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## OPTICAL PROPERTIES OF A TWISTED SMECTIC C

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**Résumé.** — Un mélange de *bis*-(4'-*n*-décyloxybenzal) 2-chloro-1-4-phénylènediamine (D. O. B. C. P.) et 5 % de cinnamate de cholestérol se comporte optiquement comme un cristal liquide cholestérique. Le pouvoir rotatoire et le pas ont été mesurés. La théorie de de Vries écrite pour les cholestériques peut être appliquée, mais l'accord entre les valeurs expérimentales et les valeurs théoriques est moins bon dans la phase smectique chirale. Il est préférable probablement d'utiliser les indices de la couche du smectique C chiral plutôt que les indices du smectique C non chiral.

**Abstract.** — A mixture of *bis*-(4'-*n*-decyloxybenzal) 2-chloro-1-4-phenylenediamine (D. O. B. C. P.) and 5 % of cholesteryl cinnamate behaves optically in a way similar to cholesteric liquid crystals. Rotatory power and pitch have been measured. De Vries' theory written for the cholesteric phase can be applied, but agreement between experimental and theoretical values is less good for the twisted smectic C phase. It is necessary to know refractive indices of the chiral smectic C layer and to use these indices rather than refractive indices of the non chiral smectic C.

It is possible to twist a smectic C by adding a cholesteric liquid crystal. For this purpose we used *bis*-(4'-*n*-decyloxybenzal) 2-chloro-1-4-phenylenediamine (D. O. B. C. P.) smectic C from 66 °C to 112 °C, nematic from 112 °C to 165 °C and 5 % of cholesteryl cinnamate. D. O. B. C. P. was first prepared by S. L. Arora, J.-L. Ferguson and A. Saupe [1]. Such a mixture is a twisted smectic C or a chiral smectic C,  $S_C^*$ , from 66 °C to 103 °C and a twisted nematic,  $N^*$ , from 103 °C to 170 °C. W. Helfrich and S. Oh Chan have also mixed D. O. B. C. P. with an optically active smectic C, but they did not study optical properties of this mixture [2]. Moreover, some chiral smectics C have been studied by W. Urbach and J. Billard [3].

**1. Smectic textures.** — First, it is necessary to define two possible textures and indicate how they are obtained.

*a)* We shall call planar the texture of a smectic in which layers are parallel to the boundary surface of the glass.

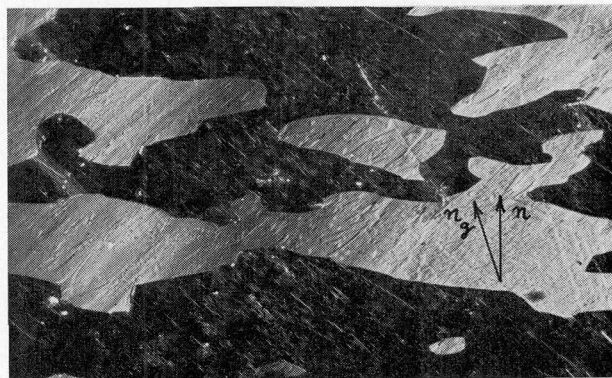
For a smectic A, molecules are then normal to the surface: In parallel light propagating normally to the surface, between crossed polarizers, there is extinction.

For a smectic C molecules are tilted with respect to the surface: In parallel light propagating normally to the surface, between crossed polarizers, there is extinction four times during a complete rotation and brightness between.

In convergent light, an interference figure of a biaxial crystal is observed [4]. Such a texture is obtained by dipping glasses in a solution of cetyltrimethyl-ammo-

onium bromide (C. T. A. B.) in chloroform [5], or, for a smectic C, by rubbing glass slides. For D. O. B. C. P., molecules are at an angle of about 45° with respect to the layers [6, 7].

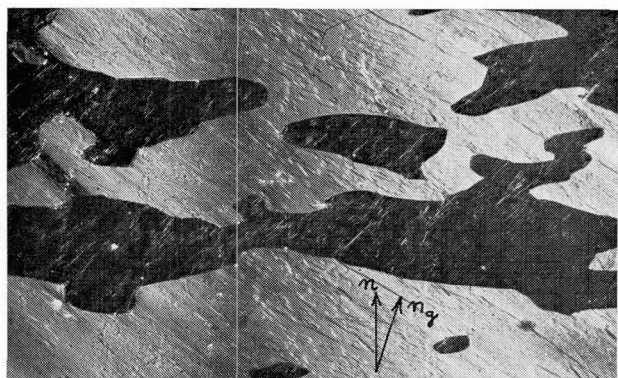
*b)* We shall denote a texture with molecules parallel to the surface (or *ear* texture, as G. Durand called it [8]) a texture in which molecules are anchored on the surface of a glass (\*). In that case the smectic layers are normal to the surface, and for a smectic C, whose molecules are tilted of  $\theta$  with respect to the layers, these make an angle  $\pm \theta$  with the director parallel to the direction prescribed by the treatment of the boundary



SLIDE 1. — Extinction for some domains when the director makes an angle  $+ \alpha$  with the vibration's direction of the polarizer.

