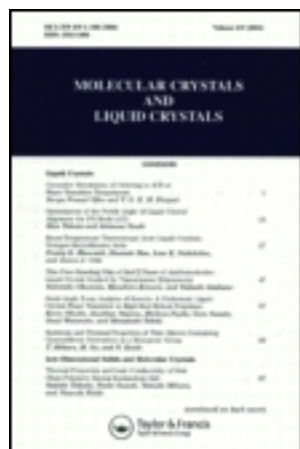


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J. Zubia^a, J. Etxebarria^b & A. Remon^b

^a Departamento de Física Aplicada II, Universidad del País Vasco, Apartado 644, 48080, Bilbao, Spain

^b Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080, Bilbao, Spain

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Temperature Dependence of the Rotatory Power and Tilt Angle in a Ferroelectric Liquid Crystal with a Cholesteric-Chiral Smectic C Phase Sequence

J. ZUBIA,† J. ETXEBARRIA and A. REMON

†*Departamento de Física Aplicada II, Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao (Spain)*

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Recently it has been shown that the tilt angle in a S_C^* phase can be determined from measurements of the optical rotatory power, birefringence and helical pitch. We have applied this procedure for studying the tilt behaviour of a ferroelectric liquid crystal which exhibits the phase sequence $N^*-S_C^*$. The tilt results are compared with those obtained for a planar sample from measurements of the angle between the dechiralization lines and buffing direction. A good agreement has been found between both sets of data, albeit the points obtained from the indirect method are much less scattered. In contrast to the tilt saturation commonly observed immediately on cooling through the $N^*-S_C^*$ transition, we have clearly noticed a slight variation of this quantity within the S_C^* phase, which cannot be appreciated from the direct angle measurements. It is argued that the apparent temperature independence of the tilt angle could be just a consequence of the wall anchoring effects in planar cells.

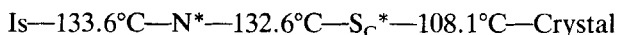
1. INTRODUCTION

Since the discovery of ferroelectricity in liquid crystals, the chiral smectic C (S_C^*) phase has been the object of an increasing amount of theoretical and experimental work. However, most of these studies have dealt with materials in which the S_C^* phase comes from a higher-temperature smectic A (S_A) phase. As is well known, this is not the only sequence giving rise to a S_C^* phase. Actually, the ferroelectric phase can be preceded by a cholesteric (N^*) or the isotropic (Is) phase. These phase transitions have scarcely been investigated so far, and the behaviour of some physical parameters in materials possessing these sequences is only partially known.

Regarding the $N^*-S_C^*$ transition, one of the most striking features that some authors have observed for the ferroelectric phase is a temperature independent tilt angle,^{1–3} often with a conspicuous value near 45° . Those results have been mainly obtained by measuring the angle between the dechiralization lines in the two domains that appear in a planar sample, where the alignment is achieved under the combined action of an electric field and a polymer coated surface.¹ It should be

noticed however that the wall anchoring effects in such samples are particularly strong. Indeed, the molecular long axes align parallel to the buffing direction, whereas the orientation of the smectic layers is determined by the molecular tilt. In this situation, it would not be surprising if the normal evolution of the tilt angle could be influenced by the bounding glass plates, especially in the case of thin samples.

Recently, it has been shown how, by measuring the helical pitch and the optical rotatory power along the helix axis in a S_C^* phase, one can obtain the tilt angle in an essentially unperturbed sample.^{4,5} In this paper we have applied this method to study the tilt behaviour in a S_C^* phase coming from an N^* phase. The molecular structure of the compound studied is shown in Figure 1. The phase transition sequence is the following:



2. EXPERIMENTAL

The cell for the rotatory power measurements was made of two glass plates coated with cetyltrimethylammonium bromide (CTAB). The thickness (60 μm) was maintained by using teflon spacers. The sample was introduced by capillary action with the material in the I_s phase. Afterwards, the sample was cooled down into the S_C^* phase at a rate of 0.1 $^\circ\text{C}/\text{min}$. Despite the transition sequence, the quality of alignment in the ferroelectric phase was fairly good. The optical activity measurements were carried out with a polarimeter equipped with a rotating analyser and a phase-sensitive detector. More experimental details can be found elsewhere.⁵

