

Blue Phases in Liquid Crystals

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The blue phases are a set of thermodynamically distinct phases that occur between the helical phase and isotropic phase of highly chiral liquid crystals. They display many striking properties, brought about by a defect lattice in their structure. In this essay, I briefly introduce liquid crystals, describe some of the properties of the blue phases, look at the theory of blue phases while avoiding mathematical details, and then describe a few of the important experiments which have helped define the blue phases and reveal their structure.

Introduction

The blue phases are a set of mesophases which occur in the temperature range between the helical phase and isotropic phase of highly chiral, thermotropic liquid crystals (Kitzerow [1]). In order to understand the properties of the blue phases, a short introduction to liquid crystals and chirality is first necessary.

The phase of a thermotropic liquid crystal is temperature dependent. As temperature is varied, the conditions on the translational and orientational order of the constituent molecules which produce the most energetically favorable system may also change. The thermotropic phases of a non-chiral liquid crystal are classified as either smectic or nematic.

Smectic phases “possess one-dimensional positional order” (Seideman [4]). Molecules arrange in layers to create a stratified structure, and there is often some sort of orientational order of the molecules within each layer. Nematic phases possess long-range orientational order, but the constituent molecules do not have long-range translational order (Seideman [4]). While the molecules in the nematic phase of a liquid crystal align parallel to one another, they are positionally disordered.

The nematic phases of liquid crystals occur at higher temperatures than the smectic phases, and when the temperature is increased even further, the liquid eventually becomes isotropic. When a liquid crystal is chiral, a chiral nematic phase, often called the helical phase, replaces the ordinary nematic phase, and new, distinct phases (the blue phases) may appear within a temperature range between the helical and isotropic phases.

A chiral object “cannot be transformed into [its] mirror image by rotations or translations” (Kitzerow [1]). A hand is an example of a chiral object. A chiral molecule and the molecule that is its mirror image are called enantiomers, (Kitzerow [1]) and when a substance is composed of a pair of enantiomers in equal amounts, it is called a “racemic” mixture. A liquid crystal is considered chiral if the molecules that compose it are chiral, and if the mixture is not racemic (Wright [3]).

Liquid crystals composed of non-chiral constituent molecules, racemic mixtures, or weakly chiral mixtures (one enantiomer exists in a slightly higher concentration than the other in the liquid), will transition from the nematic phase to the isotropic phase directly. Highly chiral liquid crystals, on the other hand, may exhibit one or more blue phases (BP) as they are heated from the helical phase to the isotropic phase. In order of increasing temperature, the blue phases are called BPI, BPII and BPIII. The different phases of chiral and non-chiral liquid crystals in the range of interest are shown in Figure 1.

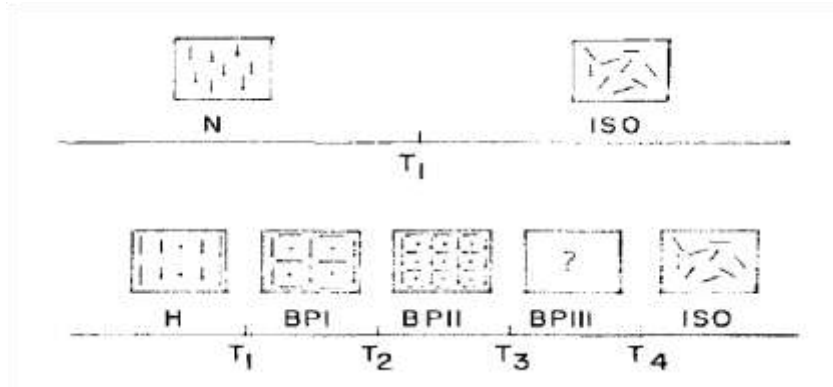


Figure 1. The phases of non-chiral (top) and highly chiral (bottom) liquid crystals slightly below, and including, the isotropic phase. Non-chiral liquid crystals transition straight from a nematic phase to the isotropic phase. Highly chiral liquid crystals have a helical phase and up to three blue phases at temperatures just below the isotropic phase. This chart was taken from Crooker [9].