(\*) For a nematic, when molecules are parallel to the boundary surface, the texture is called a planar texture. It is a very different situation for a smectic.

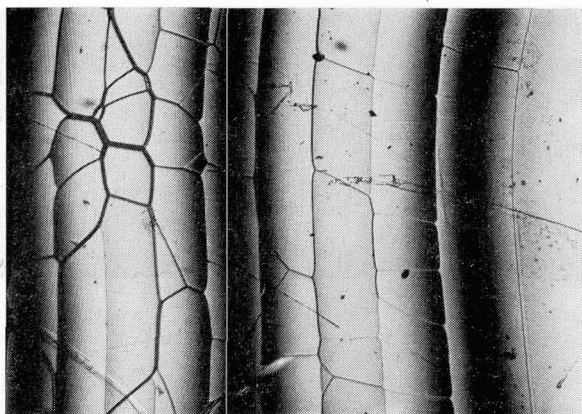
surfaces [9]. For a smectic C, such a texture has been obtained between surfaces coated by silicon monoxide [10]. We have to report that, for smectics C, the director and the high refractive index,  $n_g$ , are not always parallel. Consequently, if  $\alpha$  is the two directions' angle, between crossed polarizers, there is extinction for some domains when the director make an angle  $+\alpha$  with the vibration's direction of polarizer or analyser and for others domains when  $-\alpha$  (slides 1 and 2 for D. O. B. C. P.  $\alpha = 4^\circ$ ).



SLIDE 2. — Extinction for other domains when the director makes an angle  $-\alpha$ .

**2. Optical properties of a twisted smectic C.** — The studied mixture is optically active with negative rotatory power. A monodomain of twisted smectic C in planar texture, between a glass plate and a cylindrical lens, shows rotatory power fringes. Specific rotatory power has been measured for the sodium wavelength as a function of temperature (Fig. 1). It is decreasing, but more rapidly in the twisted nematic phase than in the twisted smectic C phase, with a weak jump at the transition temperature.

To know the pitch of this helicoidal structure, first we can measure the cholesteric pitch by Grandjean-Cano's planes between coated glass plate and cylindrical lens. This pitch varies from  $3.3 \mu$  at  $103^\circ\text{C}$  to  $2.7 \mu$  at  $165^\circ\text{C}$ . But such a sample in the chiral smectic C phase presents a very different texture as we shall see later. Between rubbed surfaces, Grandjean's



SLIDE 3. — Grandjean's discontinuities in a wedge shaped mica for the twisted nematic phase.

