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## Novel sequence with incommensurate SA phases in a new dimesogenic liquid crystal

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**Abstract.** — We present differential scanning calorimetry, optical and X-ray diffraction measurements for a new dimesogenic liquid crystal compound (KI5). The rich polymorphism of this compound includes new smectic phases and rare phase transitions. In particular the first observation in a pure compound of two incommensurate SA phases as well as cholesteric and helical smectic phases (TGB and SC\* phases) are reported. We discuss this observation in terms of the dual peculiar structural character of the molecule : a polyphilic and dimesogenic system including the concept of the central flexible spacer.

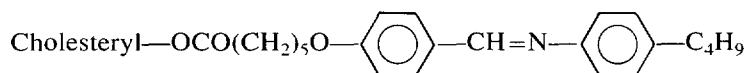
### 1. Introduction.

For many years most of the low molar mass liquid crystals had to be composed of two blocks of different chemical nature : their molecules comprised one single rigid core covalently bonded to one or two alkyl chains in a rod-like configuration. Such simple molecules are no longer the unique class known to promote nematic and smectic phases. Initially keeping the concept of two distinct parts (aromatic cores/paraffinic chains), of particular interest are dimesogenic liquid crystals which contain two similar rigid cores — joined by a central flexible alkylene spacer — and attached to which are generally two terminal alkyl chains [1-7]. Such dimers are often regarded as model compounds for semiflexible main chain liquid crystalline polymers [1-5].

At this stage the question arises of the specific roles played by three-block molecules, instead of two, in the mesophase formation. Two main ways are offered to tailor-make dimesogenic L.C. which contain three distinct and amphipatic parts. Firstly, we can introduce alternative sequences with a different chemical nature of the spacer with respect to the tails (or reciprocally). For instance, it has already been reported that the mesomorphic behavior is quite different in dimeric compounds having highly flexible siloxane containing spacer and aliphatic tails [8-12]. Moreover, taking into account the fact that chemists have devised a large variety

of polyphilic systems in conventional low molar mass liquid crystals [13, 14], we can also imagine the synthesis of dimesogenic compounds in which alkyl tails are replaced by perfluorinated (or semiperfluorinated) chains or siloxane moiety, still keeping an aliphatic spacer.

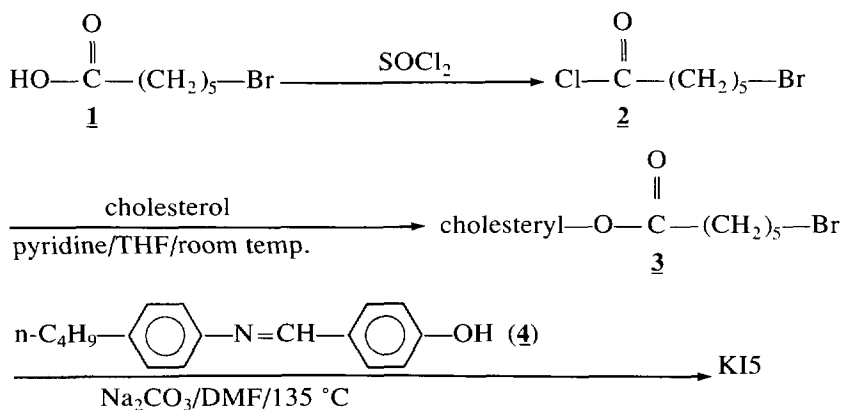
Secondly beyond the notion of dimers, one can induce novel supramolecular systems with compounds consisting of two chemically different mesogenic rigid units [15]. The polymorphism and the structural behavior of such dimesogenic LC compounds remain still open. Our strategy is to investigate the latter situation met here by the following dimesogenic compound « KI5 » :



This compound was synthesized. It exhibits a high degree of polymorphism and all the mesomorphic phases have been studied using D.S.C., microscopy and X-ray diffraction.

## 2. Synthesis.

The synthetic route to KI5 is shown in the following scheme



6-Bromohexanoic acid (**1**,  $3.77 \times 10^{-2}$  mol) was dissolved in 80 ml of purified thionyl chloride and the mixture was refluxed for 4 h. The excess thionyl chloride was removed by distillation under a reduced pressure (1 Torr). To the residue (6-bromohexanoyl chloride : **2**) added slowly at 0 °C was  $3.39 \times 10^{-2}$  mol of cholesterol dissolved in a mixture of dry tetrahydrofuran (50 ml) [16] and pyridine (5 ml) [16]. The mixture was stirred at room temperature for 12 h under dry nitrogen atmosphere. At the end of reaction, the mixture was poured into a large excess (500 ml) of 0.1 M HCl. The precipitate formed was collected on a filter and washed thoroughly several times with 0.5 M sodium carbonate and distilled water. The washed crude product **3** (cholesteryl 6-bromohexanoate) was dried at room temperature (0.1 Torr). It was then recrystallized three times from dry n-pentanol and dried at 40 °C in a vacuum oven.

Compound **4** was prepared separately [15] by refluxing for 3 h the ethanol solution (140 ml) of 4-hydroxydebenzaldehyde (0.125 mol) and 4-n-butylaniline (0.125 mol). The reaction mixture was cooled to 0 °C and the product **4** (N-(4-hydroxybenzilidene)4-n-butylaniline) thus obtained was recrystallized from ethanol.

The final compound KI5, N-[4-(6-cholesteryloxycarbonyl) pentyloxy]-benzylidene]-4-n-butylaniline, was synthesized by reacting compound **3** with compound **4**. Compound **4** ( $1.42 \times 10^{-2}$  mol) was dissolved in 100 ml of dry N,N-dimethylformamide (DMF) [16].



