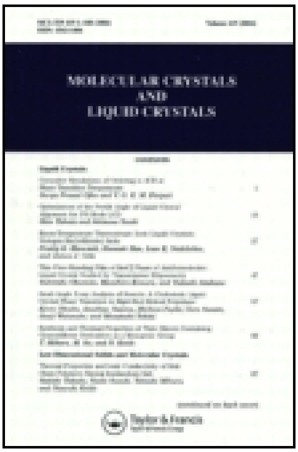

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Optical Studies on Grandjean Planes in Cholesteric Liquid Crystals

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Abstract—Optical investigations were performed to prove the idea of variable pitch in the Grandjean structure of cholesteric liquid crystals. According to this model, the helical structure is deformed in such a manner that with decreasing thickness of the wedge-shaped layer the pitch of the screw decreases, while the number of turns remains constant. At the next "step", however, the pitch gets large again and the number of turns decreases by a half. From measurements on the Grandjean structure with several derivatives of cholesterol, the values of the pitch are determined as a function of temperature and found to be in good agreement with values obtained from the wavelength at maximum reflection. This is considered as a confirmation of the model used, in particular of the assumption that the gap width is essentially equal to an integer multiple of the half pitch and the number of turns changes by one half at the optically observed discontinuities.

Cholesteric liquid crystals that are confined to a wedge-shaped space show a series of bright stripes. This periodic structure is especially well developed if the two boundary surfaces consist of mica or of glass that has been rubbed in a definite direction. The stripes follow the lines of equal thickness. An individual stripe has a sharp boundary line at the side of the wedge opening. Starting from this line in the direction of the wedge top, the colour of the reflected light changes to shorter wavelengths.

This phenomenon was described first by Grandjean[1] in 1921. Starting from the fact that the stripes are identical with the lines of equal thickness, Grandjean has given the following interpretation: In the structure of the cholesteric liquid crystal there are distinguished parallel planes, the so-called Grandjean planes. The observed system of equidistant lines arises from the intersection of the boundary surface with these planes.

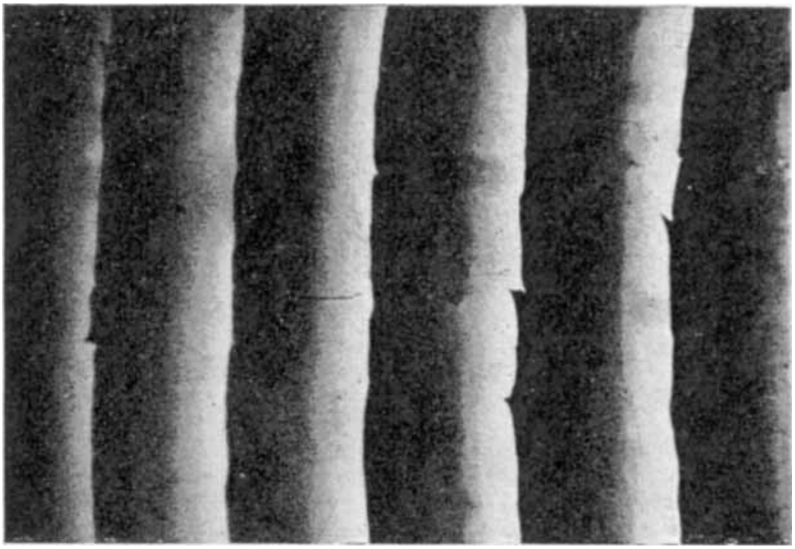

Figure 1. Microphotograph of a Grandjean structure in a cholesteric liquid crystal between two glass plates in incident white light with crossed Nicols (magnification 30 ×). The distance of the plates decreases from left to right. Within one stripe the colour changes from red to yellow (in the black and white representation of Fig. 1 from dark to bright).

However, this model is not able to explain all the optical properties of cholesteric liquid crystals. Cano[2] has given a simple consideration that shows that the explanation given by Grandjean leads to severe difficulties: there is no reason why only the superior or only the inferior boundary surface should make intersection lines with the Grandjean planes and therefore two systems of lines are to be expected. But in all cases only one system has been observed. This is such a serious objection to the hypothesis of Grandjean that one must conclude that the planes cannot exist at all.

