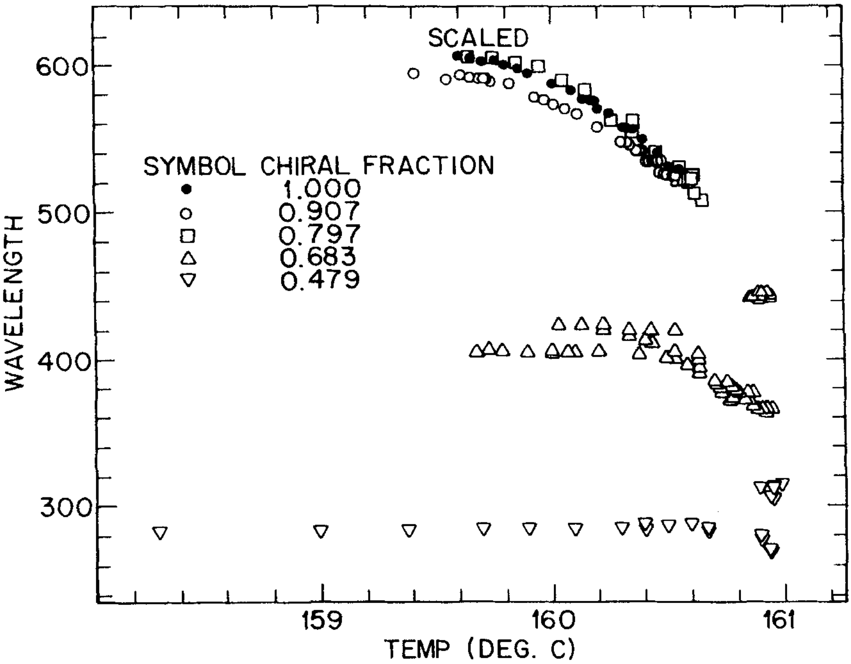

Fig. 3b. Same as Fig. 2b, but with the wavelengths multiplied by the chiral fraction.

chirality phase diagram as might be constructed from a theory, since the elastic constants and thermodynamic properties of the system don't change with chirality. However, this diagram pertains to one point in the K_2/K_1 - K_3/K_1 plane. Perhaps other points in this plane give rise to other topologies.

Acknowledgements

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[*] This material has two chiral centers/molecule, so its racemate is actually 25% (++), 25% (−−), and 50% (+−). For simplicity we ignore the presence of the (+−) species.
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[7] The CB15-6OCB mixture studied by P. Cladis and P. Finn (submitted to Mol. Cryst. Liq. Cryst. Lett.) is apperently ideal in the sense that there is probably no heat of mixing. Also, the inverse pitch is linear with composition. However, the elastic constants may change with composition, although their ratios may not. Therefore, the topology of the phase diagram may also be representative of a theoretical point in $\frac{K_2}{K_1} - \frac{K_3}{K_1}$ space.