FLEXO AND FERRO-ELECTRICITY OBSERVATION OF FERRO-ELECTRICAL MONODOMAINS IN THE CHIRAL SMECTIC C LIQUID CRYSTALS
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OBSERVATION OF FERROELECTRICAL MONODOMAINS IN THE CHIRAL SMECTIC C LIQUID CRYSTALS

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Abstract. — We have determined, on monodomain samples oriented by an electric field, the tilt angle of molecules inside the layers of ferroelectric smectic C phase of some chiral compounds (DOBAMBC, OOBABCC, HOBACPC, DOBAMBC, TDOBAMBC) and we have studied the temperature dependence of this angle. The sign of the permanent electric dipole of the molecules has also been determined. We have specified the pitch of the helix obtained without electric field.

Molecular structure and thermal phase diagram for the compounds studied in this paper

<table>
<thead>
<tr>
<th>COMPOUND AND NAME</th>
<th>THERMAL PhASE DIAGRAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10 H21-O-CH=N-CH=CH-C=O-CH2=CH2</td>
<td></td>
</tr>
<tr>
<td>P-DECYLOXYBENZYLIDENE P-AMINO 2 METHYL BUTYL CINNAMATE (DOBAMBC)</td>
<td>Cr 76° CHIRAL Sm C 95° Sm A 75° ISOTROPIC</td>
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<tr>
<td>C9 H17-O-CH=N-CH=CH-C=O-CH2=CH2</td>
<td></td>
</tr>
<tr>
<td>P-OCTYLOXYBENZYLIDENE P-AMINO 2 METHYL BUTYL CHLORO CINNAMATE (DOBAMBC)</td>
<td>Cr 46° Sm A 60° ISOTROPIC</td>
</tr>
<tr>
<td>C10 H21-O-CH=N-CH=CH-C=O-CH2=CH2</td>
<td></td>
</tr>
<tr>
<td>P-DECYLOXYBENZYLIDENE P-AMINO 2 METHYL BUTYL CYANO CINNAMATE (DOBAMBC)</td>
<td>Cr 97° Sm A 105° ISOTROPIC</td>
</tr>
<tr>
<td>C8 H29-O-CH=N-CH=CH-C=O-CH2=CH2</td>
<td></td>
</tr>
<tr>
<td>P-TETRADECYLOXYBENZYLIDENE P-AMINO 2 METHYL BUTYL CYANO CINNAMATE (DOBAMBC)</td>
<td>Cr 76° Sm A 105° ISOTROPIC</td>
</tr>
<tr>
<td>C6 H13-O-CH=N-CH=CH-C=O-CH2=CH2</td>
<td></td>
</tr>
<tr>
<td>P-HEXYLOXYBENZYLIDENE P-AMINO 2 CHLORO 2 PROPYL CINNAMATE (HOBACPC)</td>
<td>Cr 60° Sm H 64° Sm C 76° Sm A 98° ISOTROPIC</td>
</tr>
</tbody>
</table>

1. Introduction. — General symmetry arguments have allowed R. B. Meyer and coworkers [1] to foresee the possibility of ferroelectricity in the smectic C and smectic H phases if the liquid crystal molecules are chiral and have a permanent dipole moment normal to its long axis. The symmetry forces the resulting moment of each layer to be parallel to the layer and normal to the long molecular axis.

The observations made by the authors of [1], on a particular compound, showed that the molecular chirality can involve the texture chirality. Then the smectic layers pile up in a helicoidal structure and their permanent dipoles precess around the normal to the layers. If the thickness of the samples is much larger than the helicoidal pitch (~ 10 μm), the resulting permanent dipole moment of all the sample is practically zero. An electrical field of about 10^3 V/cm parallel to the layers unwinds the helix and gives an average polarisation to the sample [1, 2]. In the arrangement of reference [1] the glass slides of the sample are parallel to the smectic
layers. This sample is then a biaxial slab cut with a tilt of about ten degrees between the slab normal and the bisectrix of the two optical axis.

