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From Incommensurability to Commensurability in Smectic Phases for a Series of Dimesogenic Liquid Crystals

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(Received 9 February, accepted 5 April 1995)

Abstract. — Genuine incommensurate smectic A phases were recently discovered, among the rich polymorphism of a new dimesogenic liquid crystal compound (K15). In the present paper, we examine the role played by molecular parameters in the existence of such incommensurate state. In a series of several homologues of K15, we find that two smectic modulations exist in agreement with the phenomenological model of “frustrated smectics”. The condensation of one or the other of these modulations and their coexistence appear to be closely related to the length of the flexible spacer linking the two mesogenic moieties. We observe that only for intermediate spacer length, the elasticity of the system allows the occurrence of incommensurate SA phases.

1. Introduction

The phenomenological Landau model of “frustrated smectics” developed by Prost and Barois [1–4] is based on the existence of two incommensurate lengths in the system. The great number of fluid smectic phases experimentally discovered [5] in polar mesogens arises from the competition between these two incommensurate periodicities (L, the molecular length, and \( L' \), the length of a pair formed by dipolar association with \( L < L' < 2L \)). The impossibility to satisfy contradictory tendencies simultaneously is solved in different ways: lock-in of the two periods (bilayer \( S_{A2} \)), condensation of one period with the coexistence of incommensurate fluctuations corresponding to the other one [6, 7], escape from the incommensurability by forming two-dimensional modulated phases (antiphase \( S_A \), ribbon phase \( S_C \) [5]) and finally incommensurate \( S_{A_{inc}} \) phases, in which the two competing periodicities coexist at long range order along the layer normal. Experimentally speaking, these \( S_{A_{inc}} \) are questioned in polar systems [8–10] but only incommensurate \( S_E \) [11] or \( S_B \) [12] have been clearly observed.

Note that the molecular origine of the two natural periodicities are not necessarily those of polar systems. For example, they can also be induced by sterical frustrations [13]: in this sense, incommensurate \( S_{Ad} \) fluctuations in a monolayer \( S_{A1} \) have been observed in non-symmetric swallow-tailed mesogens [14].

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Moreover, we have recently reported the existence of genuine incommensurate S_A phases in a new dimesogenic compound without strong polar head [15]. This polyphilic dimesogenic molecule consists in two chemically different mesogenic units – a cholesteryl one and a classical two aromatic ring mesogen connected through a central paraffinic flexible spacer and this new architecture can be regarded as a three-block molecule.

Besides incommensurate smectic A, this compound ("KI5") exhibits a rich polymorphism including a blue phase, cholesteric, TGB and S_C- phases. Since the smectic arrangements are usually very sensitive to molecular details, and taking into account the peculiar role of the spacer in a dimesogenic compound [16-24] (as in polymer systems), we plan to investigate in this paper the influence of the spacer length n on the polymorphism of the "KIn" homologues:

![Chemical Structure](image)

2. Synthesis

The synthetic details for the preparation of KI5 compound were given in reference [15] and exactly the same method was utilized in the synthesis of all the rest compounds.

Special attention was drawn on the purification of the materials. The high purity of the samples was checked by high pressure liquid chromatography, elemental analysis, IR and 1H NMR spectroscopy. Moreover, since all the Schiff-base compounds are very moisture sensitive, we take care to keep them always in dry condition.

3. Experiment

The thermal and structural characterization of these new homologues was achieved through three complementary techniques: differential scanning calorimetry, optical and X-ray diffraction measurements.

The thermal behavior of the compounds was investigated using a Perkin Elmer DSC7. An initial phase identification was carried out by thermal optical microscopy using a polarizing Leitz microscope equipped with a Mettler FP52 hot stage. Observations were systematically made either without surface treatment of the substrate or with rubbed polyimide aligning agent resulting in a planar texture.

