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# Liquid Crystals

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# Structural characterization of organosiloxane liquid crystals with a transverse or longitudinal dipole

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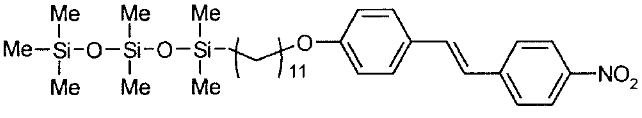
In this work we report the characterization of two organosiloxane liquid crystalline compounds by means of DSC, polarizing optical microscopy and X-ray diffraction. These compounds can be used for dye guest-host ferroelectric displays. We focus this investigation on the molecular organization of the SmC phases of the two pure compounds to help elucidate the physical behaviour of mixtures with different concentrations of the dye and the guest host. The existence of longitudinal and transverse dipoles in the molecules of the dye and the chiral guest-host respectively are responsible for the different molecular organizations in the SmC mesophases of each compound. Taking into account the experimental results and the complexity of the molecules, we present coherent models to explain the molecular arrangements in the mesophases of both compounds.

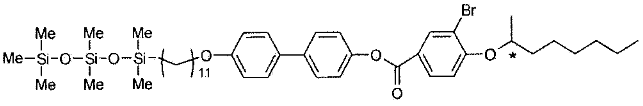
## 1. Introduction

Ferroelectric liquid crystals exhibiting chiral smectic C* mesophases at room temperature and very fast response times to a low applied electric field, are of great interest for high resolution display devices [1]. Among materials exhibiting such properties, organosiloxane derivatives have been shown recently to be particularly promising [2]. The molecular architecture of these compounds consists of three molecular moieties different in nature and linked covalently together: a classical polarizable mesogenic core with a chiral chain at one end and an aliphatic spacer at the other terminated by a siloxane group (the typical number of dimethylsiloxy groups being 1–10 repeats). Indeed, the presence of the siloxane part is enough to reduce considerably the transition temperatures and to widen at the same time the ferroelectric mesophase temperature range, without changing the response times significantly, despite a small increase of the viscosity of the compounds. Compared with classical ferroelectric mesogens without the siloxane group, the strong stabilization of the smectic C* phase induced by the terminal siloxane moiety in these compounds is related to the specific molecular arrangement within the smectic layers. It results from the formation of distinct sublayers, each of them corresponding to the specific chemical nature of each molecular moiety, which in turn superimpose to form the lamellar liquid crystalline phase [3–5]. This microsegregation between the different sublayers stabilizes the smectic phase and also confers on the material some of the rugged mechanical properties more often associated with polymeric liquid crystals.

More recently, it has been shown that low molar mass organosiloxane liquid crystalline dyes can be used for dye guest-host ferroelectric display devices [6], leading to high contrast displays. The first example reported in the literature [7] deals with an organosiloxane nitrostilbene dye which is both dichroic and fluorescent ($NO_2$-11-$Si_3$) mixed with a biphenylyl benzoate organosiloxane host (Br-11-$Si_3$). The corresponding chemical formulae are shown below:



$NO_2$-11-$Si_3$



Br-11-$Si_3$

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In order to understand better the variations of the physical properties as functions of the dye concentration in mixtures, it is necessary to establish first the molecular arrangement in the smectic phases of both pure compounds. Whilst the structural arrangement of the host is already known, that of the dye has not been determined to date. In this paper, we report a comparison between the molecular organizations of the smectic C phase of the dye and the smectic C* phase of the host. The main difference in the molecular design of these two compounds lies in the presence of a strong longitudinal terminal dipole in the achiral $NO_2$-11-$Si_3$ dye molecule and of a transverse dipole in the chiral Br-11-$Si_3$ host molecule. Thus the resulting dipole–dipole interactions lead to quite different supramolecular organizations in the smectic phases of the two compounds under consideration. We show, in particular, that the smectic C layers of the organosiloxane dye are characterized by some degree of head to head association of the aromatic cores through strong longitudinal dipole coupling, and that in the smectic A phase of the same compound, the molecules also form pairs, the degree of association being relatively low, about 0.1 to 0.2. On the other hand, the smectic C* layers of the host are made from the superposition of three separate sublayers: a monolayer of tilted aromatic cores, a sublayer made of disorganized aliphatic chains and a partially bilayered arrangement of the siloxane end groups.

