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HAL Id: jpa-00247940
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Submitted on 1 Jan 1993

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Sub-layer adequacy in smectic ordering: structural characterization of new low molar mass liquid-crystalline siloxanes

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(Received 13 July 1993, received in final form 26 August 1993, accepted 1 September 1993)

Abstract. — This paper deals with the structural characterization of a new series of smectogens the molecules of which contain three distinct parts, a cyanobiphenyl aromatic core, a central paraffin chain and a siloxane endgroup. Incompatible with one another, these parts tend to locate themselves in three separate sub-layers superposed in a partially bilayered smectic A structure. Because the siloxane endgroups have an important lateral extension as compared with the other two molecular moieties, the head to head association of the cyano endgroups is smaller than usual and the smectic layering of the aromatic cores closer to a single layer arrangement. This behaviour illustrates the necessity for the sub-layers to adapt their internal structure so as to be adequate for superposition.

1. Introduction.

The lateral register of rod-like molecules in the smectic state may profitably be viewed as a microphase separation of the aromatic cores from the paraffin chains in distinct sub-layers alternately superposed [1]. The structure of the smectic phases is then described in terms of layer and sub-layer thicknesses, of tilt of the molecules with respect to the layer normals, of molecular areas etc. Most of the smectogens considered so far in the literature are two-block in chemical nature, their molecules being composed of only two types of constituent parts, aromatic cores and paraffin chains, covalently bonded in a rod-like geometry. In structural
studies of such simple materials no special consideration of the lateral packing of the individual constituents of the molecules has, hitherto, been necessary. The reason being simply that the high flexibility of the paraffin chains permits important variations of their lateral expansion, allowing the aromatic cores a great latitude to arrange in single or double layers with molecular areas of 40 and 20 Å² respectively. Two questions arise quite naturally at this point. Firstly what happens to the structural behaviour of smectic phases if the number of distinct and incompatible parts is changed from two to three? Secondly what effect does the lateral size of the constituent parts of the molecules have on this structure? Therefore what factors influence the geometrical adequacy of smectic sub-layers to superpose on top of one another without complete alteration of their internal structural arrangement? Investigation of these problems is the aim of the present article.


The compounds studied in this work were synthesized by hydrosilylation and characterized as described in a separate paper [2]. Their full chemical formula (abbreviated in the following to 2 Si-nO-CB) is:

\[
\text{CH}_3 - \text{Si-O-Si-} \big(\text{CH}_2\big)_{n}\text{O-} - \text{C}_6\text{H}_{3}^-\text{CN}
\]

with \( n = 3, 4, 5, 6, 8, 10 \) and 11.

The thermotropic polymorphism of these compounds was studied by differential scanning calorimetry and polarizing optical microscopy and revealed the presence of a smectic A mesophase [2]. The following polymorphic schemes summarize the mesomorphic behavior of 2 Si-nO-CB.

\[
\begin{align*}
\text{n} = 3 & \quad \text{K} \xrightarrow{70.2 \degree C} \text{I} \\
& \quad \text{SmA} \xleftarrow{22.0 \degree C} \\
\text{n} = 4 & \quad \text{K} \xrightarrow{39.1 \degree C} \text{I} \\
& \quad \text{SmA} \xleftarrow{28.7 \degree C} \\
\text{n} = 5 & \quad \text{SmA} \xrightarrow{50.3 \degree C} \text{I} \\
\text{n} = 6 & \quad \text{SmA} \xrightarrow{53.8 \degree C} \text{I} \\
\text{n} = 8 & \quad \text{K} \xrightarrow{37.0 \degree C} \text{SmA} \xleftarrow{59.0 \degree C} \text{I} \\
\text{n} = 10 & \quad \text{K} \xrightarrow{37.9 \degree C} \text{SmA} \xleftarrow{67.9 \degree C} \text{I} \\
\text{n} = 11 & \quad \text{K} \xrightarrow{30.0 \degree C} \text{SmA} \xleftarrow{73.4 \degree C} \text{I}.
\end{align*}
\]