Definitely, 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 CuKα radiation of an 18 KW rotating anode X-ray generator. A flat pyrolic graphite (002) monochromator delivered a 0.5×0.5 mm² beam onto the sample. The scattered radiation was collected on a two dimensional detector Imaging Plate system (apparatus already described in [15]). In addition we use a Guinier-type focusing camera equipped with a bent quartz monochromator using CoKα1 radiation (λ = 1.79 Å) allowing accurate determination of the thermal evolution of the reticular distances.
4. Results

To clarify the discussion, we first recall the main results concerning the KI5, which constitutes the basis compound of the KIn series.

4.1. KI5 Compound [15]. — This new type of polyphilic and dimesogenic compound exhibits a quite novel polymorphism. Taking into account the different complementary characterizations, the following phase assignment has been found:

\[ \text{Crystal} \to S_{A_{inc}} \to S_{C} \to S_{A_{inc}} \to S_{C} \to \text{TGB} \to N^* \to \text{BP} \to \text{Isotropic liquid} \]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td></td>
</tr>
<tr>
<td>144.5</td>
<td></td>
</tr>
<tr>
<td>149</td>
<td></td>
</tr>
<tr>
<td>151.5</td>
<td></td>
</tr>
<tr>
<td>165</td>
<td></td>
</tr>
<tr>
<td>168</td>
<td></td>
</tr>
<tr>
<td>191</td>
<td></td>
</tr>
<tr>
<td>192</td>
<td></td>
</tr>
</tbody>
</table>

In this sequence, in addition to commensurate smectic C phases, incommensurate smectic A phases are observed and the low temperature one exists over a large temperature range.

Commensurate S_C phases are described by a quasi Bragg reflection at a wavevector \( q_1 \) (possibly with its first harmonic at \( 2q_1 \)) which extends from 0.150 to 0.155 Å\(^{-1} \) depending on the phase and on temperature. In real space, the corresponding layer spacing is around 41 Å.

From a structural point of view, the commensurate S_C – incommensurate S_A transition is clearly detected by the occurrence in the \( S_{A_{inc}} \) of three collinear incommensurate wave vectors \( q_1, q_2 \) and \( q_3 \). Just below the transition, \( q_2 \) appears like a shoulder in the \( q_1 \) peak on the intensity profile. With decreasing temperature in the large domain of the low temperature \( S_{A_{inc}} \), \( q_1 \) and \( q_2 \) progressively separate, \( q_1 \) moving to the lower values (from 0.153 to 0.143 Å\(^{-1} \)) and \( q_2 \) to higher ones. In the whole temperature range, the third wave vector \( q_3 \) keeps essentially a quasi constant position (0.319 Å\(^{-1} \)). The two reflections connected to \( q_1 \) and \( q_2 \) 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 \( q_1 \). In agreement with the theoretical prediction [4], the law of conservation of vectors: \( q_3 = q_1 + q_2 \) seems satisfied over the large temperature range of the phase. This incommensurate phase is a modulated structure in terms of soliton regions which separate phase-locked regions. Such on incommensurate phase with modulated structure is expected when the coupling between \( q_2 \) and \( q_1 \) is strong, that is to say when the ratio \( q_3/q_1 \) is close to 2 a value which is experimentally supported (\( q_3/q_1 \approx 2.1 \)), \( q_2 \) is hence the signature of a modulated structure with solitons and the periodicity of the discommensurations, \( Z = 2\pi/(q_1 - q_2) \) tends to diverge at the transition to the commensurate phase.

In the real space, the largest periodicity (\( \sim 41 - 44 \) Å), which corresponds to the wavevector \( q_1 \), can be connected to the “dimer” length and the smallest periodicity (\( \sim 20 \) Å), which corresponds to \( q_3 \), to a “monomer-like arrangement”. In contrast with polar systems, we note that the ratio of the two periods is in fact larger than two. Referring to the frustrated smectic model [4], such situation (\( q_3/q_1 > 2 \)) has to rule out an escape from incommensurability through a two-dimensional lock-in of the modulation (\( S_A \) or \( S_C \)). This is probably a basic reason of the aptitude for stabilizing incommensurate S_A phases in this dimesogenic compound.