The helical phase is associated with a pitch. Molecules are oriented uniformly in planes perpendicular to a pitch axis, but along the pitch axis, molecules are rotated with respect to one another (Figure 2). The orientation of the molecules may be described by a unit vector, $\mathbf{n}(\mathbf{r})$, called the director. A director $\mathbf{n}(\mathbf{r})$, may be used to describe the orientation of molecules in other phases of liquid crystals, such as the blue phases, as well. Due to the mirror symmetry of a plane perpendicular to the pitch axis, the directors $\mathbf{n}(\mathbf{r})$, and $-\mathbf{n}(\mathbf{r})$ are considered equal (Wright [3]). The pitch of the helical phase can therefore be defined as twice the smallest distance between planes with the same director. The relationship between the pitch of the helical phase and the chirality of the liquid crystal is given by $q = 2\pi/P$, where q is the chirality and P is the pitch (Wright [3]). The pitch of the helical phase is often used in describing the blue phases. Because the helical pitch would hardly vary across the small temperature range of the blue phases, the pitch of the blue phases can be taken to mean the pitch of the helical phase immediately before the helical-blue transition.

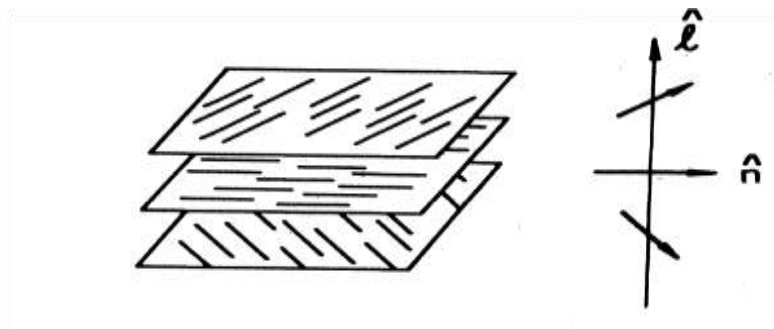


Figure 2. The helical phase. The pitch axis points upward, and the director is shown in three planes perpendicular to the pitch axis. This diagram was taken from Wright [3].

The Blue Phases

The blue phases were first observed by Reinitzer in 1888 as he cooled cholesterol benzoate. He described a “bright blue-violet colour phenomenon” which quickly appeared and disappeared over a small temperature range (Seideman [4]). However, it was not until the work of Armitage and Price in 1975 that the blue phases were shown to be stable, distinct, thermodynamic phases of liquid crystals.

The blue phases occur within a small temperature range at the boundary of the helical and isotropic phases of a highly chiral liquid crystal. BPI and BPII are known to have cubic symmetry, whereas BPIII has the same symmetry as the isotropic phase. More specifically, BPI is body-centered cubic and BPII is simple cubic (Kitzerow [1]). These symmetries are not associated with positionally ordered molecules at lattice sites; the blue phases are liquid phases, and their molecules do not have positional order. Instead, the lattice is a lattice of line defects, brought about by the orientational order of the molecules and the inability of the molecular ordering which creates a local energy minimum to be expanded globally. This will be discussed further in the theory section of this essay. The lattice constant is on the order of the pitch, which is usually in the range of the wavelength of visible light. A sample of BPI or BPII, therefore, may display a mosaic of colors. Different colored “platelets” within the mosaic correspond to “randomly oriented domains of crystalline blue phase ordering” (Wright [3]). Figure 3 shows such a mosaic.

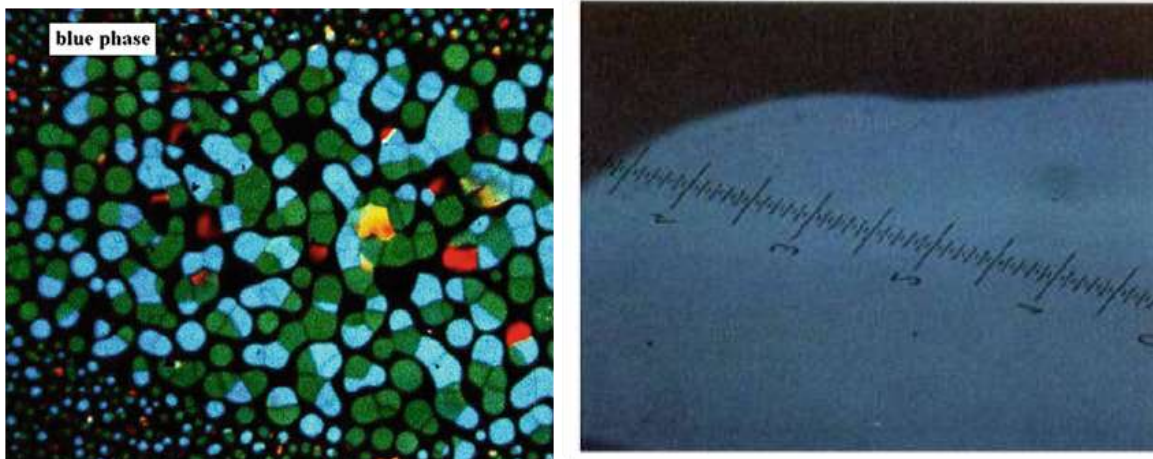


Figure 3. Left: BPI platelets. Image from Blinov [10]. Right: BPIII, the fog phase. Image from Crooker [9].