Usually, liquid crystalline derivatives of cyanobiphenyl contain two distinct parts, namely a cyanobiphenyl head group or core and a linear alkyl(oxy) chain, which are incompatible with one another and segregate in space to form the smectic layers [1, 3, 4]. The particularity of the 2 Si-nO-CB compounds is that the molecules contain three, instead of two, distinct parts, the
third being a pentamethyldisiloxane moiety. To check for the amphiphilic character of these compounds, miscibility tests were performed between \( \alpha \)-pentenyl cyanobiphenyl and the pentamer of dimethylsiloxane (tests with the dimer proved impracticable because of its high volatility). The two compounds turned out to be incompatible over a wide concentration range from room temperature up to 150 °C, suggesting that the siloxane moiety of 2 Si-\( n \)O-CB should probably also be incompatible with the aromatic and paraffin moieties of the molecules.

3. Experiment.

X-ray diffraction studies were carried out with a Guinier-type focusing camera equipped with a bent-quartz monochromator \( (\lambda_{\text{CuK}} = 1.54 \text{ Å}) \) and an INSTEC hot-stage (± 0.01 °C) used as a sample holder. Powder patterns (samples in Lindemann capillaries) were recorded with an INEL curved position-sensitive detector (exposure time : 30 min) controlled by a multichannel analyzer. Experiments were conducted by stepwise heating the samples (temperature steps of about 5 °C) from room temperature up to the clearing point. A typical X-ray pattern recorded is shown in figure 1.

![X-ray diffraction pattern](image)

Fig. 1. — Typical example of X-ray diffraction pattern: smectic A phase of 2 Si-11O-CB at 40 °C.

Dilatometry measurements were performed with a home-made dilatometer described elsewhere [5], providing the specific volume of the specimens with an accuracy of 10^{-4}. The change in volume was studied as a function of temperature, upon stepwise heating or cooling (steps of 0.1 °C every 2 min) in the temperature range from 25 °C up to 90 °C. For the volume measurements to be meaningful, the samples must first be carefully degased (several heating and cooling cycles under vacuum, from the low-temperature crystal or liquid crystal to the high-temperature very fluid isotropic liquid). Typical examples of volume vs. temperature curves recorded are shown in figures 4 and 5.

4. Results and discussion.

4.1 X-RAY DIFFRACTION. — The X-ray patterns recorded are in perfect agreement with the previous optical observations [2] describing the mesophases of 2 Si-\( n \)O-CB as smectic A in nature. They contain indeed one sharp Bragg reflection in the small-angle region, correspond-
ing to the smectic layering. In the wide-angle region they also contain one diffuse band, corresponding to the liquid-like conformation of the paraffin chains and to the disordered lateral arrangement of the aromatic cores in the smectic layers (~ 4.6 Å), and one much more diffuse band (as clearly confirmed using photographic film) at about 6.3 Å, which probably corresponds to the liquid like arrangement of the siloxane moieties [6, 7].

The smectic period measured at 30 °C for all the compounds is given in table I, along with the corresponding molecular lengths estimated from molecular modelling (Sybyl software from Tripos). The smectic period increases with the molecular length as expected, but more interestingly, it is comprised of between one and two molecular lengths (d/L ~ 1.7), which when combined with the results of the dilatometry measurements (see below) indicates a partial bilayered arrangement (A_d) for the smectic layers and, therefore, a certain degree of head to head association of the molecules through their cyano endgroups [8]. As illustrated by figure 2, for the typical example of the n = 11 compound, the smectic period clearly decreases as a function of increasing temperature, showing the tendency of the head to head association to decrease. The experimental data that will be used below are summarized in figure 3.

Table I. — Smectic period at 30 °C (d) and molecular lengths (measured by molecular simulation using Sybyl software from Tripos), L, of 2 Si-nO-CB.