Indeed, de Vries[3] succeeded in explaining the optical properties of cholesteric liquid crystals without the assumption of any distinguished planes. According to this theory, there is a maximum in the reflected intensity if $\lambda_0 = p \cdot \bar{n}$, where p stands for the pitch of the helix structure and $\bar{n}$ is an average refractive index. At the end of his fundamental paper, de Vries gives a short suggestion of the manner in which the Grandjean structure can be explained without the existence of the Grandjean planes. He suggests periodic disturbances in the screwlike structure that are caused by the boundary surfaces.

These ideas have been pursued extensively by Cano[2] in a recent paper. According to Cano, the Grandjean stripes arise in the following manner: By their surface structure, the two boundary walls prescribe the orientation of the molecules. Therefore the undisturbed helix structure with pitch p cannot be developed in general.

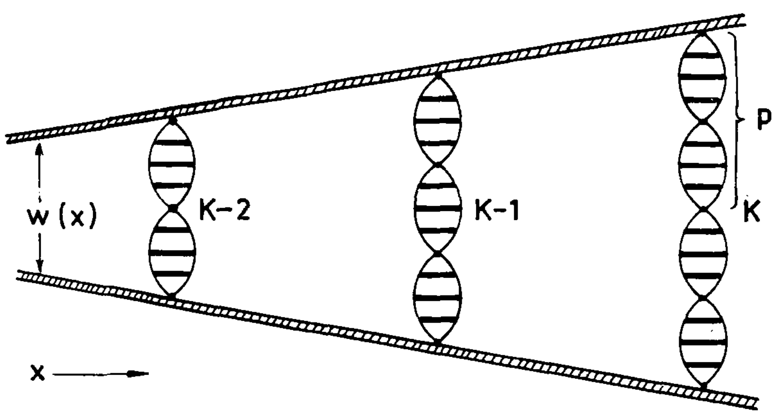

Figure 2. Cross section of the wedge showing the basic assumption that the gap width is equal to an integer multiple of the half pitch.

In Fig. 2 we see a cross section through a part of the wedge. The molecules are drawn in the form of cigars. For simplicity, we assume here the preferred orientations at the upper and lower surfaces to be equal and perpendicular to the drawing plane. Therefore we see only the heads or ends of the molecules at these points. The ends of the molecules are connected by a curve in order to obtain a better view. The development of the undisturbed helix structure is possible only at those points, where the gap width w is equal to an integer multiple of the half pitch:

$$w = k \cdot \frac{p}{2} \qquad k = \text{integer}$$

In Fig. 2 the integer k is equal to 4. We have to take the half pitch, because we assume that a turn of a molecule by π leads to an equivalent orientation, while the pitch must correspond to a full turn by 2π. Of course, the points with undisturbed pitch lie at lines of equal thickness.

Between these lines the helical structure is deformed. With decreasing gap width the pitch of the screw decreases, while the number of turns stays constant. Because of the relation $\lambda_0 = p \cdot \bar{n}$, the wavelength of the reflected light decreases also. At the next " step " however, the pitch again gets larger and the number of turns decreases by a half.

A schematic representation of this conception is given in Fig. 3a. Only those molecules are drawn that have their long axes in or perpendicular to the drawing plane. This figure shows that in the middle of the layer there are singularities with respect to the orientation, whereas at the two surfaces there are no discontinuities at all. The singularities lie on lines perpendicular to the drawing plane.

It is possible to suggest also another model of the Grandjean structure that is schematically represented in Fig. 3b. The colour of the reflected light depends on the angle between the helix axis and the direction of observation. The wavelength gets shorter if this angle increases. If we now assume that the axis of the helix inclines more and more with decreasing gap width, the observed change of colour within a Grandjean stripe can be explained and the boundary condition can be met with a constant pitch p_0. At the next Grandjean line, the helix jumps back in the vertical

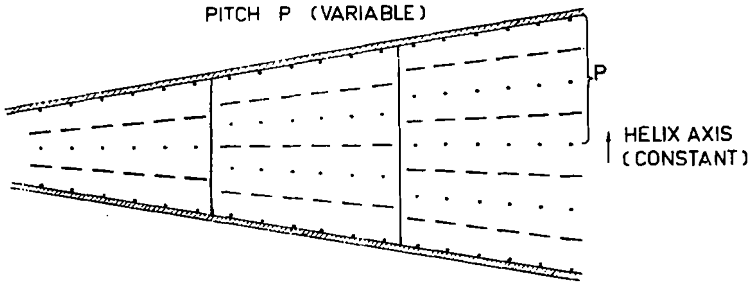

Figure 3a. Model of variable pitch with constant helix axis.