In initial observations, such as Reinitzer’s, the blue phases were observed to reflect blue light, hence they were named the “blue phases”. BPIII, in contrast to BPI and BPII, appears foggy (Figure 3) and is often referred to as the “fog phase” (Kitzerow [1]).

The blue phases have a number of additional interesting properties. For example, while blue phases are liquid phases, they exhibit a non-zero elastic shear modulus. While the magnitude of the elastic shear modulus is quite small, (about 10^6 times smaller than that of a conventional solid) it is still surprising that a liquid can resist static shears at all (Wright [3]). In addition, the blue phases possess a much higher viscosity than either the helical or isotropic phase. Their viscosity has been found to be on the order of 10^6 times larger than the viscosity of their corresponding helical phases (Wright [3]). In both cases, it is likely that the crystalline ordering of the blue phases is responsible for giving these liquids properties which one usually associates with solids.

Theory

Landau theory for the blue phases uses a traceless, symmetric tensor Q as an order parameter. This tensor is the anisotropic part of the dielectric tensor. The free energy is given in Kitzerow [1] by

$$F = \frac{1}{2} \int [aQ^2 + c(\nabla Q)^2 - d(\nabla \times Q) \cdot Q - \beta Q^3 + \gamma Q^4] d^3r$$

If one were to remove the gradient term and cross product term from this equation, a minimization of the free energy would simply give the nematic-isotropic phase transition of non-chiral liquid crystals. However, when the gradient term and cross product term are included in the equation, the minimization of the free energy quickly becomes complicated. The cubic structure of the blue phases and the lack of mirror symmetry of their constituent molecules force us to include these two terms (Kitzerow [1]). It has been shown from Landau theory that a cubic structure for BPI and BPII achieve a lower free energy than the helical phase structure at temperatures just below the isotropic phase.

To conceptually consider the problem of what sort of structure the molecules of the liquid crystal blue phases take, one can begin by considering the uniaxial, “single-twist” structure of the helical phase, as is done in Kitzerow [1]. The interaction energy of two chiral molecules is minimized when the two molecules are at a slight angle to one another. This is evident from the orientation of the molecules in the helical phase. However, in the helical phase, molecules are only at slight angles to one another along the pitch axis. Therefore, it should be possible to reduce the local interaction energy of neighboring molecules further by allowing the orientations of the molecules to twist in a second dimension, producing a biaxial helix. This configuration is also referred to as a “double-twist tube,” and an example of a double-twist is shown for clarification in Figure 4.

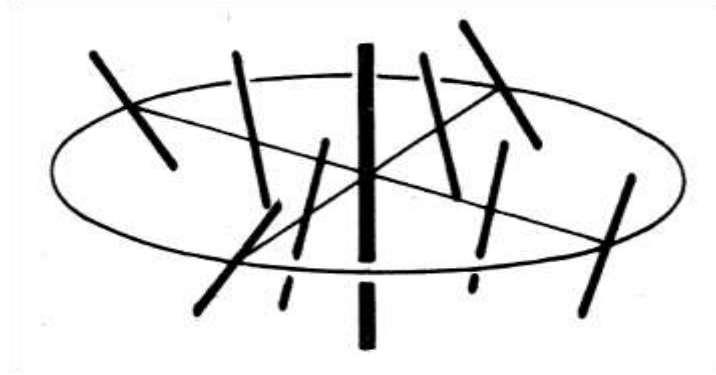


Figure 4. Double-twist. The molecules are twisted with respect to one another in two dimensions, compared to one dimensional twist in the helical phase. Taken from (Wright [3]).