Starting from this first observation of \( S_{A_{inc}} \) phases in KI5, the question of the dependence of the formation of such incommensurate fluid smectic phases upon molecular parameters is raised and the thermal and structural investigations on several homologues of KI5 can partly solve this problem. Thus, we report here the experimental results concerning the spacer length influence selecting one shorter spacer (\( n = 4 \): KI4 compound) and two longer ones (\( n = 7, 10 \). KI7, KI10 compounds).

4.2. KI4 Compound: A Shorter Spacer. — The complementary techniques allow to determine the following phase sequence:
Fig. 1. — Thermal evolution of the fundamental wavevector \( q_1 \) and its first harmonic \( 2q_1 \) in the \( S_{C^*} \) range for the KI4 compound.

Crystal \( \rightarrow S_{C^*} \rightarrow S_{C^*} \rightarrow TGB \rightarrow N^* \rightarrow BP_1 \rightarrow BP_2 \rightarrow \) Isotropic liquid
85 °C 134 °C 141 °C 142 °C 153.8 °C 154.8 °C 155.6 °C

As for KI5, the TGB is assigned from the observation of a planar texture and of a resolution limited X-ray peak, centered on the wave vector \( q_1 = 0.156 \) Å\(^{-1} \). From a textural point of view, it seems that the TGB phase is the same as for KI5.

Upon cooling, only one wave vector is observed with its first harmonic in the low temperature smectic phase and no incommensurability tendency exists in this KI4 homologous. As shown in Figure 1, the fundamental \( q \) vector remains quasi constant \( (q_1 = 0.155 \) Å\(^{-1} \) over the whole temperature range. It corresponds in real space to a layer spacing of 40.5 Å. In addition, the intensity profile in the wide angle region shows a broad diffuse band centered at \( q = 1.18 \) Å\(^{-1} = 2\pi/5.3 \) Å which indicates fluid smectic domain. The optical textures, as well as contact diagram with the reference compound KI5, allows these phases to be assigned as smectic \( C^* \) phases. At this step, we stress that further investigations are in progress to specify the type of the different \( S_{C^*} \) phases. Thus these first results yet underline the fundamental role of the spacer in such dimesogenic compounds, since a shortening of this central part from five to four methylene groups undoubtly leads to a poorer smectic polymorphism and to the disappearance of the incommensurate phases which is of course the most striking feature in the subsequent discussion.

4.3. KI7 and KI10 Compounds: Longer Spacers. — The two homologous with seven (KI7) or ten (KI10) methylene groups in the spacer exhibit a similar behavior and the same phase sequence:

KI7 Crystal \( \rightarrow S_A \rightarrow TGB \rightarrow N^* \rightarrow BP \rightarrow \) Isotropic liquid
148 °C 151.5 °C 152.5 °C 172.8 °C 173.5 °C
Fig. 2. — Thermal evolution of the fundamental wavevector $q_3$ in the $S_A$ phase for the KI7 compound. Non-condensed wavevector at $q_3/2$ corresponding to commensurate fluctuations is also reported.

KI10 Crystal $\rightarrow S_A \rightarrow TGB \rightarrow N^* \rightarrow BP_1 \rightarrow BP_2 \rightarrow$ Isotropic liquid

$104 \degree C$ $124.5 \degree C$ $125 \degree C$ $140 \degree C$ $140.6 \degree C$ $141.2 \degree C$

Once more the smectic polymorphism is largely reduced compared to KI5, since only one smectic phase exists in addition to TGB one. It seems that the TGB phases are not of the same kind for long and for short spacers. Indeed, instead of the Grandjean plane texture for KI4 and KI5, the TGB phases of KI7 and KI10 exhibit columnar textures as already reported for TGB$_A$ phase [25]. Moreover, a smectic A phase is observed for KI7 and KI10 instead of $S_C$ phase for KI4.

