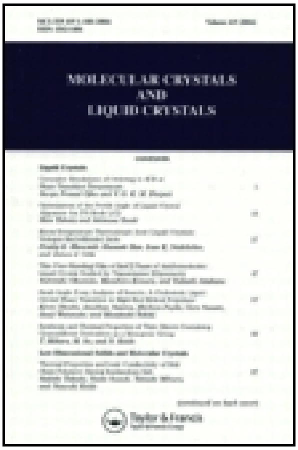

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LIQUID CRYSTAL BLUE PHASE TO ISOTROPIC TRANSITION AND ELECTRIC FIELD RESPONSE

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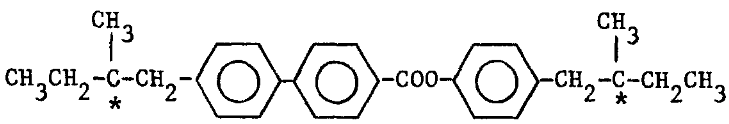
ABSTRACT: The cholesteric liquid crystal 4"-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl-carboxylate has a pronounced blue phase (BP). DSC calorimetry shows 3 peaks in the cholesteric to isotropic transition region. The phases are identified by polarizing microscopy. The BP has two forms which are separated by a first order transition. The isotropic to BP transition appears to be a form of second order transition. An applied electric field induces the transition from BP (1) to the cholesteric focal conic phase.

The cholesteric blue phase (BP) is generally found in short pitch cholesterics. It is typically stable over a temperature range ≃0.5°C prior to the first order transition to the isotropic (I) phase.[1-5] The transition from the phase associated with the focal conic (FC) texture, to the BP is also first order, but extremely weak.[6-9] Two BPs have recently been identified in a narrow temperature interval.[10] NMR, light scattering, viscosity, and optical activity exhibit unusual properties close to the BP transition.[10-13] Its isotropic optical properties suggest that the BP has cubic symmetry, which would require an anharmonic elasticity for stability.[2] An anharmonic theory has been developed.[14] Bragg diffraction experiments at UV or visible wavelengths fit a body centered cubic structure.[15] A theoretical analysis of the isotropic to cholesteric transition indicates three possible cholesteric structures.[16,17] The simplest case being the familiar molecular spiral around a unidirectional axis. Also included are a more complicated conical spiral case and finally a double spiral case.[17]

We report some experimental work on an apparent second order BP-I transition and the response of the BP to an applied electric field. Three cholesteric phases are clearly identified in accordance with the theory.[17]

Figure 1 shows a differential scanning calorimeter (DSC) thermogram of the cholesteric to isotropic transition in 4"-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl-carboxylate as supplied by BDH chemicals under the label CE2, which has the structure.[18]



The cholesteric pitch is very short at 0.1 µm because of the two chiral end groups.[18] The consequent anomalous behavior of the cholesteric-isotropic transition was noted when the compound was first synthesized.[19]

The transitions are identified by polarized light microscopy in the Mettler hot stage. The first peak at 115.9°C is a very weak (0.01 cal/gm) first order transition from a cholesteric FC texture to a form of BP. The blue phase has zero or very weak birefringence and is difficult to detect. A sample between glass slides becomes birefringent when sheared by moving the slides. Under shear, a strong birefringence is induced in the temperature range 115.9-116.9°C. This corresponds to the interval between the first and second peaks in Figure 1. At higher temperatures no observable birefringence can be induced. The hysteresis in the transition temperatures, as shown in Figure 1, is also present in the microscopy.

The main transition, BP-I, peaks at 118.7°C. There is no detectable supercooling of this transition when the machine hysteresis is taken into account. The cusp shape of the transition indicates that this is not a normal first