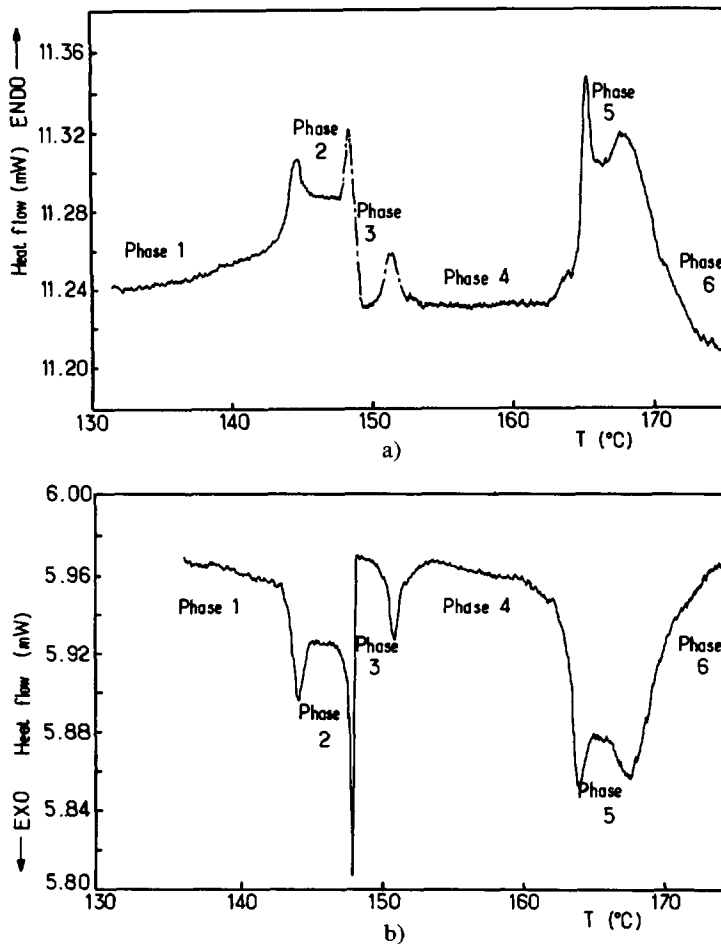


Fig. 2. — DSC thermograms for the heating (a) and cooling (b) of compound KI5 (rate 1 °C/min) suggesting the phase sequence indicated in the next. Note that in this figure the energy scale is considerably expanded by comparison with figure 1.

Cooling from the isotropic liquid resulted in the formation of an iridescent cholesteric phase, either in the form of cholesteric fan defects or of a Grandjean plane texture.

- For the subsequent observations, the substrate was treated with an aligning agent (rubbed polyimide) resulting in the formation of a cholesteric planar texture.

The transition from the cholesteric to Phase 5 was mediated by the onset of slight striations and this Phase 5 also exhibits a Grandjean texture (Plate 1 : 166 °C) similar to that of the cholesteric phase. Moreover, when the planar texture of Phase 5 was rotated between crossed polarizers, no extinction could be obtained, which is typical of a helical structure. One can also note that the pitch length increases considerably at the cholesteric-Phase 5 transition and becomes too long for the reflection to occur in the visible range.

On cooling, at 164.5 °C, focal conics of Phase 4 grow at the expense of the planar texture of the Phase 5. Subsequent cooling produced very subtle changes in this focal conic fan texture at the Phase 4 → Phase 3 transition : the Phase 4 texture seems slightly broken (Plate 2 : 158 °C) by comparison with that of Phase 3, showing a simple smooth fan texture (Plate 3 : 151 °C).

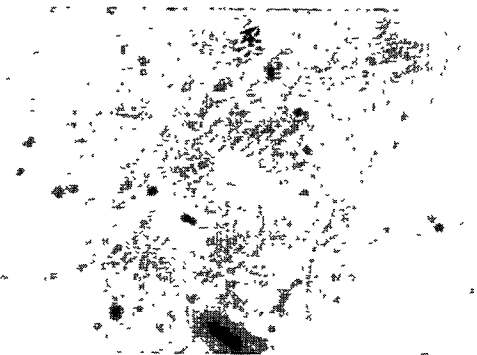


Plate 1.



Plate 2.



Plate 3.

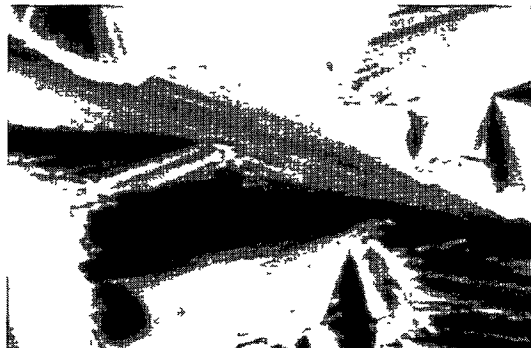


Plate 4.



Plate 5.

Microphotographs of KI5 under crossed polars. Magnification  $\times 400$ . Plate 1 : 166 °C, Phase 5 — Plate 2 : 158 °C, Phase 4 — Plate 3 : 151 °C, Phase 3 — Plate 4 : 147 °C, Phase 2 — Plate 5 : 140 °C, Phase 1. Only subtle changes are observed in the focal conic texture through the different phases. Phase 4 and Phase 2 textures appear slightly broken and have a fuzzy aspect by comparison with the Phase 3 and Phase 1 ones.

The focal conic defects are kept when cooling through the Phase 3  $\rightarrow$  Phase 2 and Phase 2  $\rightarrow$  Phase 1 transitions : Phase 2, like Phase 4, exhibits slightly broken focal conics (Plate 4 : 147 °C) and Phase 1, as Phase 3, a fan shaped texture (Plate 5 : 140 °C).

Thus, these microscopic observations give direct evidence to identify the phases 1 to 4 as smectic phases and thus we can label them as S1, S2, S3 and S4.

- If we now observe between crossed polarizers an unaligned sample (i.e. with no surface treatment), a homeotropic texture spontaneously appears with the onset of the S4 phase. Cooling down, this homeotropic (or pseudo homeotropic) texture is kept without any change till the S1 phase. Thus, according to these observations, the four smectic phases (1 to 4) appear to be like uniaxial media where the molecules are on average parallel (SA) or symmetrically disposed (SC\*) with respect to the viewing direction. In the latter hypothesis, the helical pitch must be reasonably short (less than 1  $\mu\text{m}$ ) as usually observed for cholesterol derivatives, and in this sense no dechiralisation lines can be observed by microscopic observations of planar textures. This could also explain the fuzzy aspect of plates 2 and 4. Further identifications of the different smectic phases need a structural analysis.