The helical pitch of the S_C^* phase was determined by direct microscopic observation. In this case, the sample was 200 μm thick and the glass plates were coated with nylon 6/6. The alignment was facilitated by buffing one substrate unidirectionally and cooling the material slowly through the $N^* - S_C^*$ transition in the presence of an a.c. electric field (80 v, 50 Hz). The sensitivity of the pitch to surface effects was overcome by using the method described in Ref. 6 for obtaining the free value of the helical pitch in samples with strong anchoring conditions.

3. RESULTS AND DISCUSSION

The temperature dependence of the rotatory power in the S_C^* phase is presented in Figure 2 for a wavelength $\lambda = 633$ nm. The experiment was performed when

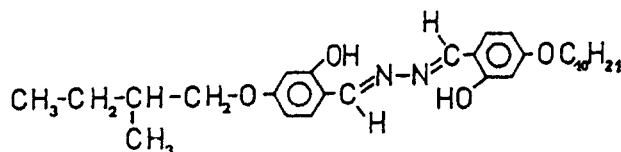


FIGURE 1 Molecular structure of the compound studied.

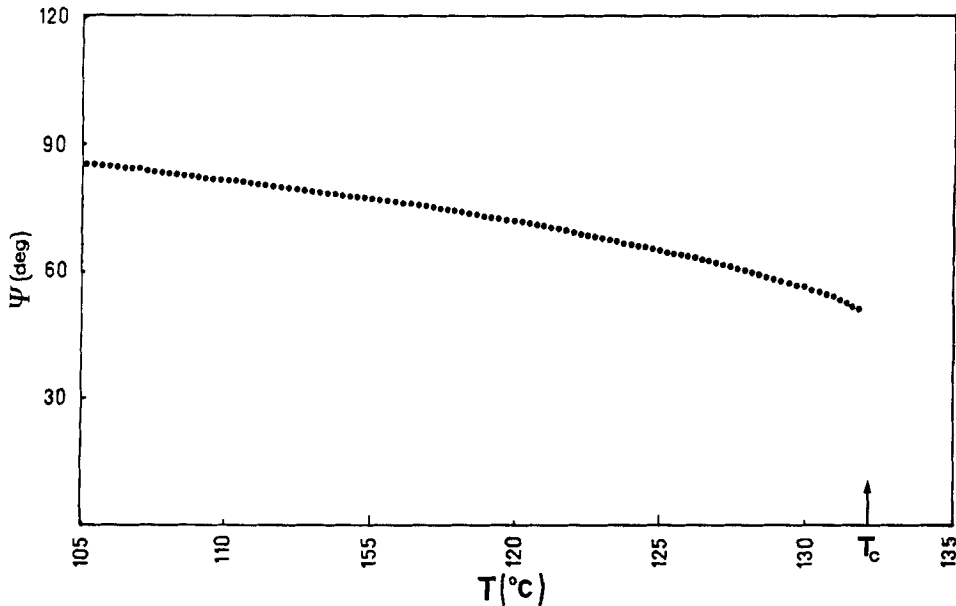


FIGURE 2 Temperature dependence of the rotation of the light polarization for a 60 μm sample at 633 nm.

heating at a rate of 0.1°C/min. The plotted results represent the optical activity due to the long range S_C^* helical structure. The optical rotation caused by the inherent molecular chirality was subtracted by taking the data relative to the rotatory power of the I_s phase. It was not possible to do any measurement for the N^* phase, because the sample alignment is disrupted about the $S_C^*-N^*$ transition.