However, no incommensurability appears in the smectic phase of KI7. Only one wave vector is condensed, but in this case, it corresponds to $q \approx 0.3 \, \AA^{-1}$, that is to say, with the notation of KI5, to $q_3$! The corresponding layer spacing slightly increases from 20.6 Å to 21.1 Å decreasing temperature (Fig. 2). In addition, commensurate fluctuations at $q/2(q \approx 0.15 \, \AA^{-1})$ are clearly observed on the pattern (Fig. 3).

Although no fluctuations at $q/2$ are detected, the homologous compound with longer spacer (KI10) exhibits similar structural properties with only one condensed wave vector in the $S_A$ phase $q = 0.28 \, \AA^{-1}$, corresponding in the real space to a layer spacing of 22 Å (Fig. 4).

5. Discussion

First of all, smectic incommensurability is only observed in the KI5 homologue. Nevertheless, two smectic modulations potentially exist in the KIn series, roughly one connected to a "small" period and a second connected to a "large" period (Tab. I).

The smaller periodicity appears to be quasi spacer length independent and corresponds i) to the underlying period of the $S_A$ phase for the longer homologous KI7 and KI10 and ii) to
Fig. 3. — Oriented X-ray diffraction pattern in the small angle region in the $S_A$ phase for KI7, in which commensurate fluctuations are clearly observed.

Fig. 4. — Thermal evolution of the fundamental wavevector $q_3$ in the $S_A$ phase for the KI10 compound.

one of the periodicities observed in the incommensurate $S_A$ phases of KI5 and connected to the wave vector $q_3$.

At a microscopic level, this small period could correspond either to the cholesteryl moiety or to the length of the aromatic mesogen including a part of the spacer. New results recently obtained on another compound could help us to solve this question. They concern a homologue of the KI5 with the same cholesteryl moiety, the same spacer ($n = 5$) but a different "second
Table I. — *The wave vectors in the different smectic phases.*

<table>
<thead>
<tr>
<th>n</th>
<th>incommensurate smectic A</th>
<th>commensurate smectic</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>no</td>
<td>$S_c^+ q_1 = 0.155 , \text{Å}^{-1} (40.5 , \text{Å})$</td>
</tr>
<tr>
<td>5</td>
<td>$q_1 = 0.153 - 0.143 , \text{Å}^{-1} (41-44 , \text{Å})$</td>
<td>$S_c^+ q_1 = 0.150 - 0.155 , \text{Å}^{-1} (41.9 - 40.5 , \text{Å})$</td>
</tr>
<tr>
<td></td>
<td>$q_2$ satellite, $q_1 = 0.315 , \text{Å}^{-1} (20 , \text{Å})$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$q_1 + q_2 = q_2$</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>no</td>
<td>$S_{\alpha} q_5 = 0.305 - 0.297 , \text{Å}^{-1} (20.6 - 21.1 , \text{Å})$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+ commensurate fluctuations at $q_{12}$</td>
</tr>
<tr>
<td>10</td>
<td>no</td>
<td>$S_{\alpha} q_1 = 0.288 , \text{Å}^{-1} (21.8 , \text{Å})$</td>
</tr>
</tbody>
</table>

mesogen”:

![Image of mesogen structure]

"KII5" for short

This KII5 compound (details will be reported in a forthcoming paper) exhibits an incommensurate smectic A phase as KI5, but with a very different large period $2\pi/q_1 \approx 52 \, \text{Å}$ and a quasi identical small one $2\pi/q_3 \approx 20 \, \text{Å}$. The latter result supports the idea that the “small” period in these systems is essentially driven by the cholesterol part.