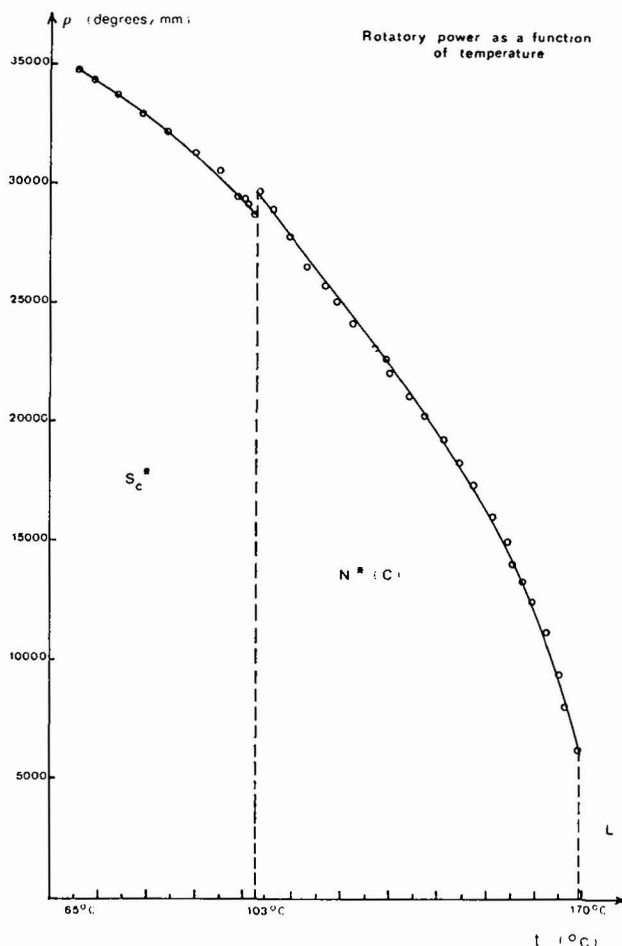
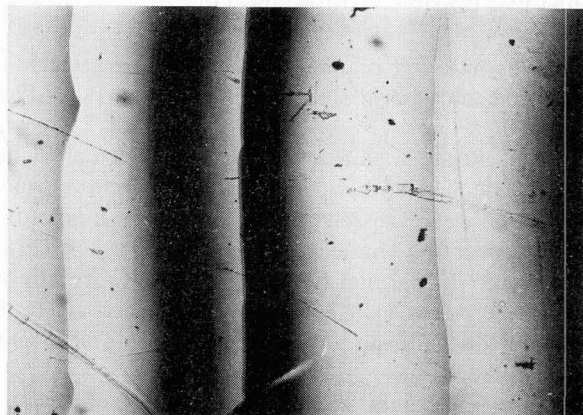


FIG. 1. — Specific rotatory power as a function of temperature for the sodium wavelength in the twisted smectic C phase and in the twisted nematic phase.

planes are not obtained but rather small fragments of disclinations that did not allow measurement of the pitch. On the other hand, in a fresh cleavage of mica, Grandjean's planes appear both for the chiral smectic C and the twisted nematic. Slide 3 shows disclinations in mica for the twisted nematic. On this slide, disclinations are double lines, that is, places where the twist increases by  $2\pi$ . Slide 4 shows, at the same place, disclinations for the twisted smectic C. They appear



SLIDE 4. — Grandjean's discontinuities at the same place for twisted smectic C phase.



when the thickness increases by one pitch interval because the conical structure obliges a rotation of  $2\pi$  to obtain an identical situation. There are always double lines.

Though variation of thickness in the wedge shaped mica is not known, the knowledge of the cholesteric structure leads to a profile of the wedge and then to the pitch in the chiral smectic C phase:  $12\ \mu$  at  $100\ ^\circ\text{C}$ . D. W. Berreman showed, using Maxwell's equations, that single domain samples of cholesteric liquid crystals and of the twisted smectic C phase have identical properties for light incident in the direction of the helicoidal axis [11], [13]. Consequently, it is possible to use, for twisted smectic C liquid crystals, de Vries' theory written for cholesteric liquid crystals [12]. We attempted to determine if agreement between theoretical values from this theory and experimental values is as good as in the cholesteric phase.

A non-chiral smectic C, for polarized light propagating normally to the layers, is a biaxial crystal whose high index makes an angle  $\theta - \alpha$  with the light's propagation direction. Indices of the privileged vibrations are given by the ellipse section of indices' ellipsoid of the wave plane.

De Vries' theory gives this expression for specific rotatory power.

$$\rho = \frac{\pi}{p} \left( 2 + \frac{m'_1 - m'_2}{\lambda'} \right) \quad (1)$$

where

$$\begin{aligned} \lambda' &= \lambda/p \sqrt{(n_1^2 + n_2^2)/2} = \lambda/pn \\ m'_1 &= \sqrt{1 + \lambda'^2} - \sqrt{4\lambda'^2 + \alpha^2} \\ m'_2 &= \sqrt{1 + \lambda'^2} + \sqrt{4\lambda'^2 + \alpha^2} \end{aligned}$$

$n_1$  and  $n_2$  are indices of the birefringent layer.

$$\alpha = (n_2^2 - n_1^2)/(n_2^2 + n_1^2).$$

Using a power expansion one obtains, if  $\alpha^2 \ll 4\lambda'^2$

$$\rho = -\frac{\pi}{p} \frac{\alpha^2}{4\lambda'^2(1 - \lambda'^2)} \quad (2)$$

that can be written :

$$\rho = -\pi p \frac{(n_2 - n_1)^2}{4\lambda^2} \quad (3)$$

if  $\lambda'^2 \ll 1$ .