<table>
<thead>
<tr>
<th>n</th>
<th>d(Å)</th>
<th>L(Å)</th>
<th>d/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>34.4</td>
<td>21.3</td>
<td>1.62</td>
</tr>
<tr>
<td>5</td>
<td>36.4</td>
<td>22.6</td>
<td>1.61</td>
</tr>
<tr>
<td>6</td>
<td>39.4</td>
<td>23.8</td>
<td>1.66</td>
</tr>
<tr>
<td>8</td>
<td>42.6</td>
<td>26.2</td>
<td>1.63</td>
</tr>
<tr>
<td>10</td>
<td>49.6</td>
<td>28.7</td>
<td>1.73</td>
</tr>
<tr>
<td>11</td>
<td>51.1</td>
<td>30.0</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Fig. 2. — Typical variation of the smectic period with temperature : sample 2 Si-11O-CB.
4.2 DILATOMETRY. — Dilatometric measurements were carried out only on those four compounds \((n = 3, 5, 8, 11)\) which were available in sufficient quantities. Figures 4 and 5 illustrate the specific case of compounds \(n = 3\) and \(n = 11\). The first shows the first order transition between the low-temperature crystal and the high-temperature isotropic liquid, characterized by a marked volume jump and a strong hysteresis upon cooling. The same type of transition takes place also for the other compounds where the melt is a smectic phase. It is useful to note the perfect reversibility of the temperature dependence of the specific volume in the isotropic (or smectic) melt, and also the occurrence of a secondary first order polymorphic transition in the crystalline state of the \(n = 3\) compound upon heating. On the other hand, figure 5 shows the first order transition between the smectic and the isotropic liquid; the
reversible volume jump measured at the transition is rather small (~ 1%), as is usual for this transition.

In the range of stability of the smectic and isotropic liquid phases, the molar volume varies linearly with temperature according to equation:

\[ V(T) = V_0(1 + \alpha T) , \]

where \( V_0 \) is the molar volume at 0 °C and \( \alpha \) the relative thermal expansion coefficient. Using a linear regression fit method, the values of \( V_0 \) and \( \alpha \) were calculated for compounds \( n = 5, 8, \) and \( 11 \) (compound \( n = 3 \) was not considered further as it does not show a smectic phase above room temperature). Inspection of table II clearly shows the linear dependence of the molar volumes on the spacer length both in the smectic and the isotropic state. With the reasonable assumption of additivity of the partial molar volumes of the constituent parts of the molecules, it is easy to calculate the partial molar volume of the methylene groups \( (V_{CH_2}/\text{cm}^3\text{mol}^{-1}) \) as a function of temperature:

\[ V_{CH_2} = 15.6 + 1.63 \times 10^{-2} T \quad \text{for the smectic and} \]
\[ V_{CH_2} = 16.1 + 1.61 \times 10^{-2} T \quad \text{for the isotropic phases} . \]

Table II. — Values of the molar volume at 0 °C \((V_0)\) and relative thermal expansion coefficient \((\alpha)\) of 2 Si-nO-CB in the smectic A and isotropic liquid phases.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( V_0 ) ((\text{cm}^3\text{mol}^{-1}))</th>
<th>( \alpha \times 10^4 ) ((\text{°C}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( S_A )</td>
<td>I</td>
</tr>
<tr>
<td>5</td>
<td>399.0</td>
<td>399.6</td>
</tr>
<tr>
<td>8</td>
<td>445.4</td>
<td>446.4</td>
</tr>
<tr>
<td>11</td>
<td>492.6</td>
<td>494.2</td>
</tr>
</tbody>
</table>
These are in good agreement with those given in the literature for paraffin chains in a disordered conformation [9].

4.3 Structural model. — The smectic A structure of the 2 Si-nO-CB compounds was suggested above to be partially bilayered ($A_d$), since its Bragg period was found to lie between one and two molecular lengths ($L < d < 2L$) [3, 10]. For the sake of clarity, it is useful to recall briefly the structural model that describes this type of layering in the case of the well-known alkoxy-cyanobiphenyls [8]. In this model (Fig. 6), the smectic layers are formed by an intimate binary mixture of single molecules pointing up and down, and of pairs of molecules (dimers) associated through their terminal cyano groups. The value of the smectic period reflects quite clearly this degree of association of the molecules, i.e. the fraction $\tau$ of molecules dimerized:

$$d \approx 2(V/\sigma)/(2 - \tau) = 2L'/ (2 - \tau).$$

![Molecular model of the smectic $A_d$ mesophase](image)