R. Duke, G. Durand and R. B. Meyer [2] have studied six compounds having the same chiral group and newly synthesized by P. Keller, L. Liebert and L. Strzelecki [3]. They measured the helical pitch, the tilt angle, the critical field and the dielectric constants versus the temperature. They proved that the C phases of these compounds also are ferroelectrical.

In the paper we report on the observation of monodomains aligned by an applied electric field in the planar geometry i.e. where the smectic layers are normal to the two sample walls.

2. The observation method. — Let us remember the molecular arrangement model and what we can measure if we observe optically a sample in a direction parallel to its smectic layers.

If the plane of the layer is taken as the \( xy \) plane, \( \theta \) is the tilt angle of the long molecular axis \( m \) (or more properly the long axis of its optical polarizability tensor) with respect to the layers normal \( z \) and \( \psi \) is the angle between \( Ox \) and the \( m \) projection on the \( xy \) plane.

Let us suppose that all the molecules are aligned through the ferroelectric coupling by an electrical field applied along \( x \). Their electric dipoles \( P \) are parallel to \( x \) and their long axis \( m \) have the direction: \( \theta \), \( \psi = \pi/2 \) or \( \psi = -\pi/2 \), according to the field sign and the orientation of \( P \) in the molecule (Fig. 1a, 1b). Reversing the electrical field turns \( m \) from \( +\theta \) to \( -\theta \) in the \( yz \) plane. The long axis of the refractive indices ellipsoid of the liquid crystal is in the same direction as the long molecular axis \( m \).

If we observe along \( x \) a slab of this liquid crystal parallel to \( yz \), we see the optical neutral lines in the direction \( \theta \) and \( \theta + \pi/2 \) or \( -\theta \) and \( -\theta + \pi/2 \). We can see if the whole sample is aligned and measure the tilt angle with an applied field. Besides the sign of \( \theta \) gives the orientation of the permanent dipole with respect to the layers normal \( z \) and the long molecular axis \( m \).

Let us now suppose that the smectic layers are piled up with the direction of tilt precessing around the \( z \) axis in a helicoidal structure of pitch \( Z \) following R. B. Meyers model (Fig. 1b). The long molecular axis projection on the \( xy \) plane makes with \( z \) an angle \( \theta' \) and

\[
\tan \theta' = \tan \theta \sin \psi = \tan \theta \sin \frac{2 \pi z}{Z}.
\]

If we observe along \( x \) a slab of this liquid crystal parallel to \( yz \), we see its optical neutral lines practically in the \( \theta' \) direction. Indeed, the liquid crystal is biaxial, but its index along \( m \) is much higher than the two others who are almost equal. Then the bisectrix of the optical axis projections is very close to the optical axis bisectrix projection (i.e. the projection of \( m \)). The direction of the optical neutral lines of the sample have to vary sinusoidally versus \( z \) with a period \( Z \).

3. Experimental. — The sample thickness (\( d = 150 \mu m \)) is chosen to avoid the helixquenching by the walls. (We have indeed observed [4] this quenching when the thickness is about the pitch (\( d = 20 \mu m \)).)

The sample walls are two glass slides coated with transparent tin oxide electrodes separated by two glass lamellas. To line up the smectic layers perpendicular to the slides a thin film of SiO is evaporated at an oblique incidence on the tin oxide coating [5]. Practically this film does not insulate electrically the electrodes from the liquid crystal.

To have a good orientation of the layers, we put the sample at a temperature near the isotropic phase in the A phase. An alternate electric field (1 Hz, 10⁴ V/cm) is applied during several minutes to sweep out the focal conics. The temperature is then lowered to reach the C phase.

The stabilization and the measurement of the temperature is made by a Mettler hotstage wich is regulated to better than \( 0.1 \) °C.