At last, we can note that Phase 5, which is located between a cholesteric and a smectic phase (S4), has a texture which closely resembles that of TGB phases [17, 18]. In any case, structural evidence for distinguishing Phase 5 from a cholesteric will be gained by X-ray diffraction experiments.

**3.2 X-RAY DIFFRACTION STUDIES.** — The identification of the different liquid crystalline phases was carried out using the characteristic features of X-ray diffraction patterns.

X-ray scattering experiments were performed using a  $\text{CuK}_\alpha$  radiation of an 18 kW rotating anode X-ray generator. A flat pyrolytic graphite (002) monochromator delivered a  $0.5 \times 0.5 \text{ mm}^2$  beam onto the sample. The scattered radiation was collected on a two dimensional detector Imaging Plate system. The sample to the detector distance was 830 mm through helium in order to lower absorption and diffusion. The instrumental resolution in reciprocal space was about  $\Delta q \approx 1.4 \times 10^{-2} \text{ \AA}^{-1}$  FWHM in both vertical and horizontal directions ( $q$  is the momentum transfer vector  $q = 4 \pi \sin \theta / \lambda$ ). The sample-detector distance could be reduced to 200 mm to investigate the wide angle region.

Lindemann tubes ( $\Phi = 1 \text{ mm}$ ) were filled by capillarity at high temperatures without an alignment procedure and sealed under dry atmosphere. The capillary tube was introduced in an

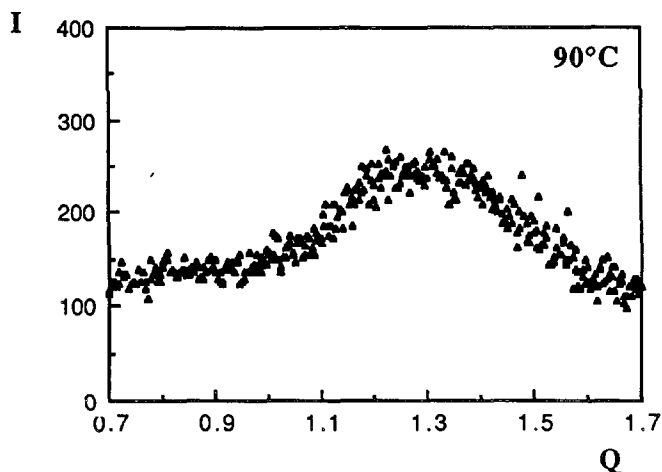


Fig. 3. — Intensity profiles at wide angle of the X-ray powder diffraction pattern of phase 1 at 90 °C.

oven whose temperature stability was  $\pm 10$  mK. The tube axis was vertical and perpendicular to the beam. Exposure times were 15 min.

As shown in figure 3, above the melting point and throughout the mesomorphic range, the intensity profiles in the wide scattering angle region show a broad diffuse band centered at  $q \approx 1.28 \text{ \AA}^{-1} = 2 \pi/4.9 \text{ \AA}^{-1}$  corresponding to only a positional liquid-like short range order within the smectic layers. This intensity profile is weakly temperature dependent. Although not very pronounced, the asymmetric shape of the intensity profile might correspond to the possible existence, according to the molecular structure, of two nearest neighbour molecular distances in the plane of the layers as yet reported for other polyphilic systems [19].

Thus all the smectic phases under study have to be referred to as « fluid smectics » and not lamellar 3D crystalline phases.

We now describe the thermal evolution of the X-ray diffraction patterns in the small scattering angle region through the sequence previously evidenced both by calorimetric and microscopic observations.

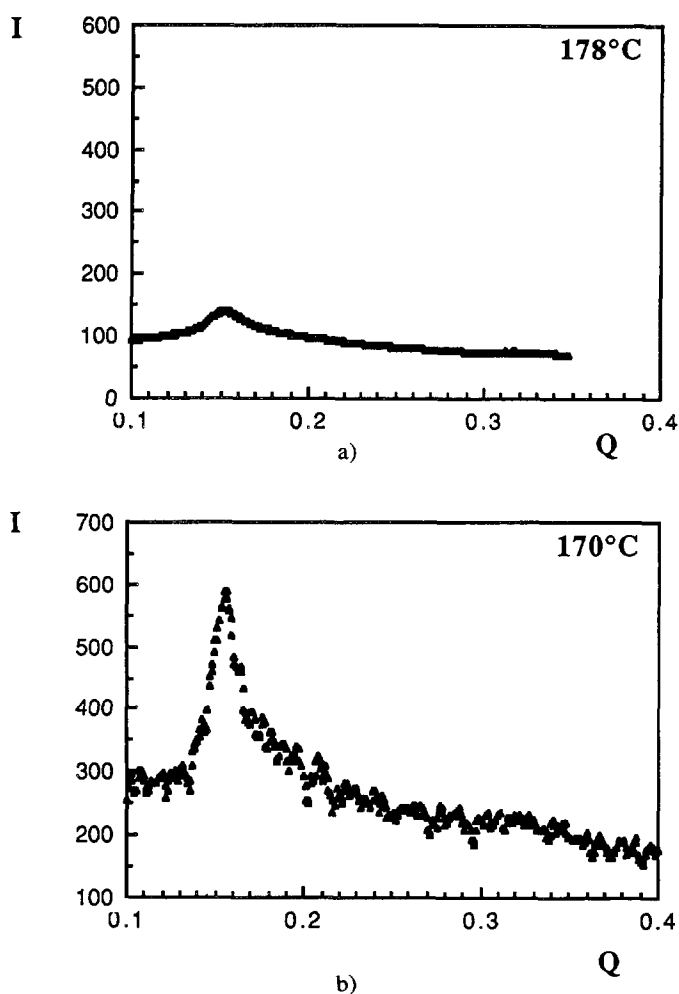


Fig. 4. — Intensity profiles at low angle of the X-ray powder diffraction patterns of the cholesteric phase a) at 178 °C, b) at 170 °C near the  $N^* \rightarrow$  Phase 5 transition (non limited resolution peak).