## 2. Experimental

The synthesis of the compounds has been described elsewhere [8]. However, before using them, we have controlled carefully their purity by chromatography and NMR.

Br-11-$Si_3$ was purified on a silica-gel column using ethyl acetate/hexane (3/97) as eluent to give a white solid. $^1H$ NMR ($CDCl_3$): $\delta$ (ppm) 8.42 (d, 1H, PhH), 8.12 (dd, 1H, PhH), 7.55 (dd, 4H, PhH), 7.25 (d, 2H, PhH), 6.96 (dd, 3H, PhH), 4.55 (m, 1H, $-CH-O-$), 4.01 (t, 2H, $-CH_2-O-$), 1.82 (m, 2H, $-C\underline{H}_2-CH_2-O-$), 1.56–1.30 (m, 29H, aliphatic protons), 0.90 (t, 3H, $CH_3$), 0.54 (t, 2H, $-Si-CH_2-$), 0.09–0.03 (m, 21H, $-S-CH_3$).

$NO_2$-11-$Si_3$ was purified on a silica-gel column using ethyl acetate/hexane (5/95) as eluent to give a yellow solid. $^1H$ NMR ($CDCl_3$): $\delta$ (ppm) 8.20 (d, 2H, PhH), 7.60 (d, 2H, PhH), 7.48 (d, 2H, PhH), 7.23 (d, 1H, $-CH=$), 7.00 (d, 1H, $-CH=$), 6.92 (d, 2H, PhH), 3.99 (t, 2H, $-CH_2-O-$), 1.80 (m, 2H, $-C\underline{H}_2-CH_2-O-$), 1.45–1.20 (m, 16H, aliphatic protons), 0.53 (t, 2H, $-Si-CH_2-$), 0.09–0.03 (m, 21H, $-Si-CH_3$).

Powder X-ray diffraction (XRD) patterns were recorded using a Debye-Scherrer camera with a bent quartz monochromator ($K_{\alpha 1}$ radiation, $\lambda = 1.54$ Å), and INEL curved position-sensitive gas detector and an INSTEC hot stage (±0.01°C), associated with a data acquisition and temperature controlling computer system. The compounds were enclosed in sealed Lindemann glass capillaries. The X-ray patterns were registered on both cooling and heating as a function of temperature. All patterns were obtained with an exposure time of at least one hour.

Polarizing optical microscopy (POM) was performed using a Leitz-Orthoplan polarizing microscope associated with a temperature controlled hot stage. In general the optical microscopy observations were performed using thin preparations of the compounds between two glass plates without any treatment or spacers. In order to clarify the nature of some mesophases, complementary observations were performed using silane treated glasses (to induce a surface orthogonal alignment of the molecules in the case of N or SmA mesophases). All the observations were performed on both increasing and decreasing the temperature.

Differential scanning calorimetry measurements were performed using a Perkin-Elmer DSC7 apparatus. For measurements below 10°C we have modified the cooling system using liquid nitrogen as the cold source.

## 3. Mesomorphic behaviour

### 3.1. *Br-11-Si*$_3$

Under the polarizing microscope, a smectic C* phase appears at 86°C when cooling from the isotropic phase. The texture of this mesophase is characterized by a form of schlieren texture. At 49°C, a transition to another mesophase, Mx, can be detected through a change in the optical texture with a decrease in the transmitted light.

The DSC traces (see figure 1) registered on heating and cooling confirm the observations made under the microscope. Three first order phase transitions associated with low values of latent heat seem to indicate the presence of at least two mesophases, since the transitions at 86 and 49°C are perfectly reversible. On lowering the temperature, a supercooling effect (about 20°C) is observed before the last transition. As a consequence, the polymorphic behaviour of this compound is the following:

$$\mathrm{I} \underset{86^{\circ}\mathrm{C}}{\longleftrightarrow} \mathrm{SmC^*} \underset{49^{\circ}\mathrm{C}}{\longleftrightarrow} \mathrm{Mx} \underset{-60^{\circ}\mathrm{C}}{\overset{-40.5^{\circ}\mathrm{C}}{\leftrightarrows}} \mathrm{Cr?}$$