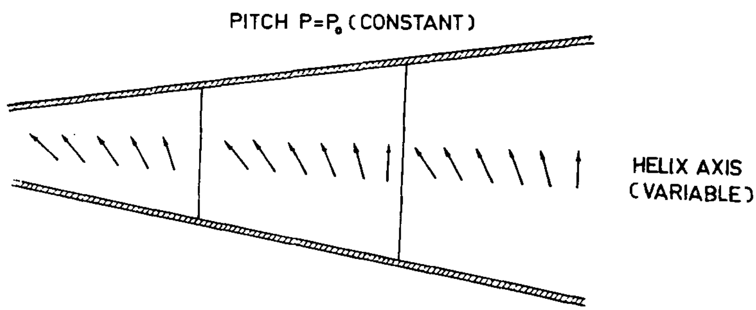

Figure 3b. Model of variable helix axis with constant pitch.

direction, whereas the number of turns in the screw structure decreases by a half.

Now it is easy to test this model by a simple experiment (Fig. 4). We call the angle of incidence and of reflection Θ and the angle between the Grandjean stripes and the plane of incidence ϕ. Then the colour of reflection should depend on the angle ϕ with constant angle Θ. We have performed this experiment with the result that there is no dependence on the angle ϕ. With that we have shown that the interpretation of the Grandjean structure by means of inclined helix axes is not possible. On the other hand, the assumption of variable pitch fits well all experimental observations. Therefore we adopt this hypothesis.

Our optical investigations on Grandjean structures had the aim to determine the value of the pitch of the helix structure and its dependence on temperature. For this purpose we prepared thin layers between freshly cleaved mica or rubbed glass plates. The Grandjean structure was observed through a microscope and photographed. On the photograph, the distance between the Grandjean lines was measured. We did not fill the wedge-shaped

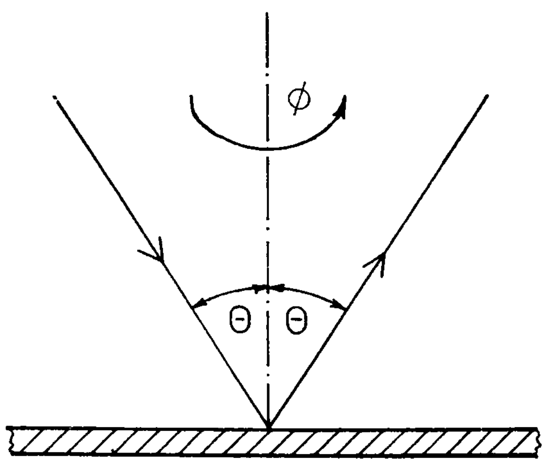

Figure 4. Angles in the experiment to test the model of variable helix axis.

gap completely with substance. In the free space there were interference lines by means of which we were able to determine the angle of the wedge.

The pitch p is given by

$$p = 2\,a \sin \alpha,$$

where α is the wedge angle and a the distance between two Grandjean lines. The measurements were made at different temperatures.

There is still another method to measure the pitch of the helix.

Since

$$p = \frac{\lambda_0}{\bar{n}}$$

p can be calculated from the wavelength at maximum reflection, when the refractive index $\bar{n}$ is known. In the de Vries theory, $\bar{n}$ is a special average value but for our purpose it is sufficiently exact to measure $\bar{n}$ in the ordinary manner with a refractometer. This has been done. The maximum reflection was determined by a spectral photometer.

Measurements were made with several derivatives of cholesterol: cholesteryl proprionate, cholesteryl n-valerate, a mixture of cholesteryl nonanoate and chloride, and pure cholesteryl nonanoate. The results are graphically represented in Fig. 5 to Fig. 8. The crosses are from measurements of the Grandjean structure. The circles represent the values obtained from the reflection maximum. The agreement between the two measurements is good. In some cases there is a systematic deviation of about 5%.