At high temperatures in the cholesteric phase, the diffraction pattern exhibits a clearly broad ring (larger than the resolution) of radius  $q = 0.150 \text{ \AA}^{-1}$  (corresponding to  $41.6 \text{ \AA}$  lattice spacing), whose intensity increases near the  $N^* \rightarrow$  Phase 5 transition (Figs. 4a and 4b). Inspection of figure 4b indicates large smectic fluctuations in the cholesteric phase.

In Phase 5, the ring narrows. The scattering vector of the maxima remained unchanged  $q = 0.150 \text{ \AA}^{-1}$ . The intensity is spread uniformly over the ring. The smectic character of Phase 5 is evidenced by the observation of one resolution limited X-ray peak (Fig. 5). Combined to the microscopic observations, it appears reasonable to assign this phase to be a TGB one.

On cooling below  $164 \text{ }^\circ\text{C}$  in the *S4* phase, the X-ray diffraction patterns in the small angle region equally show one ring (Fig. 6 : the intensity profile indicates a resolution limited peak) the radius of which increases from  $q = 0.150 \text{ \AA}^{-1}$  at  $164 \text{ }^\circ\text{C}$  to  $q = 0.153 \text{ \AA}^{-1}$  at  $151 \text{ }^\circ\text{C}$ . The temperature dependence of this first order diffraction maximum corresponds to a small diminution of the layer spacing from  $41.8 \text{ \AA}$  to  $41 \text{ \AA}$  with decreasing temperature, and this indicates the existence of a fluid tilted smectic phase of  $SC^*$  type, which is in agreement with the optical texture. We can note in figure 6 that the intensity over the ring is not perfectly uniform indicating a slight deviation from a typical X-ray powder diffraction pattern of a smectic phase.

At  $150 \text{ }^\circ\text{C}$ , in the temperature range of the *S3* phase detected from the DSC thermogram (Fig. 2), the X-ray pattern exhibits two very unexpected and striking features.

- Firstly, the sample spontaneously orientates (Fig. 7a) leading to one principal domain with smectic planes lying horizontally (and to a lower extent in the vertical direction generated by a second domain of minor importance). Such marked anisotropy of the molecular organization is clearly observed by the presence of one set of three meridional reflections (resolution limited).

- Secondly, these three collinear modulations are simultaneously condensed with incommensurate wave vectors at the position  $q_1 = 0.143 \text{ \AA}^{-1}$ ,  $q_2 = 0.175 \text{ \AA}^{-1}$  and  $q_3 = 0.319 \text{ \AA}^{-1}$  in the reciprocal space, as shown in the intensity profile (Fig. 7b). They correspond in the real space to different periodicities of wavelengths  $43.8 \text{ \AA}$ ,  $35.8 \text{ \AA}$  and  $20 \text{ \AA}$  respectively. According to microscopic observations (which strongly suggest a smectic A phase) and to this

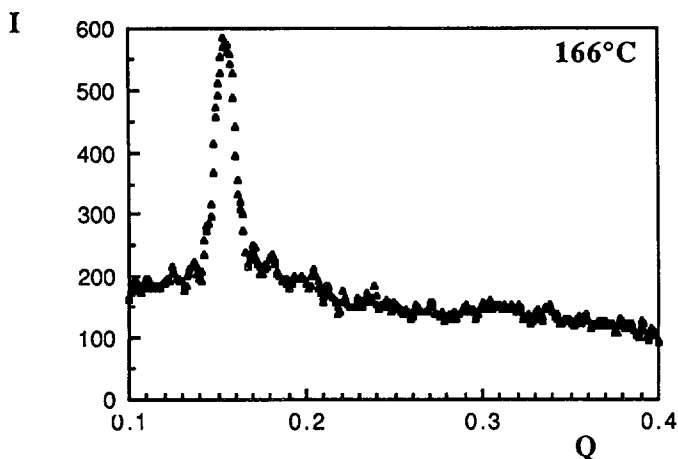


Fig. 5. — Intensity profile at low angles of the X-ray diffraction pattern of Phase 5 at  $166 \text{ }^\circ\text{C}$  (resolution limited peak).

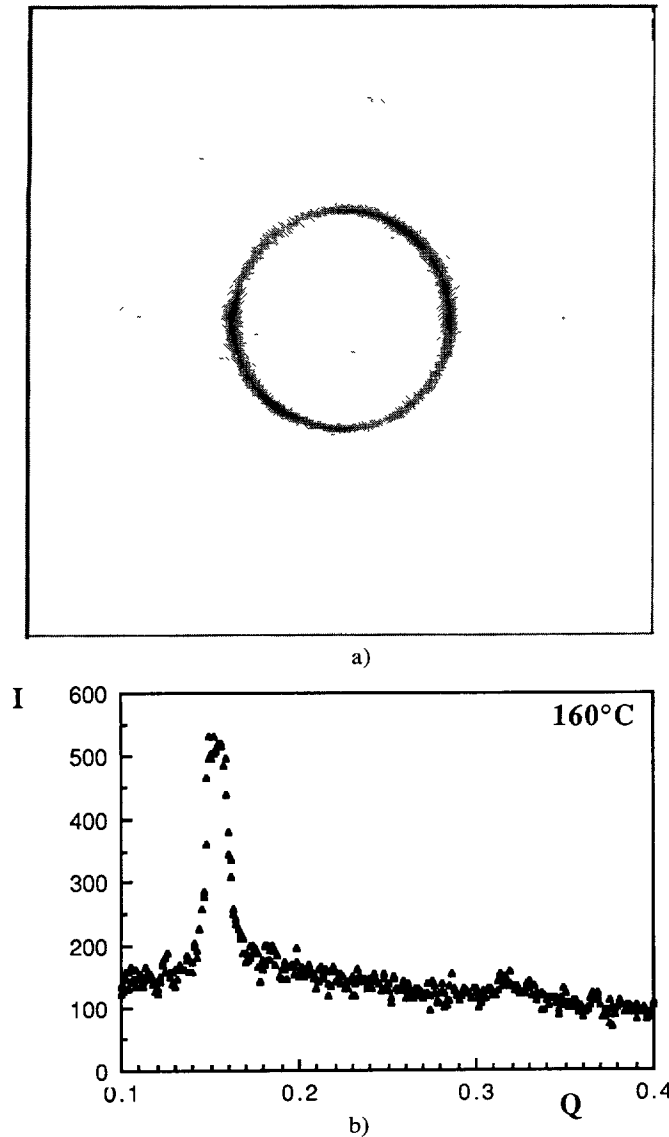


Fig. 6. — X-ray diffraction pattern in the small angle region in the S4 phase at  $160^\circ\text{C}$  (a) with the corresponding intensity profile (b).