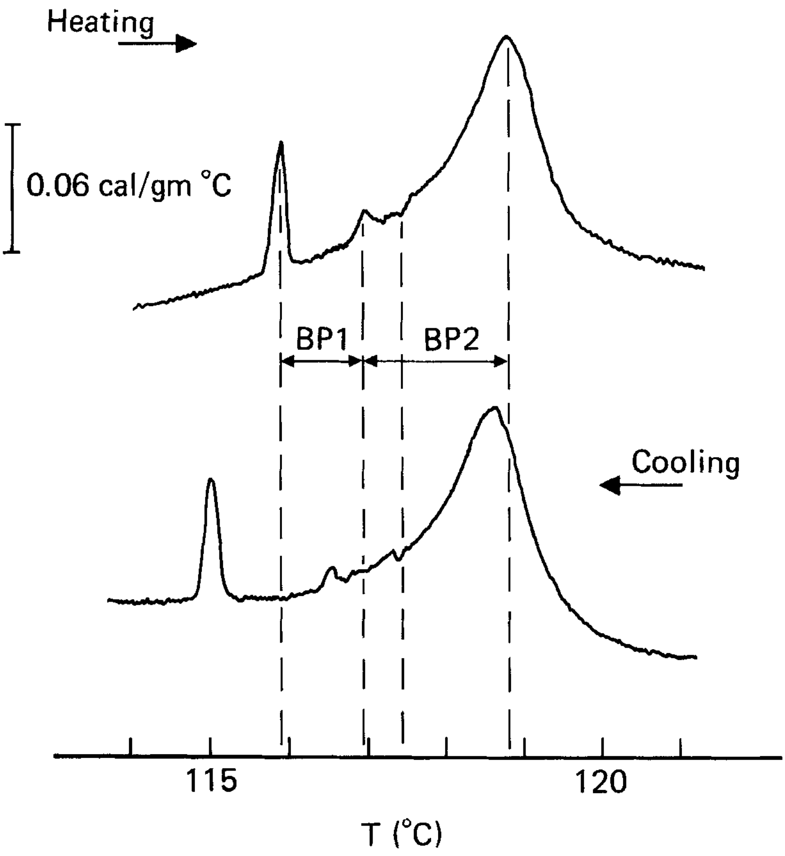


FIGURE 1

Heating and cooling thermograms for CE2 cholesteric to isotropic transition showing blue phases BP1 and BP2. Sample 19.7 mg; DSC 0.62°C/min, 0.1 mC/sec.

order liquid crystal transition. Figure 2 shows the typical form of a cholesteric BP-I transition. In comparison, Figure 1 shows a gradual transition from the isotropic side. Within experimental limit the transition is continuous and thus a form of second order phase transition. However, more precise thermodynamic measurements are required to clarify the situation.

The second peak at 116.9°C indicates a very weak (0.002 cal/gm) first order transition between two blue phases. The higher temperature BP shows no birefringence under shear or electric field.

Broad peaks are found in impure cholesteric to isotropic transitions. However, the very sharp peak at 115.9°C implies high purity. An analysis of the DSC solid melting thermogram indicated a molecular purity greater than 99.9%. The small deflection at 117.4°C was not observed with the sample removed, but since there is no detectable hysteresis in this effect it is most probably instrumental.

Electrooptic experiments were performed using cells formed from indium tin oxide coated glass plates, parallel spaced and sealed at 7 µm with mylar epoxy spacers (Ablestick). An audio frequency voltage of maximum amplitude 280V rms could be applied, while the cell was microscopically observed in the Mettler hot stage.

At temperatures below 115.9°C the sample shows a FC fan texture of violet color in transmitted light between crossed polarizers. An applied voltage changes the color slightly. In the temperature range 115.9-116.3°C the sample could be voltage driven from the optically extinct BP to a FC fan texture of identical appearance and color to that existing below 115.9°C. When the voltage is applied the fan texture appears via a nucleation and growth process. On removal of voltage the growth process reverses and the BP is restored. The voltage required to induce the transition increases with temperature from 100 to 250V rms, limited by electric breakdown. The response is insensitive to frequency in the a.f. range. The dielectric anisotropy ($\Delta\varepsilon$) is not known, but the molecular structure suggests negative $\Delta\varepsilon$. This is consistent with the fan texture voltage response.[20]