The size of a double-twist tube that will produce a locally favorable energetic structure is limited. As the local twist is increased, the tube becomes strained and distorted (Kitzerow [1]), and the double-twist structure is no longer favorable over the single-twist structure of the helical phase, so we can't have simply one large double-twist tube as the structure of a blue phase. Instead, the liquid crystal consists of many of these double-twist tubes, arranged in a lattice that corresponds with the known cubic symmetry of the blue phases. But it is impossible to extend such a lattice in three dimensions. The directors associated with one double-twist tube cannot always line up with the directors of neighboring double-twist tubes. The only way this problem can be resolved is by adding a lattice of line-defects to the structure. As it turns out, this system, which can be thought of as either a lattice of double-twist tubes or a lattice of line-defects, is still energetically favorable in the temperature range of BPI and BPII. The idea of this sort of lattice was first proposed by Meiboom [8] et. al., who mathematically showed that such a system was energetically favorable.

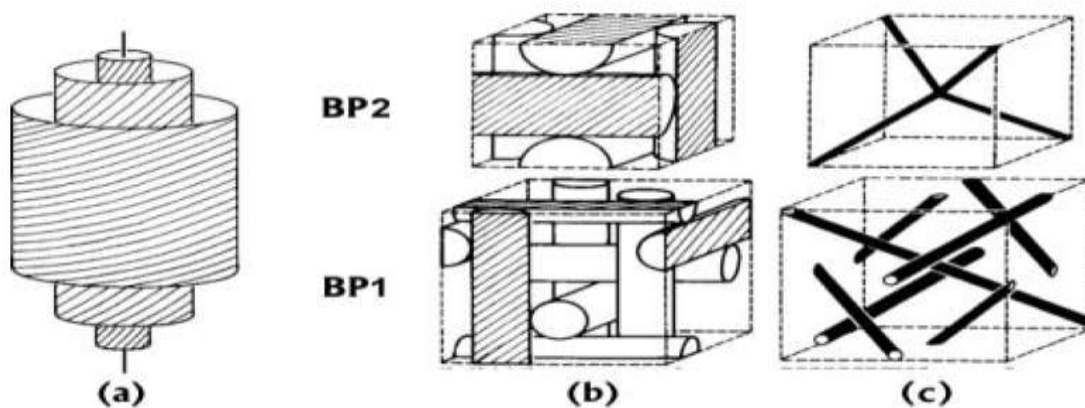


Figure 5. (a): Double twist-tube. (b): Double-twist tubes arranged a unit cell. (c): corresponding line defects in a unit cell. Taken from (Kitzerow [2]).

Experiment

The first experiment which proved that the blue phases are distinct, thermodynamic phases of highly chiral liquid crystals was performed by Armitage and Price in 1975. They measured the density of a liquid crystal as a function of temperature and found a discontinuity in the density measurement at the temperature of the helical phase-blue phase boundary. Their experimental setup and results are shown in Figure 6.