The optical neutral lines determination is made with a Leitz polarizing microscope. Its accuracy is better than \( 1^\circ \).

The layers direction is obtain by locating the neutral lines when the sample is in the A phase.

4. Results. — 4.1 Pitch measurement. — Turning the sample between two crossed polarizers on the microscope stage shows parallel black lines regularly spaced. The figures 2b, 2c and 2d represent schematically this pattern for three particular polarizers orientations. For two orientation \( \theta'' \) and \( -\theta'' \) symmetrical to \( z \)

\[
\tan \theta'' = \tan \theta \sin \psi = \tan \theta \sin \frac{2 \pi z}{Z}.
\]
OBSERVATION OF FERROELECTRICAL MONODOMAINS IN THE CHIRAL SMECTIC C

Fig. 2. — a) Model for the chiral smectic C texture in absence of electric field. This arrangement is seen along the x direction. b, c, d) shows the patterns seen between two 90° crossed polarizers, for three particular angles they make with z (+ θ ; 0 ; − θ).

The light beam is along x.

the contrast is maximum. The black lines for θ" are just in the middle of these for − θ". Between these positions the pattern is blurred. If the polarizers are in the z direction and the pitch large, the microscope can resolve twice narrow lines.

θ" is not located with a better accuracy than 30 % but with this uncertainty we found that θ" is equal to θ obtained by X Ray measurements [2]. The interest of this observation is to confirm the helicoidal structure and to answer the question of reference [2]: is the lines spacing equal to the pitch or half the pitch? The answer is: this spacing is equal to the pitch in a uniform structure in all cases except when the polarizers are normal to the layers but in this case the lines are quite difficult to see.

On figure 3 the black dots show the pitch versus the temperature obtained by this method for the TDOBAMBCC. The continuous curve drawn for comparison was obtained by [2]. They measured on multidomain textures where they saw the half pitch. By our method it is possible to go closer to T

To prove the helicoidal structure by measuring the θ' variation versus z it should be necessary to have compounds the pitch of which is very large to allow a good precision for measuring θ' and z. Indeed in this experiment we cannot use the better resolution power of the microscope because the light ought to be nearly parallel. We are restricted to use a aperture of 0.2.

4.2 MONODOMAINS, TILT ANGLE. — We apply an electrical field of about 10³ V/cm on the sample, corresponding to some dozen of volts between the glass slides. Increasing the voltage, if the polarizers are in the θ" direction, we see the light lines flowing out of the microscope field merging eventually in some focal conics which can remain. By adjusting a little the polarizers direction in θ" we make black the whole observed sample part.

Multiplying by ten the field value does not change the orientation θ". If we change the field sign, the black lines flow out. Turning the polarizers to − θ" gives the observed sample part black again. Repeating the field application keeps the values θ" and − θ" with an accuracy of ± 1° and does not move the defects. Nevertheless there is a hysteresis for the field. It is necessary to apply a light larger field to orient in one way if the sample was in the other. The field amplitude to put out the lines can be twice lower after ten orientations than for the first.

We plot on figure 4 our measurements of θ" for the DOBAMBC, the HOBACPC, the TDOBAMBCC and the DOBAMBC versus T − T

Fig. 3. — Pitch of the helix versus T − Tc in an uniform texture. Tc is the smectic A to smectic C transition temperature. The full line curve shows for comparison the data of reference [2] obtained on a multidomain texture. The dots are our data.

and the DOBAMBC versus T − Tc for the same sign of the electrical field. We have also plotted for comparison the values of the tilt angle from X Ray measure-
ments from reference [2] for the DOBAMBC and the TDOBAMBCC. The uncertainty upon the angles is \( \pm 1^\circ \) but the largest contribution to the uncertainty comes from \( T_c \). The degradation of the compounds gives a decrease of \( T_c \) which can reach 6 d\( ^\circ \)C for the four first days of a sample. We can estimate that during an experiment this give a possible shift of about \( \pm 0.5 \) d\( ^\circ \)C for \( T - T_c \). With the correction of \( T_c \) the degradation does not affect the data and we found the same results for a new sample and for the same sample after one week.