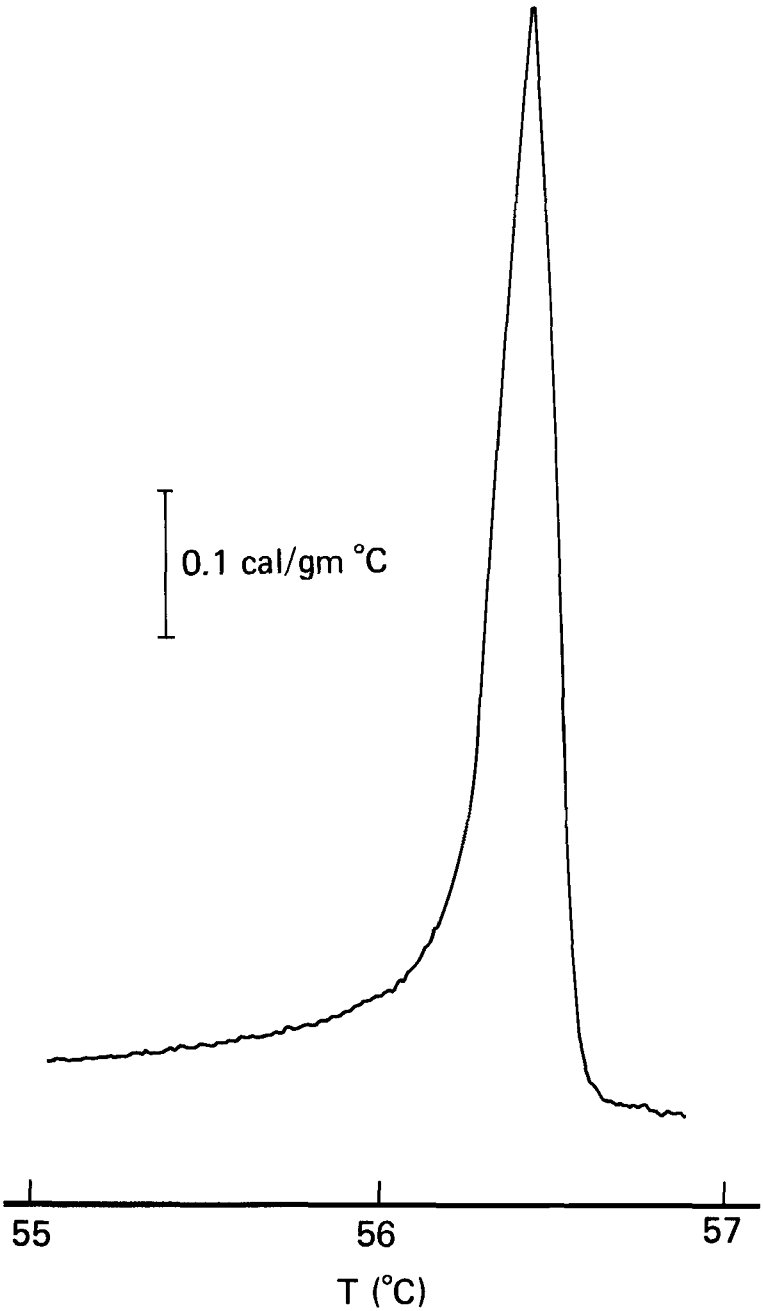
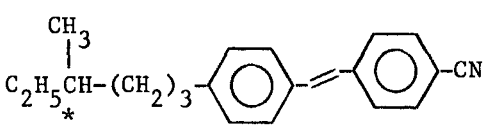


FIGURE 2
Thermogram for 4-alkyl-4'-cyanostilbene cholesteric to isotropic transition. Sample 23.7 mg; DSC 0.31°C/min, 0.1 mC/sec.

An ordinary (unidirectional spiral axis) cholesteric can be unwound by an applied electric field $E=(K/\varepsilon_0\Delta\varepsilon)^{1/2}\pi^2/P$, where K is an elastic constant, P is the pitch length and $\Delta\varepsilon$ is positive.[20] As is well known, the ordinary cholesteric orients the unidirectional twist axis parallel to the field when $\Delta\varepsilon$ is negative. The BP involves more than one twist direction, which implies that it can be partially unwound into a single twist, ordinary cholesteric, for negative $\Delta\varepsilon$. This might also be the case if $\Delta\varepsilon$ were positive, since in this case the initial response of an ordinary cholesteric is to orient the axis perpendicular to the field, but with increasing field the pitch unwinds, hence optical extinction. However, an important distinction between $-\Delta\varepsilon$ and $+\Delta\varepsilon$ is apparent; in the former the spiral axis is voltage driven to one dimension, while in the latter case the axis adopts two dimensions in a plane perpendicular to the field, before unwinding completely.

The elastic constant K always decreases with increasing temperature, which would imply that the pitch is decreasing since the critical field rises. However, a description of the BP requires higher order elastic constants, which may increase in magnitude with temperature.[2,14]

The thermogram shown in Figure 2 refers to chiral 4-alkyl-4'-cyanostilbene.[21]



This compound has a narrow BP region of 0.2°C which shows a platelet texture.[5] The thermogram shows no discernable peak at the BP transition. The reflected color changes from green to red with increasing temperature, implying Bragg reflection via a pitch length ≃0.4 μm assuming a refractive index ≃1.5.

The $\Delta\varepsilon$ is not known, but the molecular structure implies a large $+\Delta\varepsilon$. This allows the pitch to be unwound before electric breakdown. An electrooptic sample with ITO electrodes separated 40 μm gave the data presented in

Figure 3. This shows the voltage required to unwind the cholesteric twist as a function of temperature difference (ΔT) from the transition point. The falling elastic constant and increasing pitch agree with the decrease of critical field with temperature.