In this equation, $\sigma$ and $L'$ are the cross-sectional area of the aromatic cores and the length of the single molecules in the mesophase (see Ref. [8]). It is useful adding that with this model, the average molecular area of the paraffin tails is:

$$S \approx (2 - \tau)\sigma.$$

The situation in the present work, although fundamentally the same, is more complex. Indeed, the polyphilic molecules are composed of three distinct parts incompatible with one another and consequently they tend to segregate in three separate superposed sub-layers. As a result, the paraffin chains situated in the centre of the molecules, can only arrange themselves in single layers, whereas the terminal (aromatic or siloxane) parts are capable of forming either single or double layers, or eventually partially bilayered structures (Fig. 7). The question now is to decide whether the three types of segregated sublayer can superpose themselves in a smectic structure without special constraints, due to the fact that their respective molecular areas are not all compatible with one another (stacking « adequacy » of the sublayers). The molecular area ($\sigma_{ar}$) of the aromatic cores standing upright in the layers is of about 22 Å², that ($\sigma_{par}$) of the disordered paraffin chains may vary from 20 up to over 40 Å² depending upon the conformation, and that ($\sigma_{sil}$) of the short, nearly globular in shape, siloxane moieties is large, around 43 Å² [11]. In the simple case of the two-block smectogens, the lateral molecular coverage of the surfaces is imposed by the aromatic cores and is comprised between $\sigma_{ar}$ and 2 $\sigma_{ar}$ depending upon the single- or double-layered arrangement of the cores in the sublayers. Such a coverage is of course compatible with the natural spreading of the disordered
Fig. 7. — Different types of arrangement of the three distinct parts of the molecules: (a) both aromatic and siloxane parts are arranged in double layers, (b) the aromatic parts are arranged in single layers and the siloxane parts in double layers and (c) partially bilayered structure of the aromatic and the siloxane parts.

flexible paraffin chains, as currently observed in thermotropic and lyotropic liquid crystals. In the complex case of the three-block smectogens considered in the present work, the significant bulkiness of the siloxane moieties poses a serious problem of packing. For instance, with the siloxane moieties arranged in single layers, the molecular coverage of the surfaces is \( 2\sigma_{\text{sil}} = 86 \, \text{Å}^2 \), which is too large and hardly compatible with the lateral spreading of the (rather short) paraffin chains and also totally inconsistent with the upright arrangement of the rigid aromatic cores in single or double layers.

To consider this point further and to describe the detailed molecular structure of these smectic A phases it is useful to calculate, from the experimental data, not only the smectic period, but also the molecular coverage of the smectic layers. Because of the mutual incompatibility of their constituent parts, the three-block molecules must pile up in layers, pointing alternately up and down (Fig. 8); as a result of the two-sided symmetry of the smectic layers, their molecular coverage corresponds to the area occupied in the smectic planes by two molecules:

\[
S = \frac{2V}{Nd}
\]

where \( N \) is Avogadro’s number. Knowing the values of the molar volume \( V \) (Tab. II) and the smectic period \( d \) (Fig. 3), it is easy to calculate \( S \) as a function of temperature for the three compounds analyzed: \( n = 5, 8, \) and 11 (Fig. 9).

Inspection of figure 9 shows that the calculated molecular coverage \( S \) ranges from about 32 up to 39 Å². These values suggest the following comments regarding the molecular packing in each one of the three sublayers of the smectic structure (Fig. 8). Concerning the paraffin sublayers, the \( S \) values are in perfect agreement with what is known of the lateral expansion of paraffin chains in a disordered conformation and are therefore consistent with the single-layered arrangement proposed. Concerning the aromatic sublayers, the \( S \) values are between
Fig. 8. — Schematic representation of the smectic A layers of 2 Si-nO-CB. The central part of the smectic layers is arbitrarily chosen to be formed of the aromatic sublayers, with the aromatic cores (rectangles) arranged in a partially bilayered structure. This central part is fringed with the disordered paraffin chains (waxy lines) arranged in single layers. The siloxane moieties (ellipses) are located within distinct sublayers in a double-layered arrangement, some of them being squeezed out into the paraffin sublayers.