X-ray analysis, Phase 3 can now be claimed to be an incommensurate SA phase. Indeed, the spontaneous preferred orientation of the sample in the X-ray beam provides unambiguously the relative orientation of the  $q_1$ ,  $q_2$  and  $q_3$  vectors which appear to be collinear in one single domain. Although the mosaicity is typically a few degrees the absence of off-axis reflections rules out any additional translational order in the plane of the layers and hence this S3 phase cannot be a biaxial antiphase ( $\tilde{A}$ ,  $A_{\text{cre}}$ ,  $\tilde{C}$ ) [20]. However, the law of conservation of vectors is also satisfied:  $q_3 = q_1 + q_2$  over the small temperature interval of the S3 phase. Thus, this condition initially set for biaxial lockins [21, 22] seems necessary to the formation of the layers even in an incommensurate SA phase in which the three vectors are collinear.

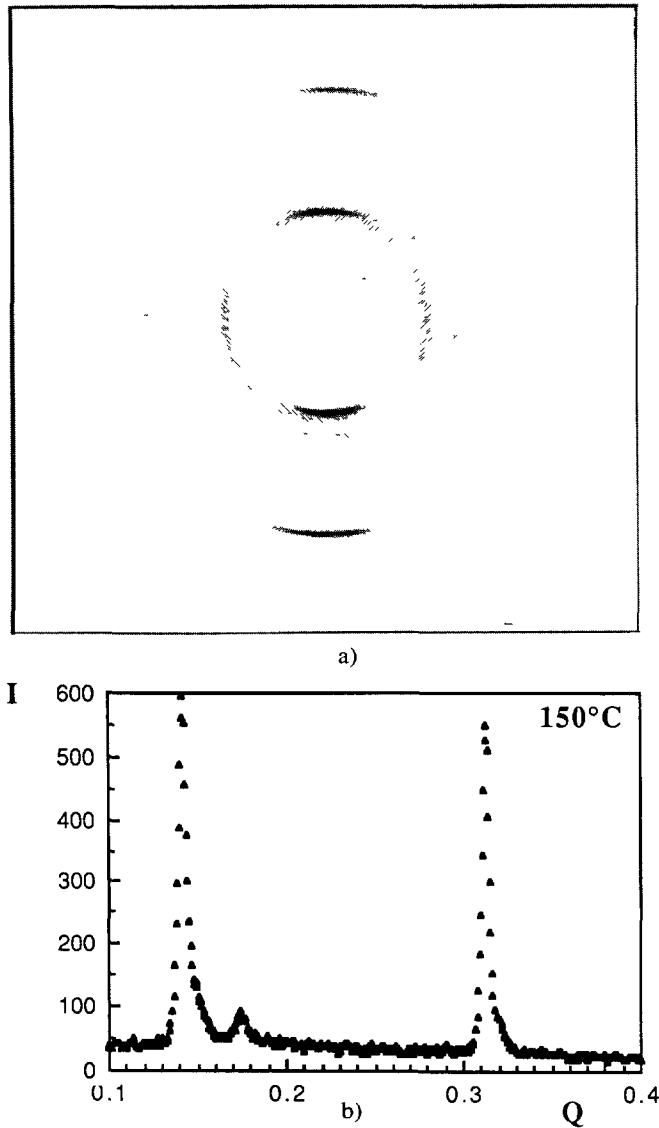
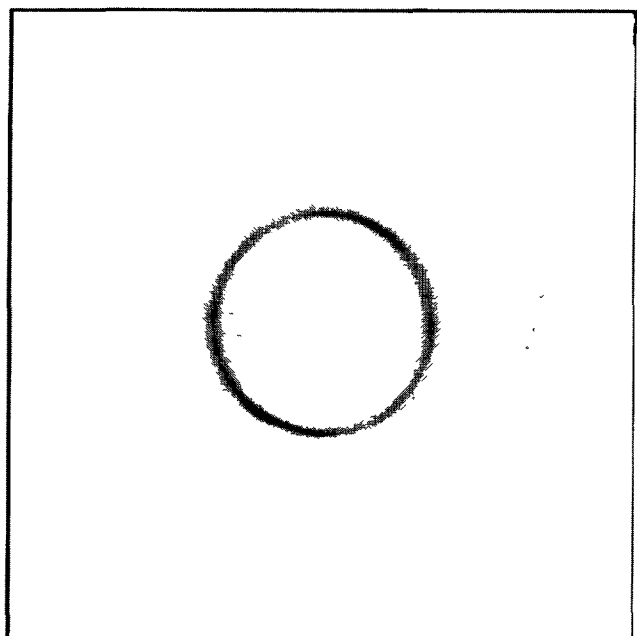


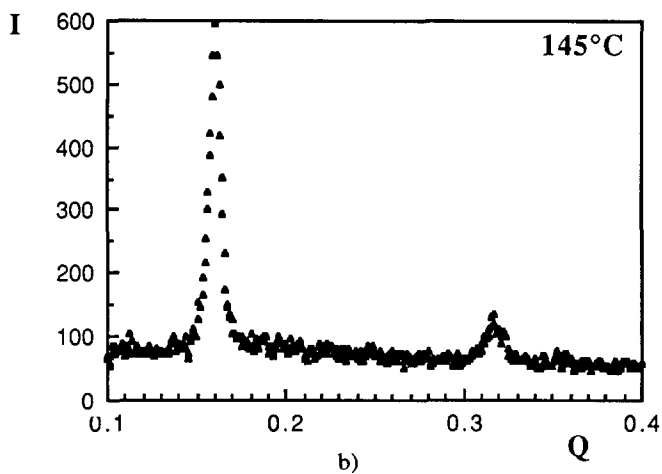
Fig. 7. — a) X-ray diffraction pattern in the small angle region in the  $S_3$  phase at  $150^\circ\text{C}$ . The sample spontaneously orientates leading to one principal domain with smectic planes lying horizontally. b) Corresponding intensity profile along the vertical direction.