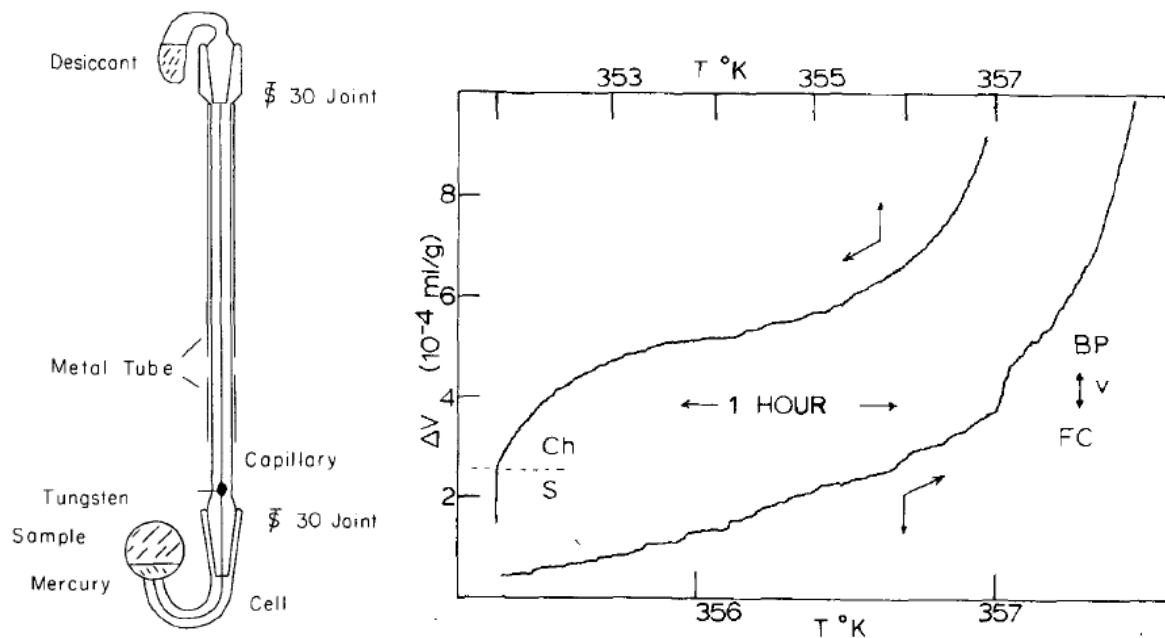


Figure 6. Left: Experimental Setup: A mercury capillary dilatometer. Right: Plot of density vs. temperature. The lower curve was obtained while increasing temperature and corresponds to the temperature scale on the bottom of the graph. The discontinuity in density is shown by the arrow slightly above 357K. These images were taken from Armitage [6,7].

Armitage and Price used a mercury capillary dilatometer to measure the density of a highly chiral liquid crystal as a function of temperature. The liquid crystal sample was sealed above the mercury, in the bulb at the bottom of the dilatometer. The bulb was placed in an oil bath, which was slowly heated. As the sample was heated, its volume changed, and this change in volume forced the mercury up the capillary tube (Armitage [7]). Armitage and Price measured the height of the mercury as a function of temperature, and from this data were able to obtain the density vs. temperature plot shown in Figure 6. Their data shows a discontinuity in the density as the liquid crystal transitioned from the helical phase to BPI (Armitage [7]). This discontinuity is indicative of a thermodynamically distinct blue phase.

Measurements of heat capacity of liquid crystals as a function of temperature performed by Thoen have been described as some of the most compelling early evidence that the three blue phases are in fact thermally distinct phases of chiral liquid crystals (Kitzerow [1]). Thoen applied a constant heating power to a sample of cholesteryl nonanoate, heating the sample from the helical phase to the isotropic phase. The experimental setup was such that heat leaks from the sample were negligible compared to the heat input. Thoen carefully measured the temperature as a function of time and used numerical differentiation to obtain the rate of change in temperature as a function of temperature. From this, Thoen plotted the heat capacity (total heating power divided by rate of change in temperature) per mole as a function of temperature. His results are shown in Figure 7.

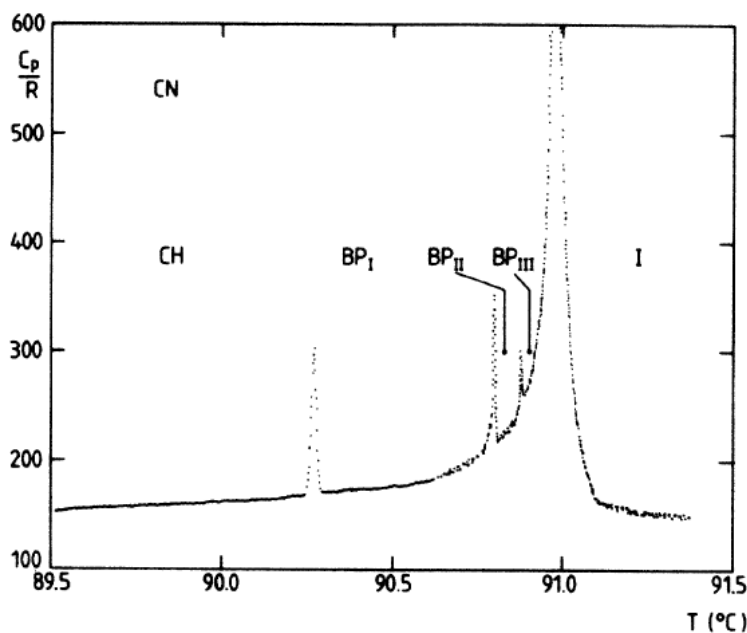


Figure 7. Reduced heat capacity per mole as a function of temperature for cholesterol nonanoate. The Helical phase (CH), BPI, BPII, BPIII and the isotropic phase (I) are clearly distinguished. Plot taken from Thoen [5].

Thoen's data clearly shows the existence of three separate phases between the helical and isotropic phases of a highly chiral liquid crystal. The blue phases shown here span a temperature range slightly less than 1°C as expected. Additionally, by showing the existence of latent heats, Thoen was able to verify that all the transitions associated with the blue phases are of first-order (Thoen [5]).

