

What was observed by Julius Planer in 1861?

L. Lisetski

Institute for Scintillation Materials, STC "Institute for Single Crystals" of the National Academy of Sciences of Ukraine, Kharkiv 61001, Ukraine

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In 1861 Julius Planer published a paper in which he described his observations of selective light reflection in monotropic cholesteric liquid crystal phase of cholesteryl chloride that he synthesized. We repeat his experiments and report in modern interpretation what indeed was observed by Planer at that time.

Key words: *cholesteryl chloride, monotropic cholesteric liquid crystal phase*

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Julius Planer studied cholesteryl chloride, a substance that, according to modern data obtained by differential scanning calorimetry (DSC) and polarization microscopy, has a melting point at approximately 95–96°C; when the formed isotropic liquid is cooled, at approximately 65–67°C (data from various sources differ within 1°C, which is a normal situation for mesogenic substances), it undergoes phase transition from isotropic liquid to cholesteric liquid crystal phase [1]. The cholesteric phase of cholesteryl chloride is monotropic, i. e., it can be observed only upon cooling. Under further cooling, the cholesteric phase is converted into a crystalline solid. Upon heating of the formed crystals, their crystalline state persists until ~96°C, when they melt to the isotropic liquid state.

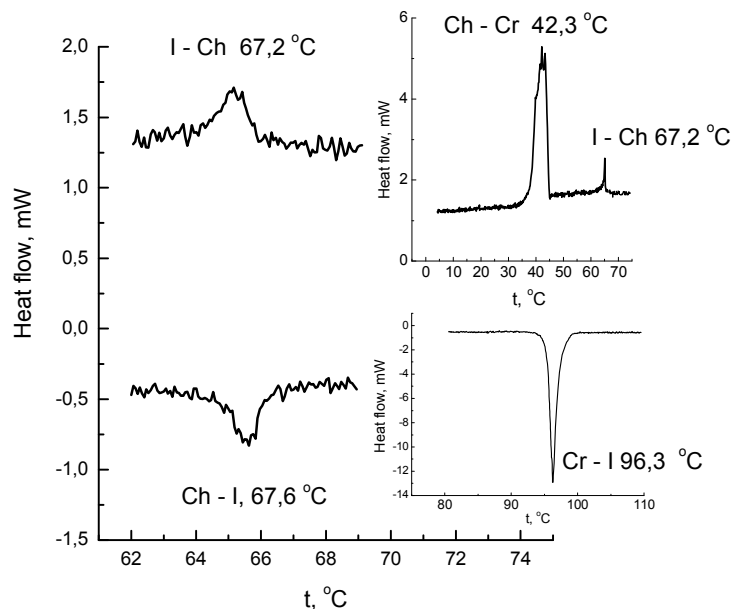


Figure 1. DSC data on the phase transitions of cholesteryl chloride. Cr-I: crystal to isotropic (melting); I-Ch: isotropic to cholesteric (cooling); Ch-I: cholesteric to isotropic (heating); Ch-Cr: crystallization of the supercooled cholesteric phase.

Our DSC results (Mettler TA 3000, Switzerland) are shown in figure 1. On cooling from the isotropic melt, a cholesteric phase is formed at approximately 67°C. Upon further cooling, the cholesteric phase persists until approximately 42°C, when crystallization occurs. If we resume heating while still remaining in the cholesteric phase, we see the cholesteric-isotropic transition at a temperature slightly higher than on cooling. In subsequent cycles of cooling and heating, isotropic-cholesteric and cholesteric-isotropic transitions are reversible if we do not cool down the sample to about approximately 42°C; then, one should heat the sample up to approximately 96°C to get the crystalline substance melted.

A natural property of a cholesteric phase is helical twisting of the orientationally ordered chiral molecules. The cholesteric helix is characterized by its helical pitch p value. The incident light falling onto the cholesteric helix is divided into two circularly polarized waves - the right-hand and left-hand ones. The wave of the same handedness as the cholesteric helix propagates (nearly) freely, and the wave of the opposite handedness is (nearly) fully reflected. In the case of normal incidence, the wavelength of maximum selective reflection λ_{\max} is related to the helical pitch by a simple formula $\lambda_{\max} = np$, where n is the average refractivity index. In textbooks and review papers, the phenomenon of selective reflection is often considered as the one similar to Bragg diffraction (X-rays scattered on angstrom distances in a crystal lattice, and visible light similarly scattered at the helix period distances). In several theoretical papers, however, selective optical properties of cholesterics were directly derived starting from Maxwell equations and helically changing dielectric tensor. By a certain will of Providence, helical pitch values in cholesterics based on cholesterol derivatives (cholesterol esters as well as cholesteryl halides, including cholesteryl chloride) fall into the range ensuring λ_{\max} in the visible range (or rather close to it, in near UV or near IR ranges).