Cooling further down through the  $S_3 \rightarrow S_2$  transition, the orientation of the sample is disrupted. In addition, the X-ray pattern of the  $S_2$  phase in the small angle region displays two rings (Fig. 8a) with commensurate wavevectors (Fig. 8b). These are the first and second order Bragg reflections on the layers. The fundamental  $q$  vector extends from  $q = 0.153 \text{ \AA}^{-1}$  at  $149^\circ\text{C}$  to  $0.155 \text{ \AA}^{-1}$  at  $145^\circ\text{C}$ . Thus in the real space, the layer spacing is slightly depressed from  $41 \text{ \AA}$  to  $40.5 \text{ \AA}$  with decreasing temperature: this behaviour, in agreement with the optical observations, suggests once again the occurrence of a fluid tilted smectic phase, that is to say, the identification of the  $S_2$  phase to a  $S_C^*$  phase.

At lower temperatures, with the onset of the  $S_1$  phase, three wave vectors  $q_1$ ,



a)



b)

Fig. 8. — X-ray diffraction pattern in the small angle region in the S2 phase at 145 °C (a) with the corresponding intensity profile (b).

$q_2$  and  $q_3$  are again observed : just below the S2  $\rightarrow$  S1 transition,  $q_2$  appears like a shoulder in the  $q_1$  peak on the intensity profile (Fig. 9). As the sample was cooled down further,  $q_1$  and  $q_2$  progressively separate.  $q_1$  moving to the lower values and  $q_2$  to higher ones. In the whole temperature range, the third wave vector  $q_3$  keeps essentially a quasi constant position. Upon cooling in the S1 phase, the sample has a natural tendency to orientate and at 110 °C the X-ray pattern shows that the smectic planes are mainly stacked horizontally : well-oriented patterns of a same principal domain are thus obtained (Fig. 10a). It results that the three wave vectors  $q_1$ ,  $q_2$  and  $q_3$  appear collinear. Thus the S1 phase is characterized by three collinear

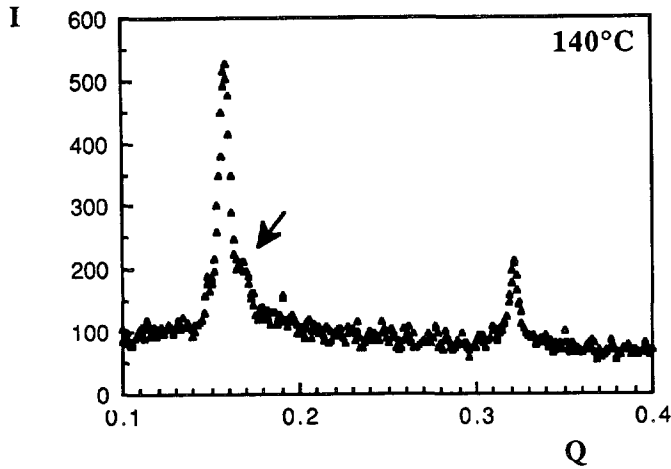


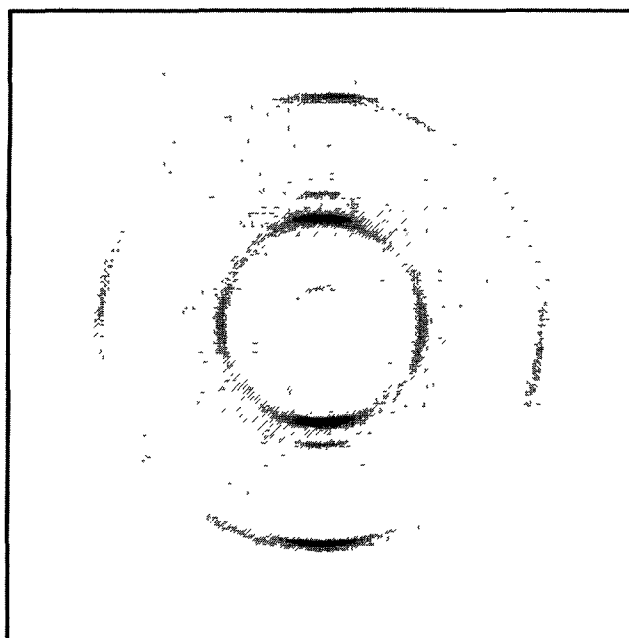
Fig. 9. — Intensity profile in the S1 phase showing three wavevectors  $q_1$ ,  $q_2$  and  $q_3$ :  $q_2$  appears like a shoulder on the  $q_1$  peak near the S2  $\rightarrow$  S1 transition (140 °C).

incommensurate wave vectors (Fig. 10b) and keeping in mind the corresponding microscopic textures, we have assigned this phase S1 to be a one-dimensional modulated incommensurate smectic A phase. The two reflections connected to  $q_1$  and  $q_3$  show relative intensities of about the same order of magnitude, while the third reflection corresponding to the wavevector  $q_2$  appears as a satellite of weaker intensity around  $q_1$ . It is important to note that the sum of the values of the wave vector values  $q_1$  and  $q_2$  remain constant and equal to the  $q_3$  value over the large temperature range of the S1 phase. One can also note that  $q_1$  decreases with  $T$  from  $0.153 \text{ \AA}^{-1}$  at  $144 \text{ }^\circ\text{C}$  to  $0.143 \text{ \AA}^{-1}$  at  $90 \text{ }^\circ\text{C}$  and this last value obtained at low temperature in S1 corresponds to the  $q_1$  position in the S3 phase. All these X-ray results strongly suggest that the S1 phase and the S3 phase are the same type of incommensurate SA phase. This is also in agreement with the similarity of their optical textures.