In the KIn series, the larger periodicity corresponds: i) to one of the modulations observed in the incommensurate phases of KI5 and connected to the wave vector $q_1$, ii) to the fundamental periodicity for commensurate smectic C phases of KI5 and for the smectic C phase of KI4 and iii) to the non-condensed commensurate modulation at $q/2 (\approx 42 \, \text{Å})$ for the smectic A phase of KI7.

Thus, this larger periodicity remains located in the real space between 40 and 44 Å and since the nature (tilted or not) of the smectic phases varies with the spacer length it seems difficult to discuss its evolution from a quantitative point of view. Nevertheless, the quite different periodicity connected to $q_1$ observed in the incommensurate $S_{\alpha}$ phase of the KII5 compound (52 Å) shows that this “large” periodicity (in contrast with the “small” one) appears to be strongly dependent on the overall chemical formula (molecular length of KII5 from SASM model in the most extended conformation: 50 Å).

Note that the basic reason for the lack of this period for KI10 is the strong decoupling between the two mesogenic moieties due to the large flexible spacer. To sum up, the condensation of either of these two smectic modulations or their coexistence in the same compound appears to be closely related to the parameter “spacer length”.

For short spacer, the period is the “large” one and the very low intensity of the first harmonic for KI4 shows that the “mesogenic-sublayers” are not well-defined in this case compared to the “dimesogenic” layers: the chain which joins the two mesogens does not play the role of a “decoupling” spacer (in the sense of the L.C. polymers). In an intermediate regime depicted by the KI5 behavior depending on temperature, the elasticity of the system allows either an escape
Table II. — *Melting entropies of the KIn homologous.*

<table>
<thead>
<tr>
<th>n</th>
<th>4</th>
<th>5</th>
<th>7</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>melting entropy</strong></td>
<td>K-SC</td>
<td>K-S_{A_{inc}}</td>
<td>K-S_A</td>
<td>K-S_A</td>
</tr>
<tr>
<td><strong>ΔS /R</strong></td>
<td>10.4</td>
<td>6.4</td>
<td>12.0</td>
<td>13.4</td>
</tr>
</tbody>
</table>

from the incommensurability by introducing a tilt angle or the occurrence of incommensurate S_A phases when the spacer plays only partially its decoupling role between non symmetric mesogens. In this sense, the conformational study of the spacer as a function of temperature seems promising. For long spacers the escape from incommensurability originates from the large decoupling between the two mesogenic parts which behave as independent moieties forming one S_A phase with an “average” mesogenic layering order. In such S_A phase, we show that the local order of the “dimesogenic” layers vanishes as the spacer length increases from KI7 to KI10. Furthermore it seems that there is no tilted phases (S_C and TGB_C) if the larger modulation is not condensed.

All these results underline the fundamental role of the length of the spacer in the polymorphism of this series, especially in the occurrence of incommensurate smectics since only KI5 exhibits S_{A_{inc}} in the homologues studied (KI4, KI5, KI7, KI10). As depicted in Table II, the melting entropy evolution underlines the specificity of this incommensurate S_A which appears more ordered than the classical A or C smectics due to the modulated structure of soliton regions.

Moreover the unusual mesogenic moiety constituted by the cholesteryl part, its non-aromatic nature connected with its planar shape and its strong ability to interact favourably with the aliphatic chains probably allow a peculiar local arrangement which supports the coexistence of the two underlying periodicities in an incommensurate fluid smectic. Once more, we stress that one modulation remains constant and directly connected to the molecular length of the cholesteryl moiety.

Finally it is not surprising to get an incommensurate S_A phase in the new compound KI15 since it possesses the same spacer length and the same cholesteryl moiety as KI5, in addition to a strong dismeectogenic potential.

**Acknowledgments**

J.-I Jin and Y.-K. Yun would like to express their thanks to the Ministry of Education, Republic of Korea, for the support of this research (Project No. BSRI-94-3406) through the Basic Science Research Institute of Korea University.

**References**