The BP platelet texture in the region 0-0.2°C, disappears with increasing voltage, then slowly reforms when the voltage is removed. In the unwound state the sample is extinct between crossed polarizers. For $\Delta T > 0.2$°C the FC texture dominates, but the platelet texture can be induced and stabilized by an applied voltage. The voltage is raised to unwind the pitch, then reduced slightly or the temperature is lowered and the platelet texture is seen to grow. The voltage induced platelet texture extends over a range $\Delta T \simeq 1$°C.

The supercooled BP, which is extinct between crossed polarizers, can be voltage driven into the FC state, further increase of voltage unwinds the pitch giving extinction again. Experimentally the critical field is not well defined. Once initiated, an unwound region will spread. A high $+\Delta\varepsilon$ confers a nonuniform electric field which is always higher in the unwound regions. The well-known hysteresis in cholesteric to nematic field driven transition is present here.[20] The experimental difficulties are compounded by a photochemical instability in the material.[21] Any subtlety in the temperature-voltage relation is masked by the above effects. However, it appears that the critical field decreases continuously without sudden changes in slope or discontinuities as the BP is approached.

The platelet dimensions are ≃20 μm and have red, green or blue colors typical of interference behavior. However, as is well known, rotating the sample has no effect on the color,[5] implying that the color is determined by rotary dispersion. The platelets may exist in a narrow region close to the surface and be stabilized by surface interaction. In this case the field induced platelet texture may be a mere removal of the FC texture, allowing the platelets to be seen. However, we note that the platelets are seen on both parallel or perpendicular aligning surfaces.

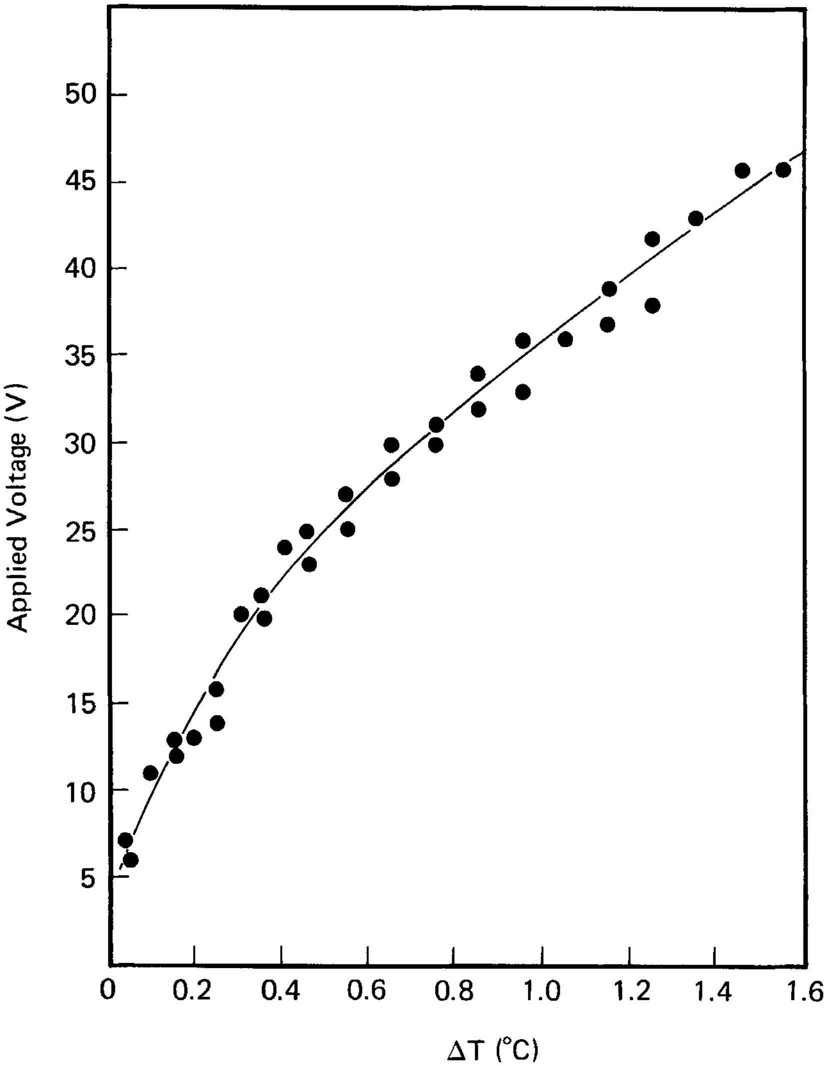


FIGURE 3

Voltage to unwind cholesteric pitch of 4-alkyl-4'-cyanostilbene as a function of the temperature difference ΔT from the isotropic point. Electrode spacing 40 μm.

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