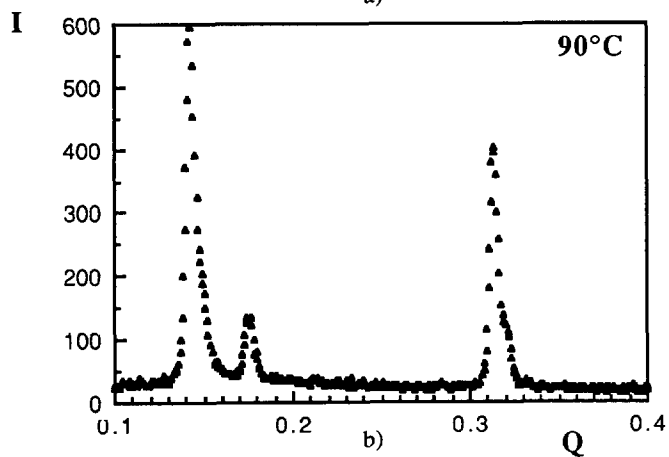
In addition, the largest periodicity ( $\sim 44 \text{ \AA}$ ), which corresponds to the wavevector  $q_1$ , can probably be connected to the molecular length of KI5 ( $l = 46 \text{ \AA}$  measured with SASM models in the most extended conformation). Taking into account the large difference of molecular area of the two mesogenic parts we can assume a head-to-tail arrangement with a complete overlapping of the molecules: such an arrangement would satisfy space filling conditions as well as layering periodicity. Moreover, one can note that this periodicity is larger in the two incommensurate phases than in the  $S_C^*$  phases (which is also consistent with the occurrence of SA-like incommensurate phases), and if we assume the same overlapping in  $SA_{\text{inc}}$  and  $S_C^*$  phases, tilt angles can be evaluated from X-ray results:  $20\text{-}22^\circ$  are found in both  $S_C^*$  phases with respect to the  $SA_{\text{inc}}$  phase (S3).

The smallest periodicity found in the incommensurate SA phases  $\left(\frac{2\pi}{q_3} \sim 20 \text{ \AA}\right)$  could correspond either to the length of the cholesteryl moiety or to the length of the aromatic mesogen including a part of the spacer (see Fig. 11). From a molecular point of view, this layered superstructure, corresponding in fact to a sublayer order, could originate from the similarity of the two mesogenic groups lengths. At last, the  $q_2$  satellite appears like a signature connected to the incommensurability and which could not be assigned to a molecular characteristic length.

We can summarize the X-ray results throughout the smectic range from the evolution of the wavevectors  $q$  reported in figure 12 as well as of the periodicities in the real space in figure 13.



a)



b)

Fig. 10. — a) X-ray diffraction pattern in the small angle region in the S1 phase at 90 °C. The sample has been spontaneously orientated leading to one principal domain with smectic planes lying horizontally. b) Corresponding intensity profile along the vertical direction.

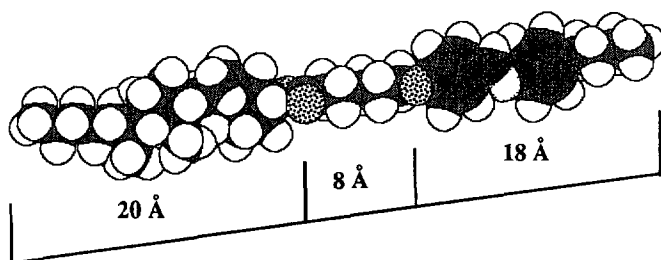


Fig. 11. — Molecular model of compound KI5.

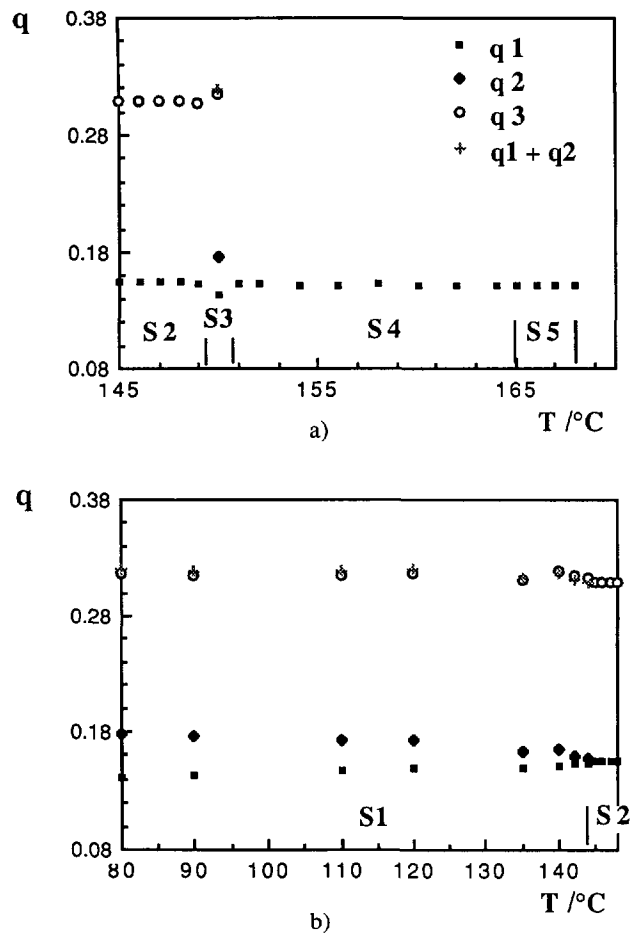


Fig. 12. — Evolution of the wavevectors over the whole temperature range of the smectic phases. In the S1 and S3 phases, the sum  $q_1 + q_2$  is reported by comparison with  $q_3$ .

#### 4. Conclusion.

A new type of polyphilic and dimesogenic compound has been synthesized and shown to exhibit a quite novel polymorphism. Taking into account the different complementary characterizations, we can make the following phase assignment for the KI5 compound :

$$\text{Crystal} \rightarrow \text{SA}_{\text{inc}} \rightarrow \text{S}_{\text{C}}^* \rightarrow \text{SA}_{\text{inc}} \rightarrow \text{S}_{\text{C}}^* \rightarrow \text{TGB} \rightarrow \text{N}^* \rightarrow \text{Isotropic liquid} .$$

The TGB was assigned from the following four main arguments : i) it is located between a cholesteric and a  $\text{S}_{\text{C}}^*$  phase ii) it exhibits a planar texture like the cholesteric one iii) it possesses an helical structure and iv) X-rays give structural evidence for a fluid smectic. We stress that X-ray diffraction on powder sample cannot distinguish between  $\text{TGB}_{\text{A}}$  and  $\text{TGB}_{\text{C}}$ . Nevertheless we can note that a  $\text{TGB}_{\text{A}}$  phase has been detected in an optically active comb like polymer having a derivative of cholesterol as side chains [23].