Fig. 9. — Temperature dependence of the molecular area of 2 Si-5O-CB (down triangle), 2 Si-8O-CB (up triangle) and 2 Si-11O-CB (square).
\[ \sigma_{\text{af}} \text{ and } 2 \sigma_{\text{af}} \text{ with } \sigma_{\text{af}} \text{ of about } 22 \text{ Å}^2, \text{ and clearly indicate a partially bilayered arrangement with a fraction of cores dimerized (} \tau = 2 - S/\sigma_{\text{af}} \text{) in the range from 0.25 to 0.50. This would be consistent with the lack of strong second or higher order 00} L \text{ reflections in the X-ray diffraction pattern, figure 1, because of the diffuse scattering interface. As for the siloxane sublayers, the } S \text{ values, significantly smaller than the size (~43 Å}^2) \text{ of the siloxane endgroups, suggest for these groups a double-layered arrangement, with some of them squeezed out into the neighbouring paraffin sublayers. A crude extrapolation of } S \text{ to } n = 0 \text{ at } 40 \text{ °C (Fig. 10), shows the molecular coverage to attain a value of about } 42 \text{ Å}^2, \text{ that is the expected value for the lateral packing area of the siloxane endgroups when all of them are forced to be located into their specific sublayers. This extreme situation corresponds to the arrangement of the aromatic cores in single layers and therefore to the total absence of association of the cyano endgroups. It is worth noting in this context the depression of } \tau \text{ as a function of increasing temperature, in agreement with previous observations on alkoxy-cyanobiphenyls [8]. Apparently, there exists a strong competition between the tendency of the cyano endgroups to associate pairwise, and thus to decrease } S, \text{ and the tendency of the siloxane endgroups to segregate into distinct layers, and thus to bring about the opposite effect.}

![Graph](image)

Fig. 10. — Evolution of the molecular area } S \text{ with the number of carbon atoms } (n) \text{ at } 40 \text{ °C.}

Interestingly, the } \tau \text{ values of the aromatic cores found here are smaller than the values usually measured with alkoxy-cyanobiphenyls (} \tau = 0.5 [8]). \text{ This demonstrates the important steric role of the siloxane endgroups which, with a tendency to segregate into distinct sublayers as required by the amphiphilic character, contribute to the lateral expansion of the layers and consequently to an increase of the molecular coverage } S. \text{ Figure 11 illustrates this effect, showing the strong dependence of } \tau \text{ upon the length of the paraffin chains. Indeed, the thinner the paraffin sublayers, the less room for the siloxane endgroups to « dissolve » therein, and the more the siloxane endgroups are located into their nominal sub-layers.}

5. Conclusion.

The present work deals with the mesomorphic behaviour of a new class of three-block smectogens the molecules of which contain a cyanobiphenyl aromatic core, a central paraffin chain and a siloxane endgroup. It describes the smectic A structure observed as resulting in the superposition of three separate sublayers formed of the three molecular moieties, and gives the
degree of head to head association of the molecules through the cyano endgroups as a function of temperature and length of the paraffin spacer. The main conclusion drawn is related with the « adequacy » of the sublayers to superpose. The molecular moieties in the sublayers being covalently bonded with one another, their surface coverage must be exactly the same in all three sublayers. Now, the siloxane endgroups are laterally bulkier than the aromatic cores. As a result, the headwise association of the cyano endgroups is smaller than usually observed, and the smectic layering of the aromatic cores closer to a single-layered arrangement. The lateral spreading of the layers so obtained permits the proper superposition of the sublayers.

Acknowledgments.

The authors wish to thank Dow Corning, Barry (UK), for supporting this work, Joanna Newton for use of her siloxane samples and Benoit Heinrich for his assistance during the dilatometry experiments.

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