As can be seen, the optical activity presents a monotonous increase with temperature as we move away from the $S_C^*-N^*$ transition point. These results can be interpreted by making use of the De Vries approach for the rotatory power in liquid crystal materials. In the case of a S_C^* phase, it can be shown that the rotatory power ρ for light propagating along the helical axis can be written as

$$\rho = -(\pi p/4\lambda^2) (\Delta n)^2 \sin^4\theta \quad (1)$$

provided that the vacuum light wavelength λ is much smaller than the product of the pitch p and the average of the so-called local refractive index.⁷ This condition is fulfilled in our case throughout the range of the S_C^* phase as will be shown below. In Equation (1), θ and Δn stand for the tilt angle and optical anisotropy respectively. According to this expression, the temperature dependence of θ can be extracted from measurements of ρ , p and Δn .

Our pitch measurements are shown in Figure 3. As can be seen, the p value in the S_C^* phase is temperature independent within the experimental resolution, although a tendency of the pitch to increase was noticed very close (less than 0.1°C) to the $S_C^*-N^*$ transition temperature. The p results for the N^* phase are given

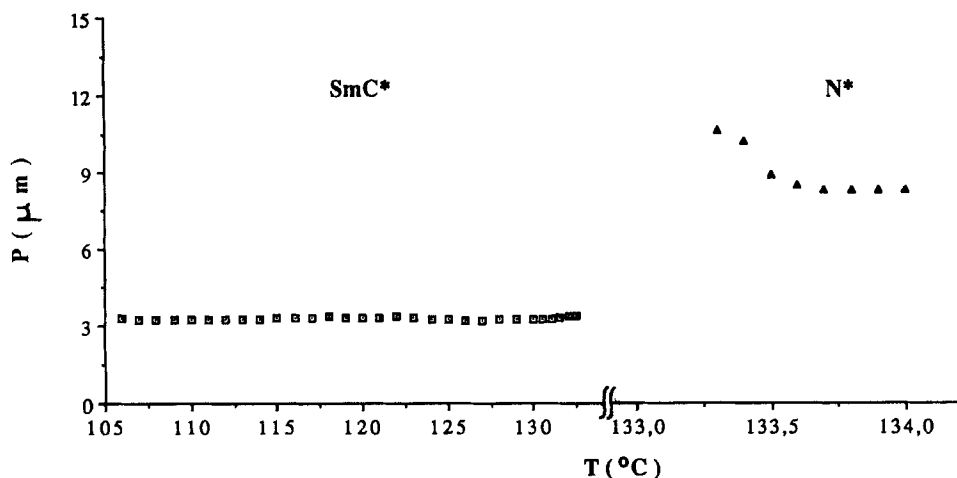


FIGURE 3 Temperature dependence of the helical pitch in the N^* and S_C^* phases.

for the sake of completeness. These measurements were performed by using the well known Grandjean-Cano wedge method. The pitch values are much higher than those for the S_C^* phase and tend to increase near the $N^*-S_C^*$ transition, as is commonly observed in materials with transitions between N^* and smectic phases.⁸

The same wedge-shaped cell used for these measurements was employed to obtain the birefringence of the S_C^* phase. In the thinnest part of the cell, the helicoidal structure was completely unwound and, presumably due to polar surface interactions,¹ a monodomain specimen was produced. Therefore, the birefringence could be estimated from the measurement of the spacing between the consecutive fringes that appeared on the regions near the wedge apex when the sample was viewed with monochromatic light between crossed polarizers.⁹ The birefringence was determined to be $\Delta n = 0.18$ for $\lambda = 633$ nm and, as usually happens within a smectic phase, showed no appreciable change with temperature.¹⁰

As a result of the above measurements, the conclusion is reached that it is the tilt angle variation within the S_C^* phase which causes the change of the rotatory power with temperature. The θ values calculated from Equation (1) are represented with open squares in Figure 4.

We also tried to determine the tilt angle by employing the usual electro-optic method.¹¹ However, and presumably because of the extremely small polarization of the material,¹² we could not bring the sample to extinction without producing serious electrohydrodynamic instabilities. Nevertheless, we have included the results obtained by measuring the complementary angle of that which the pitch lines made with respect to the buffing axis. As can be seen in Figure 4, both sets of data are in reasonable agreement, although the points obtained by the direct method scatter considerably. According to these results and within the experimental resolution ($\pm 2^\circ$, originated by a slight deviation of the pitch lines from exact parallelism), the tilt angle could be perfectly constant.