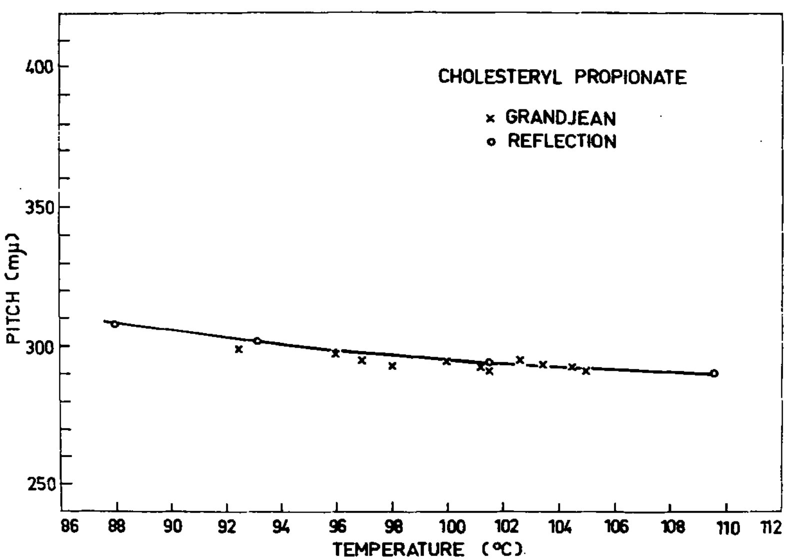

Figure 5. Pitch of the helix as a function of temperature for cholesteryl propionate.

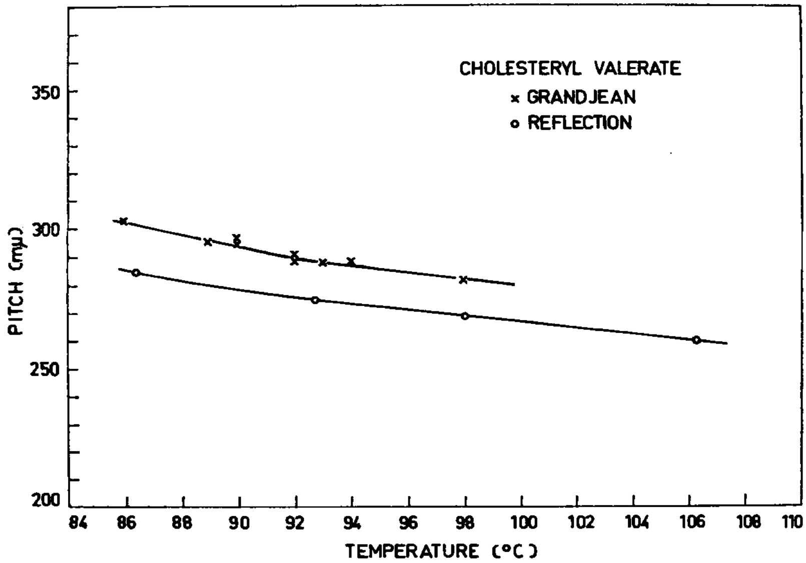

Figure 6. Pitch of the helix as a function of temperature for cholesteryl *n*-valerate.