While these two experiments proved that the blue phases were thermodynamically distinct, they did not provide information on the structure of the blue phases. The initial experimental work done to determine the structure of the blue phases was performed through Bragg scattering experiments. An example of Bragg scattering data is shown in Figure 8. The

peaks in selectively reflected light corresponded to cubic lattices in BPI and BPII, but researchers found it difficult to use Bragg scattering techniques to determine whether the phases contained body-centered cubic symmetry or simple cubic symmetry [9].

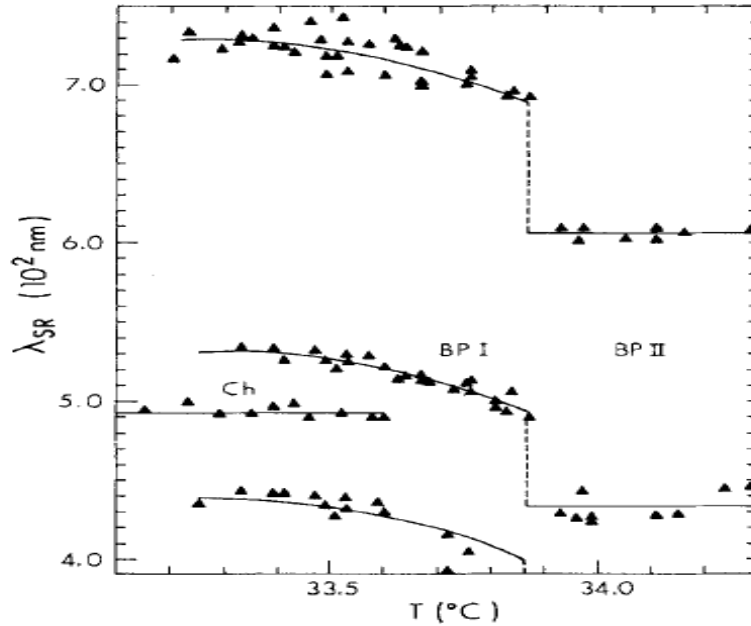


Figure 8. Selective reflection wavelengths versus temperature for a chiral liquid crystal. Plot taken from Crooker [9].

To distinguish the particular type of cubic symmetries of BPI and BPII, researchers (Onusseit and Stegemeyer for BPII, and Marcus for BPI and BPII) grew large, defect-free crystals and inferred the blue phase symmetries from the single-crystal symmetries (Wright [3]). These single-crystals were some of the most compelling evidence for the body-centered cubic structure of BPI and the simple cubic structure of BPII. A few examples of single crystals are shown in Figure 9.

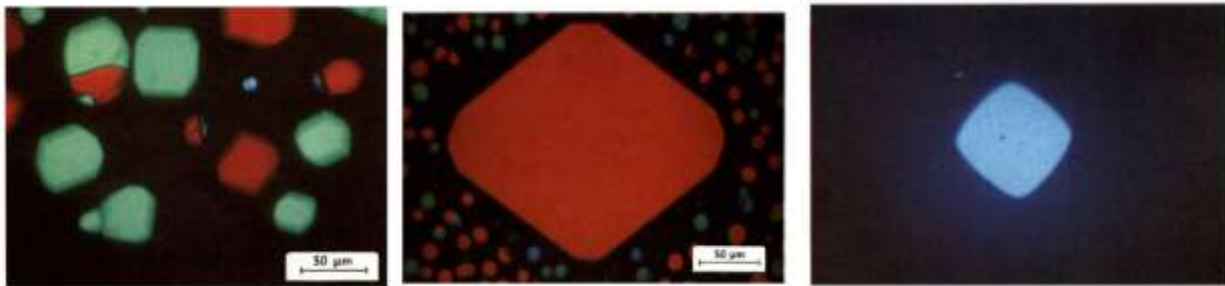


Figure 9: Three images of single crystals. The left and center are in BPI. The right is in BPII. Images were taken from Stegemeyer [11].

Discussion

Although it took about 100 years for any significant research to be performed on blue phases after Reinitzer's discovery in 1888, BPI and BPII are now well understood. There is still, however, a great amount of uncertainty concerning the structure of BPIII. BPI, BPII and BPIII are not actually the only blue phases. Additional blue phases can arise when the liquid crystals are put in electric fields. Information on these additional blue phases can be found in many pieces of literature (Wright [3], Kitzerow [1]).

It is quite surprising that the attempts of molecules to orient themselves at slight angles to their neighboring molecules can result in a complicated lattice of double-twist tubes and a corresponding lattice of line defects, which in turn give the blue phases unique optical properties and some physical properties rarely associated with liquids. But it is precisely these unique properties which make blue phases so fascinating and interesting to research.

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