It is evident that the layer spacings in the commensurate smectic phases (TGB and the two  $\text{S}_{\text{C}}^*$ ) are comparable ( $\approx 41 \text{ \AA}$ ). A complete description of the  $\text{S}_{\text{C}}^*$  phases would need X-ray

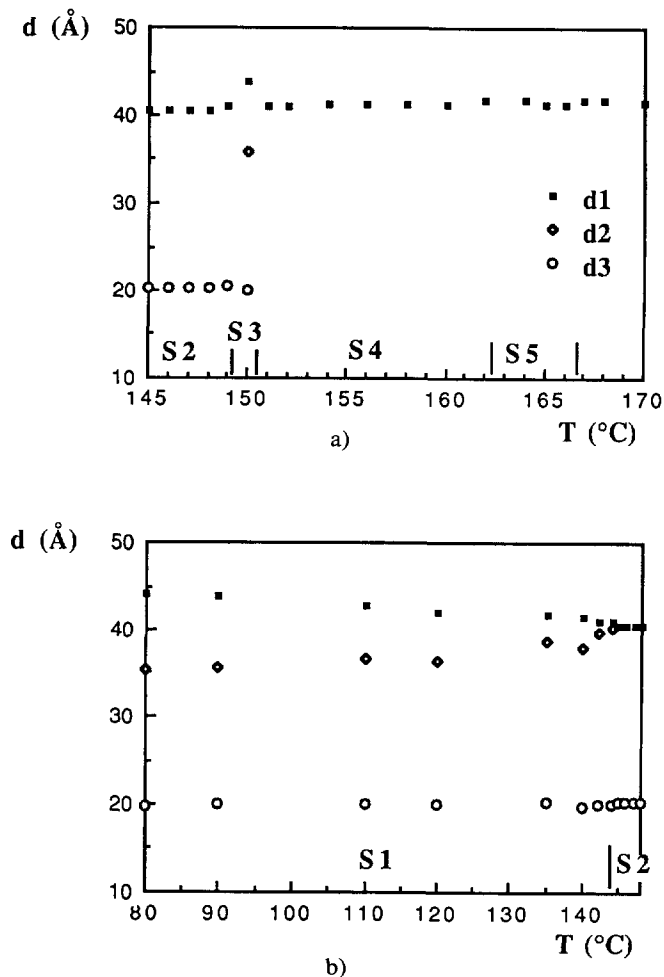


Fig. 13. — Evolution of the periodicities  $d$  corresponding to the different  $q$  vectors over the whole temperature range of the smectic phases.

diffraction on aligned samples. Moreover these phases, if they are  $S_C^*$  could be ferroelectric. We can note that preliminary electro-optic investigations reveal multistable switchings in the S4 phase different from those observed in the S2 one.

As yet reported in the upper text, the onset of each  $SA_{inc}$  phase gives rise to a principal spontaneous alignment of the sample held in a Lindemann glass capillary. This is a very intriguing but favourable situation which enables us to prove, from the two-dimensional X-ray patterns, the collinearity of the three incommensurate wavevectors which coexist in these smectic phases.

Combining chirality, mesogenic rigid groups and a central aliphatic part, the helical structures  $N^*$ , TGB and  $SC^*$  could be expected in the K15 compound. In contrast, the formation of incommensurate smectic A phases was rather unexpected. It is very likely that the occurrence of the incommensurate smectic A phase is independent of molecular chirality and, by comparison with conventional mesogens, the novelty of the K15 compound originates from its *dual peculiar structural character* inextricably linked : a polyphilic system together with a dimesogenic aspect including the concept of the central flexible spacer. Nevertheless, there is



no particular reference to the effect that these molecular geometries (or others) have on the stabilization of the incommensurate fluid smectic phases.

In these incommensurate SA phases, the coexisting wavevectors are not independent : they satisfy a general additivity rule for the formation of the smectic layered structures. This one-dimensional lock-in condition can bring out the Prost and Barois « frustated smectics » model predicting incommensurate SA phases [22, 24-26]. In essence, this phenomenological model is based on the existence of two natural periodicities and their molecular origins are not necessarily those of polar systems. Basically, the existence of two incommensurate intrinsic periodicities can be envisioned at the microscopic level from head to tail physical associations of polar molecules as initially noticed by Prost [27] or from distinct smectogenic groups chemically (and partially) coupled as it is the case here. In terms of elasticity, if the sublayer order ( $q_3$ ) corresponds to a higher stiffness than the layering order ( $q_1$ ), the model predicts that a satellite ( $q_2$ ) can be visible around  $q_1$  and hence  $q_3 = q_1 + q_2$  and our results corroborate this condition.

In fact, some analogous behavior between polar systems and KI5 compound can be pointed out :

i) incommensurate « monolayer » fluctuations in a « partial bilayer » SA phase have been evidenced in a pure polar compound [28] ;

and ii) assuming that the S3 and S1 phases are the same incommensurate  $SA_{inc}$  phase, the analogy may be also extended to the reentrant phenomenon, very common in polar systems. On the other hand, we can note that the incommensurate SA phases previously reported in binary diagrams of polar compounds [29-32] have been recently proved to be merely coexistences of two SA phases [33-35].

In the light of the new results presented here, this argument cannot be put forward. First of all the present system is a pure compound instead of a mixture. Secondly, the S1 phase exists over a large temperature range and thirdly a significant discontinuity of the wavevectors is observed at the transitions towards the S1 and S3 phases.

Finally, in this regard of the first observation of  $SA_{inc}$  phases in KI5, we stress that the dependence of the formation of such incommensurate phases upon molecular parameters is still unclear in fluid complex. Physical chemistry investigations are currently in progress on several homologues of KI5 to solve in part this problem. This effect is just one of the many exciting phenomena that will probably be unearthed in incommensurate fluid smectic liquid crystals.

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