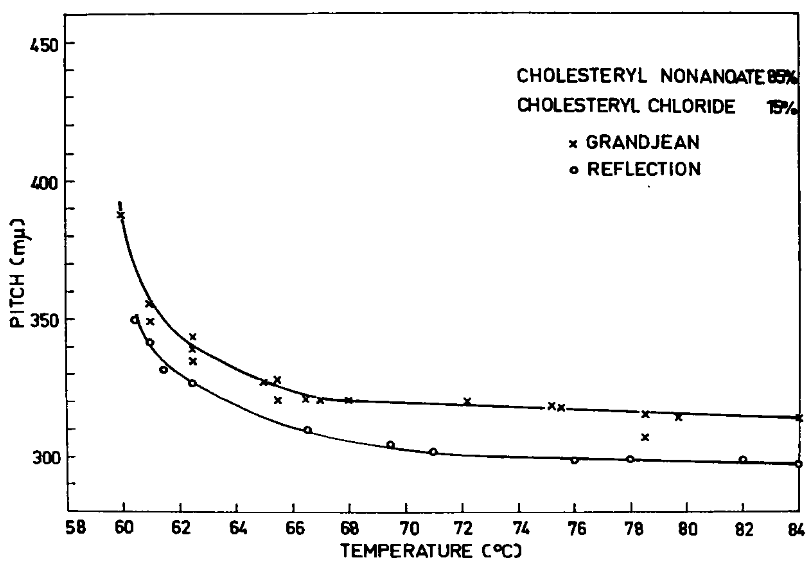

Figure 7. Pitch of the helix as a function of temperature for a mixture of cholesteryl nonanoate and cholesteryl chloride.

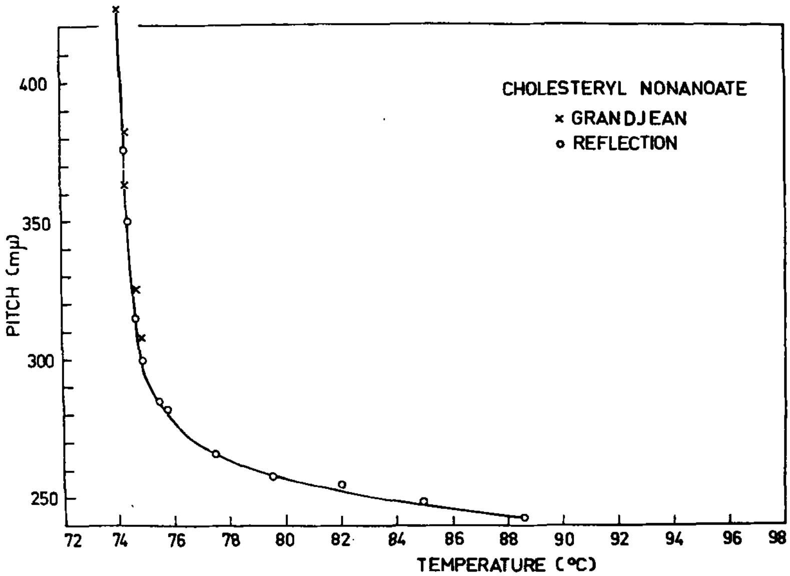

Figure 8. Pitch of the helix as a function of temperature for cholesteryl nonanoate.

This is due to the error in the determination of the extremely small wedge angle. The wavelength of maximum reflection as a function of temperature has already been measured by Fergason[4] for cholesteryl nonanoate. Because of the very steep slope of the curve it is hard to compare with our values. Even a small difference in the purity of the material will cause a large deviation. However, a shift of only 0.6 °C in the temperature scale is sufficient to let our values coincide with those of Fergason in the whole range.

The values of the pitch with cholesteryl nonanoate rise very rapidly at low temperatures. This is very interesting. We must remember that the substance has a transition point at about 74 °C. Below this temperature, the substance is in the smectic phase. In this phase there is no more a helix structure. Now we see from our measurements, that the screw begins to untwist a few degrees above the transition point. In this manner the different structure of the smectic phase is being prepared already in the cholesteric phase.

There is also another point of interest. We have used two ways to determine the pitch p that are completely independent. The first one started from the relation

$$w = k \cdot \frac{p}{2} \qquad w = \text{gap width}$$

and led to the formula

$$p = 2a \cdot \sin \alpha \qquad \begin{array}{l} a = \text{distance between two Grandjean lines} \\ \alpha = \text{wedge angle} \end{array}$$

whereas the second one used the relation

$$p = \frac{\lambda_0}{\bar{n}}$$

We think that it is one of our most important results to have verified the relation that the gap width must be an integer multiple of $p/2$ and not of p itself. As yet, there has been a certain confusion about this point in the literature. As the result of our measurements we can say that a turn of a molecule by π around the helic axis leads to an equivalent orientation.

Acknowledgment

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REFERENCES

1. Grandjean, F., *C. R. Acad. Sci.* **172**, 71 (1921).
2. Cano, R., *Bull. Soc. Franc. Mineral. Crist.* **91**, 20 (1968).
3. De Vries, Hl., *Acta Cryst.* **4**, 219 (1951).
4. Fergason, J. L., *Mol. Cryst.* **1**, 293 (1966).