Anyway the absolute value of \( \theta^\circ \) are very close for the DOBAMBC, the HOBACPC and the DOAMBCC at the same \( T - T_c \). Moreover those values are practically the same as those obtained by reference [2] with X Ray measurement on the helicoidal structure. For the TDOBAMBCC we find a 30 % lower result than reference [2], it is for us a question.

The fact the whole sample is black between two crossed polarizers oriented in the \( \theta^\circ \) direction induces us to think that the sample with a applied field is a monodomain.

\( \theta^\circ \) is the tilt angle in the monodomain, because, if a thick transition layer should be between the wall and the sample center which turns adiabatically the light polarization, the thickness of this layer should vary with a large applied field changing the value of \( \theta^\circ \).

Nevertheless the dispersion of the field value needed to put out the lines suggests that in this geometry this field is not only the critical field to unwind the helix but also the field necessary to destroy a wall anchoring.

On the other hand, from the facts that \( \theta^\circ \) does not vary and the defects does not move with repeated field applications, we deduce that the orientation of the smectic layers does not change with the field.

From the accordance of \( \theta, \theta^\prime \) and \( \theta^\circ \), two measurements of the tilt angle without applied field and one with we deduce that the field unwinds the structure varying \( \psi \) without any variation of \( \theta \). The molecules align them turning on a cone of angle \( \theta \) and axis \( z \).

4.3 Permanent dipole orientation. — The direction of the molecular axis changes with the sign of the applied electric field. This is a proof that the orientation of the molecules is due to the alignment of their permanent dipole \( P \) by the field. The direction of orientation of the molecule versus the field gives us the direction of \( P \) versus the tilt angle vector (rotation vector from \( z \) to \( m \)).

We find that though the compounds were synthetized from the same chiral group the orientation of the dipole are not the same.

For the : DOBAMBC, OOBAMBCC, HOBACPC (the first compound and these in which a chlorine was added on the cinnamate radical or on the assymetrical carbon, cf. table of the formulas).

The permanent dipole is in the opposite direction of the tilt angle vector oriented usually.

For the : DOBAMBCC and TDOBAMBCC (those in which a nitril group was added) the permanent dipole is in the same direction than the tilt angle vector oriented usually.

The substitution of a nitril group at the place of a proton or of a chlorine reverses the sign of the permanent dipole. We can think that the permanent dipole of this group is in the opposite direction to the dipole of the other molecular part.

This is a possible explanation of the data of reference [2]:

for the

<table>
<thead>
<tr>
<th>Compound</th>
<th>( P_0 ) (Debye/( ^\circ )C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOBAMBC and OOBAMBCC</td>
<td>( P_0 = 0.02 ) Debye/( ^\circ )C.</td>
</tr>
<tr>
<td>DOBAMBCC and TDOBAMBCC</td>
<td>( P_0 = 0.005 ) Debye/( ^\circ )C.</td>
</tr>
</tbody>
</table>

(\( P_0 \) is the sample polarisation divided by the number of the molecules and for a tilt of 1 rad.).

5. Conclusion. — By alignment with an applied electric field in the C phase we have obtained monodomains samples of ferroelectrical chiral smectic C. We measured on these monodomains the tilt molecular angle in the layers. We find that the sign of \( P \) (the permanent dipole orientation) can be opposite for different compounds with the same chiral group. It is demonstrated that the striations spacing observed in our uniform texture, in the absence of any applied electric field, corresponds to the helix pitch, while in a multi-domain texture this spacing would correspond to half the pitch.

After these progress in the optical observation technic of this phase if similar progress are made in the electrical conditions we could measure the permanent polarization with accuracy.

We wish to thank G. Durand for very helpful discussions.

References