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Characterization of reentrant cholesteric, cholesteric and chiral smectic phases of three recent polar mesogens

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Résumé. — L'article expose les variations du pas dans les phases torsadées de trois mésogènes polaires récents présentant du polymorphisme rentrant : (α) $KN_{re}^* S_A N^* I$; (β) $KS_F^* S_c^* N_{re}^* S_A N^* I$; (γ) $S_A N_{re}^* S_{Are} N^* I$. Les valeurs obtenues confirment la divergence du pas à l'approche d'une phase S_A et la divergence du pas à chaque extrémité d'une phase cholestérique comprise entre deux phases S_A et S_{Are} ; le pas de la phase S_c^* conserve une valeur finie aux transitions $S_c^* - N_{re}^*$ et $S_F^* - S_c^*$. Les mesures directes du pas par la méthode de Grandjean-Cano sont confirmées par l'étude de l'activité optique : la comparaison des résultats permet de décrire les variations de la biréfringence des diverses phases étudiées.

Abstract. — Measurements of pitch variations are performed over the twisted phases of three recent pure polar mesogens exhibiting reentrant polymorphism : (α) $KN_{re}^* S_A N^* I$; (β) $KS_F^* S_c^* N_{re}^* S_A N^* I$; (γ) $S_A N_{re}^* S_{Are} N^* I$. Numerous and precise values confirm pitch divergence near S_A , pitch divergence at each side of cholesteric phase when sandwiched between S_A and S_{Are} phases. S_c^* pitch keeps a finite value at $S_c^* - N_{re}^*$ and $S_F^* - S_c^*$ transitions. Direct measurements of pitch, performed by Grandjean-Cano method are confirmed by optical activity study : such comparison gives informations about birefringence variations.

1. Introduction.

In opposition to most of cholesteric mesophases, for which the helical pitch decreases with increasing temperature, the pitch of a reentrant cholesteric generally increases. Billard [1] puts in evidence the strong increase of the pitch near the $N_{re}^* \rightarrow S_A$ transition, from the observation of contact preparations between — a compound presenting a nematic reentrant mesophase and — a cholesteric mesogen. Chilaya [2] also measured the helical pitch divergence in reentrant and normal cholesteric phases of mixtures of nematics and optically active

dopants, using Bragg diffraction on focal conic textures or selective reflexion spectra on planar textures.

We present here precise and detailed pitch variations measurements of the N_{re}^* and N^* phases of three pure compounds, presenting the following phase sequences : (α) $KN_{re}^* S_A N^* I$; (β) $KS_F^* S_c^* N_{re}^* S_A N^* I$; (γ) $KS_A N_{re}^* S_{Are} N^* I$. The S_c^* phase of the (β) compound is also studied.

2. Studied compounds.

The studied compounds are

with the following phases sequences (°C) :

with

with

The properties of β and γ are expected to be more interesting because their N_{re}^* phases are situated between two smectic phases: $S_c^* S_A$ for β and $S_A S_{Are}$ for γ .

3. Principles of experimental methods.

All measurements are performed on a polarizing microscope.

3.1 THE GRANDJEAN-CANO TEXTURE. DIRECT MEASUREMENT OF THE PITCH. — The Grandjean-Cano [6, 7] planar texture can be obtained in a cholesteric weak angle prism: the cholesteric is introduced between two glasses orienting the molecules at the surfaces in a unique direction perpendicular to the edge; equidistant parallel defects appear at thicknesses $d_k = p/4 + k \frac{p}{2}$; they separate constant width steps in which the twist angle is $k\pi$. According to temperature variations, pitch variations induce a displacement of the Grandjean-Cano defects and a modification of their distance. So microscopic measurements of the steps width, associated with the angle of the prism, give the mean pitch value and its variation with the temperature.

3.2 THE APPARENT ROTATORY POWER IN GRANDJEAN-CANO SAMPLES. — The apparent rotatory power of cholesterics is given by the de Vries [8] expression:

$$\Omega = -\frac{\pi}{4} \frac{\Delta n^2 p}{\lambda^2 (1 - \lambda^2/n^2 p^2)}.$$

When the pitch is large ($p \gg \lambda$) this expression can be simplified and the rotatory power is proportional to the pitch:

$$\Omega \cong -\frac{\pi}{4} \frac{\Delta n^2}{\lambda^2} P. \quad (1)$$

This expression is not valid when the pitch grows and approaches the Mauguin's limit $p_M = \frac{2\lambda}{\Delta n}$ [9]. The rotatory power then saturates slightly [10].