If one applies this expression to the cholesteric phase where  $n_2 - n_1$  is  $n_g - n_p$  at  $103\ ^\circ\text{C}$ , for

$$n_2 - n_1 = 0.265$$

(nematic birefringence)

$$\begin{aligned} p &= 3.3\ \mu \\ \lambda &= 0.5893\ \mu \end{aligned}$$

one finds :

$$\rho = 30\ 000^\circ/\text{mm}$$

while experimental rotatory power is  $29\ 000^\circ/\text{mm}$ .

For the chiral smectic C phase, where  $n_2 - n_1$  is  $n - n_m$  ( $n$  to be calculated from the indices' ellipsoid),

applying expression (3) at  $102.8\ ^\circ\text{C}$ , for  $n_2 - n_1 = 0.120$  (smectic C birefringence in planar texture)

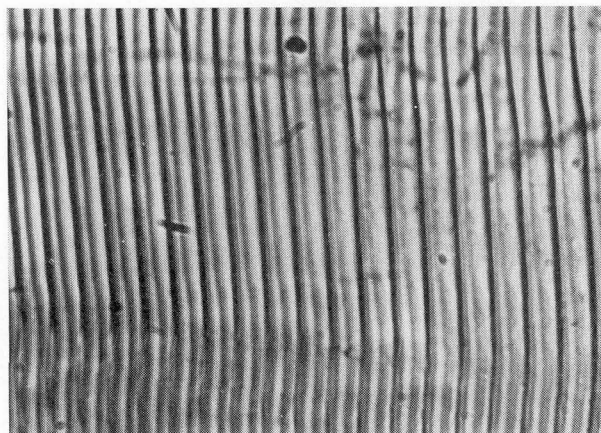
$$\begin{aligned} p &= 12\ \mu \\ \lambda &= 0.5893\ \mu \end{aligned}$$

one finds :

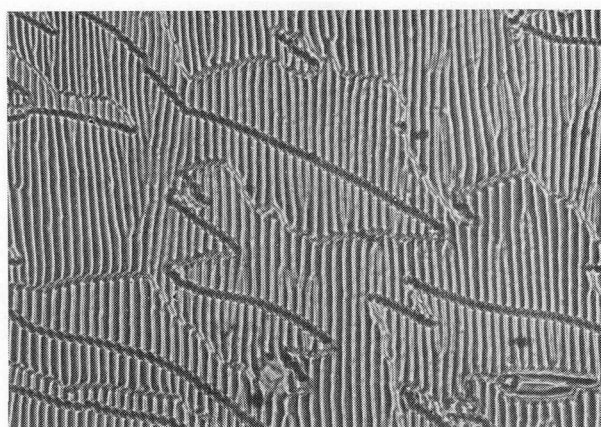
$$\rho = 22\ 000^\circ/\text{mm}$$

while experimental rotatory power is  $28\ 900^\circ/\text{mm}$ . Agreement between experimental and theoretical values is suitable but less good for chiral smectic C.

First, in that case  $\lambda'_{S\&C}$  is about  $\frac{1}{2} \lambda'_{N*}$ , and thus the expression (3) is probably less valid than in the twisted nematic phase. It is necessary to measure refractive indices of the layer to apply the more accurate expression (1). But it is also possible that a cholesteric mixed with a smectic C modifies the refractive indices more than when mixed with a nematic. If the texture is imagined as constructed of alternating layers of non-chiral smectic C and cholesteric, the smectic C indices used in the calculation are  $n$  and  $n_m$ , the indices of the cholesteric layer are  $n_e$  and  $n_o$ , where,  $n_e$  is  $\gg n$  so that  $n_e - n_o$  is greater than  $n - n_m$  and therefore, probably real birefringence is greater than the non-chiral smectic C birefringence.



SLIDE 5. — Periodic lines observed between two coated glasses (periodicity =  $25\ \mu$ ).



SLIDE 6. — Periodic lines observed in a drop on a coated glass (periodicity =  $6\ \mu$ ).

At last, various defects have been observed, but not yet interpreted. Slide 5 shows lines obtained between two coated glasses. Periodicity of these lines is about  $25 \mu$  (twice the pitch). Slide 6 shows another kind of lines in a drop of a coated surface. Periodicity of these lines is about  $6 \mu$  (Half-pitch).

3. **Conclusion.** — This paper on the twisted smectic C phase can be considered as a starting work.

De Vries' theory for the cholesteric phase can be applied to the chiral smectic C phase, but agreement is less good. To improve agreement it is necessary to use refractive indices of the chiral smectic C and not of the non-chiral smectic C.

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