A readily observed manifestation of λ_{\max} in the visible range is a bright color of a cholesteric liquid crystal. This color is best seen when the cholesteric has a so-called planar texture, i. e., the helical axis is normal to the boundary surfaces. The optimum geometry for observation (and spectral measurements) of selective reflection is realized when a thin layer of the cholesteric liquid crystal is placed between two parallel substrates. The bottom surface is usually made non-reflecting (black) for better visual observation (selective reflection), and the top surface is transparent (glass). When both boundary surfaces are transparent (glasses), selective transmission spectra can be easily

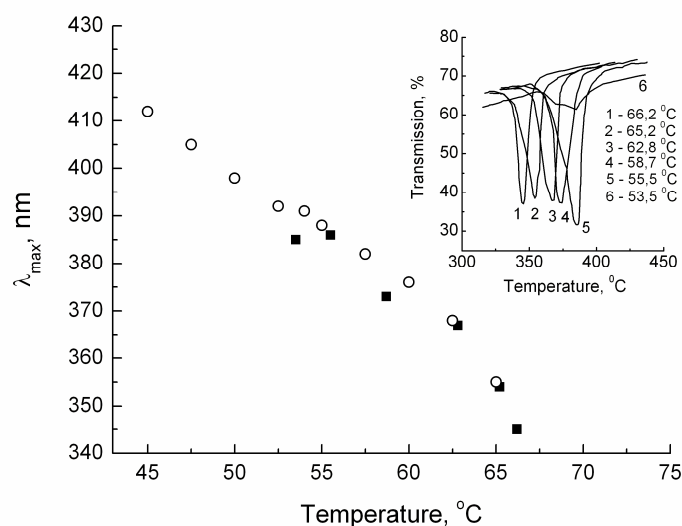


Figure 2. Wavelength of selective reflection maximum λ_{\max} as function of temperature. Solid squares: data of our measurements. Open circles: data taken from [2]. The insert shows the actually measured selective reflection spectra at several temperatures.

measured by a spectrophotometer. Both at selective reflection and at selective transmission, the measured λ_{\max} values are the same and are determined by the helical pitch (the value of n only slightly varies with temperature and cholesteric substance, and is assumed as $n = 1.5$ in most papers). It should be noted that the observed color can depend upon the observation angle.

A sufficiently good planar texture is formed when the upper glass is just slightly moved in horizontal direction over the cholesteric mixture. (More elaborate procedures include application of a thin polyvinyl alcohol film upon the glass, rubbing it in one direction with soft tissue and introducing the cholesteric mixture between the two glasses by capillary forces). However, if one simply takes a brush or spatula and applies the viscous cholesteric mixture upon a substrate, the texture formed is often sufficiently good to observe bright colors.

Selective reflection spectra of cholesteryl chloride in the monotropic cholesteric phase were measured in [2], as well as in our laboratory. The measured λ_{\max} values were approximately 400 nm, slightly increasing at lower temperatures. A visual observation shows a dark-blue or violet color, with signs of green appearing, probably due to non-uniform cooling of the sample.

Results of our measurements of selective reflection spectra in the cholesteric phase of cholesteryl chloride are shown in figure 2 (Hitachi 330 spectrophotometer, cell thickness of 10 μm). The spectra are narrow (approximately 10-20 nm wide, similar to typical cholesterol ester mixtures, which corresponds to low birefringence of cholesteryl chloride as non-aromatic mesogenic substance). In this set of measurements, selective reflection spectra were noticeably broadened on approaching approximately 53°C, when crystallization occurred. With thicker cells (30–50 μm), a further supercooling of the monotropic cholesteric phase (down to approximately 45°C) was possible (as it was observed in [2]).

Taking the above considerations into account, one can easily “decipher” the Planer’s paper [3], “translating” it into modern terms. It is absolutely certain that Planer observed the selective reflection from a planar texture of the monotropic cholesteric liquid crystalline phase of cholesteryl chloride. Of course, he could never guess that he, in fact, observed a novel state of matter – the liquid crystal state. For him, it was just a peculiar feature of a peculiar substance, without any attempts of generalizing. It should be noted that Friedrich Reinitzer, the “official” discoverer of liquid crystals, knew about this paper by Julius Planer. In fact, it is included into the list of references in his paper [4] officially known as the first publication on liquid crystals.

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Що спостерігав Юліус Планер у 1861 році?

Л. Лисецький

Інститут сцинтиляційних матеріалів НТК "Інститут монокристалів" НАН України,
Харків 61001, Україна

У 1861 р. Юліус Планер опублікував статтю, в якій він описав свої спостереження селективного відбивання світла в монотропній холестеричній фазі синтезованого ним холестерилхлориду. Ми повторили його експерименти і повідомляємо в сучасній інтерпретації, що в дійсності спостерігав Планер у той час.

Ключові слова: *хлорид холестерилу, монотропна холестерична рідкокристалічна фаза*