In Grandjean-Cano prism samples, measurements are done in the middle of the steps; there only, the

pitch gets its « natural » value p . Rotation of the analyser gives optical rotation θ_k in the k -th step; thickness is $e_k = kP/2$. So rotatory power is calculated as $\Omega = \theta_k/(kP/2)$.

Optical rotation measurements need special care when pitch approaches Mauguin's limit: ellipticity fluctuations of analysed light become important, reaching maximum values when rotation is close to $(l + \frac{1}{2})\pi$; good extinctions with a linear analyser need to choose a k -th step where θ is close to $l\pi$.

For our three compounds, (1) is sufficient. So pitch temperature dependence can be controlled by rotatory power temperature dependence, if the material birefringence is constant in the studied phase.

3.3 THE ROTATORY POWER OF PLANAR DROPS. — The rotation of the polarisation plane can be measured on flat planar drops [10] for instance. All measurements are performed at the same point of the drop. If the free surface shape of the drop does not change with temperature, the thickness remains constant. So optical rotation variations are representative of the rotatory power variations. Temperature pitch dependence can then be controlled or completed like in the previous section.

4. Experimental studies.

4.1 GENERALITIES. — The slides are first rubbed on a felt support impregnated with diamond paste diluted in alcohol (dimension of the grains $\cong 1 \mu\text{m}$; 40 go and return). The slides are then carefully cleaned with alcohol; and finally wiped with a soft paper, respecting the same direction as the rubbing one. The cleanness of the slides is very important to insure the planar texture: indeed the studied compounds are polar and exhibit a clear tendency to homeotropy, giving undesirable finger prints texture.

The lower glass is a $75 \times 20 \text{ mm}$ slide. The upper glass is a fragment ($30 \times 5 \text{ mm}$). One edge of the upper glass is lifted up by a thin glass slide ($150 \mu\text{m}$); the angle of the prism is then about $0.2-0.3^\circ$. A little drop of product is placed near the edge of the prism. The sample is introduced in the

FP₂ Mettler stage, at a temperature where the substance is cholesteric. The drop melts and the prism is filled by capillarity.

4.2 THE COMPOUND α : $\text{KN}_{\text{re}}^* \text{S}_A \text{N}^* \text{I}$.

4.2.1 Reentrant cholesteric phase. — The introduction temperature is close to 92 °C ; there, the mesophase fluidity enables an easy filling of the prism. On the other hand, $\text{N}_{\text{re}}^* \text{S}_A$ transition is far enough to avoid pretransitional effects, and it is easy to obtain 6-10 regular Grandjean steps. Then, a slow temperature decrease enables to approach the $\text{K} - \text{N}_{\text{re}}^*$ transition within one degree ; the displacement of the Grandjean lines often eliminates some defects in the parallelism of the lines (if necessary, it may be useful to do temperature cycles). It is now possible to observe and measure the lines distance temperature dependence over the whole N_{re}^* range when the temperature grows, and to measure simultaneously optical rotations in the middle of some steps.

4.2.2 High temperature cholesteric phase. — Near the $\text{N}_{\text{re}}^* - \text{S}_A$ transition, the first step ($k = 0$) invades the whole preparation, giving a perfectly planar S_A . This texture is stable if the temperature increase speed is sufficient (if not, the S_A becomes rapidly homeotropic). When homeotropy is avoided, the Grandjean texture reappears after the $\text{S}_A - \text{N}^*$ transition. The pitch decrease can be observed if the temperature variation is fast. But, in this high temperature cholesteric phase, the Grandjean lines rapidly disappear, a finger print texture appears ; the measure of the pitch variations is then impossible.

For this reason, the high temperature phase is studied in the following way : a new preparation is built and introduced in the stage at the studied temperature. The Grandjean texture generally lasts 10 to 30 s ; this is sufficient for only one measurement of the steps width ; for another temperature, it is necessary to built another preparation.

To avoid the dispersion resulting from studied cells multiplicity, the rotatory power variations are observed on a single drop for which the quality of the planar texture remains generally good over the whole N^* temperature range. (This drop is deposited on a rubbed glass.)