What now remains to be decided is whether this unchanging behaviour is only due to the lack of resolution in the angle measurements or is also caused by

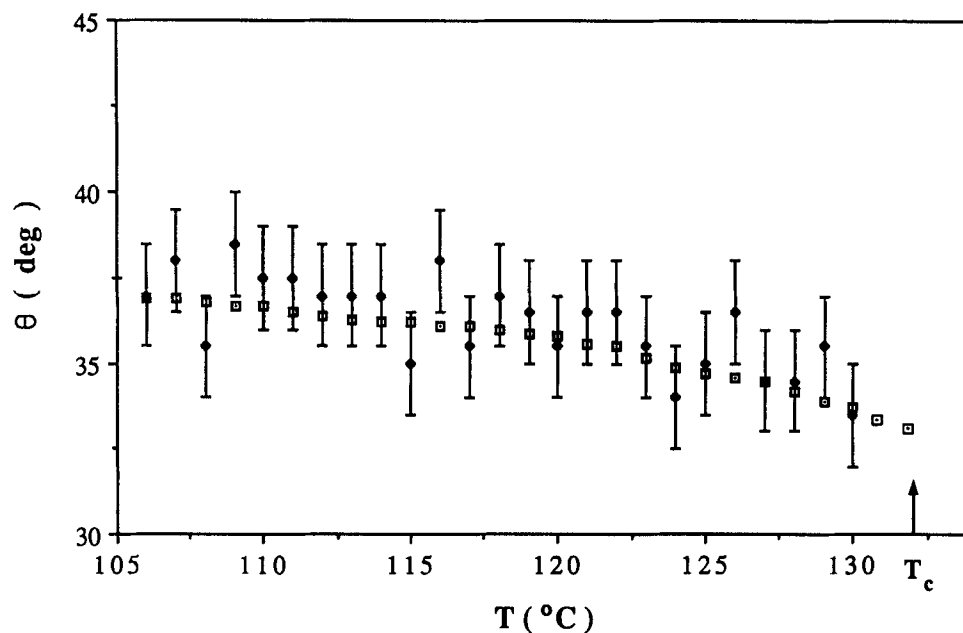


FIGURE 4 Temperature dependence of the tilt angle in the S_C^* phase. Open squares: data deduced from the rotatory power, pitch and birefringence. Full circles: results obtained by measuring the angle between the buffing direction and the normal to the pitch lines.

boundary effects. A clear answer to this question cannot be given at present. Nevertheless, it is hard to believe that the boundary plates have no influence on the tilt results. As has been pointed out above, in materials with the $N^*-S_C^*$ sequence, the alignment process compels the molecular axes to lie along the buffing direction. Furthermore, the assumption that twice the tilt is equal to the angle between the dechiralization lines of the symmetrically grown domains^{1,2} implies that, if the tilt is to change, the smectic planes (and not the molecular director) must reorient at each temperature. In principle, this process seems to be less favourable from an energetic point of view than the opposite one (molecular reorientation while the smectic planes remain fixed) that is found for materials with the more frequently studied $S_A-S_C^*$ sequence. On the other hand however, the pulling force towards the buffing direction has been found to be very strong in these materials (especially in thin samples), where some peculiar effects, such as monostability or layer switching about 90° under application of a.c. fields have been observed.³ In either case, the mechanism for tilt variation in planar cells appears to be strongly limited.

In summary, we have shown that the indirect tilt determination from rotatory power data can give results more precise than those obtained with the method commonly used in the case of materials possessing the $N^*-S_C^*$ sequence. Likewise, some systematic errors that may arise in planar cells are eliminated. The necessity of using electric fields, which can produce instabilities, induce tilt variations or even shift the transition temperature,¹³ is also avoided. The method could be

especially appropriate for studies near the transition point, where accurate experimental information would be highly desirable.

Acknowledgments

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