4.2.3 Results. — For the N_{re}^* phase, the pitch clearly increases and diverges at the S_A transition (Fig. 1). The optical study confirms pitch measurements (Fig. 2) and gives the left-handedness of the structure. In the N^* phase the pitch diverges near the S_A , decreases and gets a quasi constant value over a wide temperature range. The dispersion is due to the multiple studied samples.

The rotatory power is susceptible to correct the direct measurements of the pitch near the S_A phase. The strong decrease of the rotatory power beyond 190 °C is due to the birefringence decrease near liquid phase.

4.3 THE COMPOUND β : $\text{KS}_F^* \text{S}_c^* \text{N}_{\text{re}}^* \text{S}_A \text{N}^* \text{I}$.

4.3.1 Cholesteric phases. — The sample is introduced in the stage in the middle of the N_{re}^* temperature range (135°) ; then cooled to 125 °C and heated. For this second compound β , the tendency to homeotropy is less than for α . It is possible to study

Fig. 1. — α Compound (described in Sect. 2) : variations of the pitch versus temperature.

Fig. 2. — α Compound (described in Sect. 2) : comparison of reduced rotation and reduced pitch variations. a) In N_{re}^* phase, the birefringence is constant. b) The birefringence falls near liquid state.

the two N^* phases with the same sample provided that the S_A phase is rapidly crossed.

Generally, after more or less time, the sample finally loses his Grandjean texture and finger-prints appear near the $N^* I$ transition. This is irreversible and Grandjean lines no more reappear in the N^* phases when the temperature is decreased. However, an interesting phenomenon then occurs, in the S_c^* phase : cooling the N_{re}^* in the finger-print texture gives regular Grandjean-Cano 2π disclinations in the S_c^* phase, allowing the S_c^* pitch study. Indeed, two conditions are here simultaneously satisfied : the homeotropy tendency orients the screw axis of the S_c^* phase perpendicular to the sample plane, and the rubbing of the glasses orients the projection of the director at the interfaces. So the total twist angle is $2k\pi$, leading to 2π disclination lines, equidistant and parallel to the edge of the prism. Regions with $(2k+1)\pi$ lines can also be observed.

4.3.2 The S_c^* phase. — The Grandjean-Cano geometry in the S_c^* phase can also be obtained directly : rubbed glasses are covered with a surfactant favouring the homeotropy (HTAB for

example). The sample is introduced in the stage in the S_c^* temperature range ($121^\circ C$). The Grandjean-Cano pseudo-homeotropic texture of the S_c^* is very stable over the whole S_c^* range. The steps width variations give the values of the S_c^* pitch.

In the S_F^* phase, the Grandjean-Cano lines are still visible, but no more move when the temperature changes.

Notice endly that in the S_c^* phase, the indicatrix is not perpendicular to the screw axis, but tilted at the « tilt angle » θ . The extraordinary index, for the waves propagating along the screw axis is :

$$n'_e = \left(\frac{\cos^2 \theta}{n_0^2} + \frac{\sin^2 \theta}{n_e^2} \right)^{-1/2} ;$$

the birefringence $\Delta'n = n'_e - n_0$, is then weaker than $\Delta n = n_e - n_0$, and the apparent rotatory power $\left(\Omega \approx -\frac{\pi}{4} \Delta'n^2 \frac{P}{\lambda^2} [11] \right)$ is much weaker than in the N^* phases. So, the preparation in the S_c^* phase is not coloured, and the Grandjean-Cano steps are not very visible.

4.3.3 Results. — The figure 3 gives the variations of the pitch in the three twisted phases. In the S_c^* phase the pitch increases slowly with the temperature increase. After the $S_c^* - N_{re}^*$ transition, the pitch is about $4 \mu m$ ($2 \mu m$ in the S_c^*), first decreases slowly, and rapidly increases and diverges near the $N_{re}^* S_A$ transition. In the N^* phase, the pitch diverges at the S_A transition, and decreases.

The comparison of pitch and rotatory power variations reveals a weak decrease of the birefringence in the N_{re}^* (Fig. 4a) phase : $\Delta n = 0.23$ at $125^\circ C$ and 0.20 at $148^\circ C$. In the N^* phase the birefringence strongly decreases when approaching the liquid phase : $\Delta n = 0.19$ at $159^\circ C$ and 0.13 at $167^\circ C$. In the three twisted mesophases, the right rotatory power indicates a right-handed helix.

4.4 THE COMPOUND γ : $KS_A N_{re}^* S_{Are} N^* I$. — For the γ compound the tendency to homeotropy is as strong as for the first one α . The experiment can still be performed with two samples.

For the reentrant cholesteric phase, the sample is introduced at $120^\circ C$, as far as possible of the S_A transitions. The sample is cooled to $113^\circ C$ near the S_A transition, and then heated over the whole N_{re}^* range. The Grandjean texture is generally stable and all measurements are performed with one sample. When crossing the S_{Are} phase, the texture becomes homeotropic, and the Grandjean texture does not appear in the high temperature N^* .

In the N^* phase, the Grandjean texture is obtained only if the sample is introduced in the stage near the clarification point, when the mesophase has a sufficient fluidity. Pitch variations over the N^* phase are then obtained on cooling with the same sample.

Fig. 3. — β compound (described in Sect. 2) : variations of the pitch *versus* temperature.

Fig. 4. — β compound (described in Sect. 2) : comparison of reduced rotatory power and reduced pitch variations.
a) The birefringence is quasi constant in the N^*_{re} phase.
b) The birefringence falls near liquid state.

Near the S_{Are} phase, irrevocable finger-points often appear.

We mention at last another difficulty : the stilbene group is very light-sensitive ; if the sample is lightened by the white light of the microscope, the configuration of the molecules change from trans to cis ; in the lightened place, the thermodynamic, the structural and the optical characters change ; the reentrant N^* phase can even disappear if the exposure is too long. This difficulty can be solved by reduction of the incident light flow with an interferential filter ($5\,640\text{ \AA}$), filter besides necessary for the rotatory power study ; a slight alteration is still visible : at the end of a series of experiments, the transition occurs at temperatures different from those measured by calorimetry [5, 4] (Sect. 2) : 127°C instead of 131°C for $N^*_{re} \rightarrow S_{Are}$ and 223°C instead of 217°C for $S_{Are} \leftarrow N^*$ (Figs. 5 and 6).

Results. — The figure 5 gives the pitch variations in the two cholesteric phases ; the reentrant phase exhibits two divergences of the pitch, near the $S_A - N^*_{re}$ (113°C) and $N^*_{re} - S_{Are}$ (127°C) transitions ; the pitch is minimum near 120°C .

The rotatory power variations confirm the pitch measurements (Fig. 6a) and gives the sign, left, of the helicity. In the N^* phase, the pitch diverges near the S_A phase (223°C) and is quasi constant from 235°C to 275°C . The rotatory power variations (Fig. 6b) reveal a strong decrease of the birefringence above 240°C .

5. Conclusions.

Precise and detailed measurements of the twist are performed on three pure compounds presenting

Fig. 5. — γ compound (described in Sect. 2) : variations of pitch *versus* temperature.

Fig. 6. — γ compound (described in Sect. 2) : comparison of reduced rotatory power and reduced pitch variations.
a) The birefringence is quasi constant in the N_{re}^* phase.
b) The birefringence falls near liquid state.

different sequences of phases, and having a reentrant cholesteric phase. In the high temperature cholesteric phase, the pitch is infinite near the $S_A - N^*$ transition, and gets a quasi constant value up to the liquid phase. Rotatory power measurements reveal a strong decrease of the birefringence.

In the reentrant cholesteric phase of the α compound, (sequence $KN_{re}^* S_A N^* I$) the pitch is quasi constant far from the S_A , and diverges near the $N_{re}^* - S_A$ transition. For β (sequence $KS_F^* S_c^* N_{re}^* S_A N^* I$), the pitch slowly decreases from a limite value at the $S_c^* - N_{re}^*$ transition, shows a minimum, and increases to diverge at the $N_{re}^* - S_A$ transition.

For γ ($KS_A N_{re}^* S_{Are} N^* I$), the pitch has two divergences and a minimum. For the three products, similar values of pitch appear in the two cholesteric phases.

The pitch measurements are performed on prismatic cells with Grandjean-Cano planar texture. Except for the N^* phase of β , a unique sample is used for the whole temperature range. The rotatory power is studied to control or complete the pitch measurements and to give the sense of the helix (left for α , γ ; right for β).

The S_c^* phase of β is studied by an original method: the strong tendency to be homeotropic (which is a serious disadvantage to get Grandjean planar texture in the N^* phases) leads to a pseudohomeotropic texture in the S_c^* phase, with regular 2π disclinations permitting the S_c^* pitch measurements.

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