The XRD results were registered on cooling the sample from the isotropic phase to ~20°C and on heating it from 20°C to the clearing point. In this way it was possible to analyse the structure of the two mesophases detected below the clearing point. Due to experimental limitations in our apparatus, it was not possible to

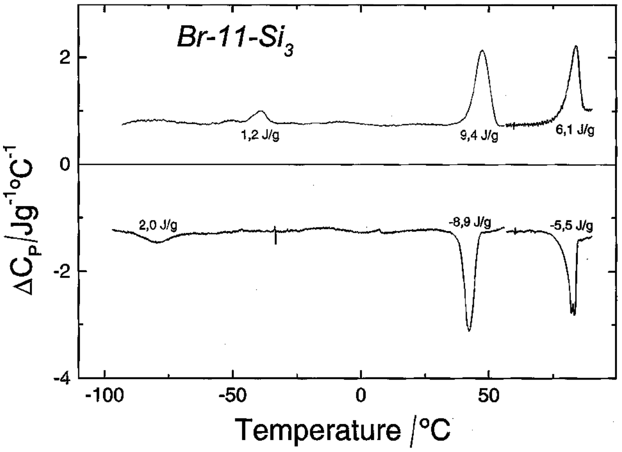


Figure 1. DSC traces of Br-11-Si$_3$ registered on heating (top) and cooling (bottom) rates of 5°C $min^{-1}$.

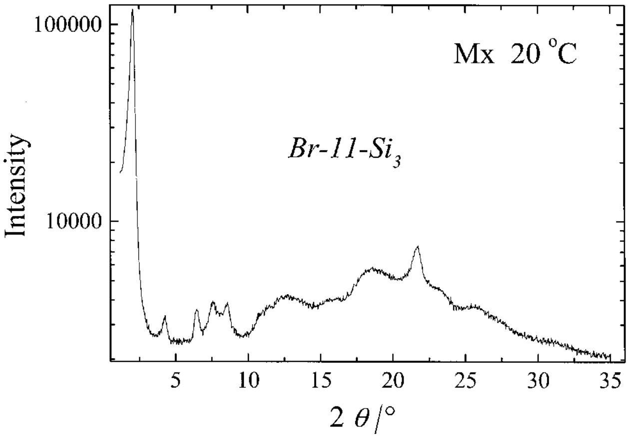


Figure 3. X-ray diffraction pattern registered in the Mx mesophase of Br-11-Si$_3$.

obtain X-ray profiles for temperatures lower than 20°C. The X-ray profiles registered for the two mesophases are clearly different (see figures 2 and 3). However, for each temperature in both phases, the X-ray profiles obtained on increasing or decreasing the temperature are identical. This proves the reversible mesomorphic behaviour of the compound under study.

The profile observed in figure 2 is characteristic of a smectic state with liquid-like layers. The two sharp peaks in the small angle region, in the ratio 1 : 2, correspond to a lamellar organization with a spacing of about 38.5 Å; two diffuse bands (at 6.8 and 4.4 Å), in the wide angle region, correspond to two distinct molecular lateral interactions. The first diffuse band at 6.8 Å corresponds to interactions between siloxane groups, and the second at 4.4 Å to those between aliphatic spacers and also mesogenic groups. The electro-optical results previously reported [8] confirm that this high temperature mesophase (above 49°C) is SmC* in nature.

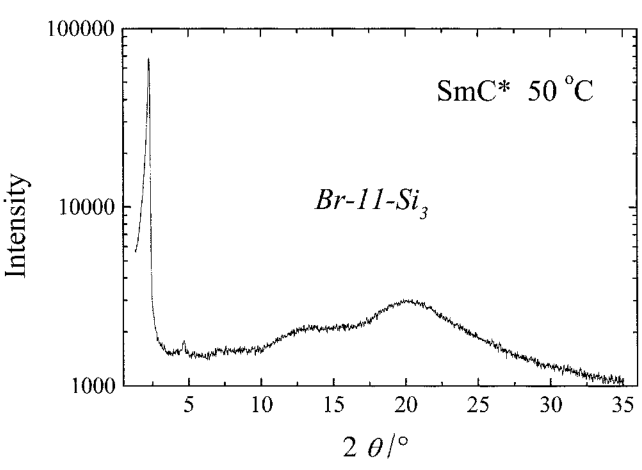


Figure 2. X-ray diffraction pattern registered in the smectic C* phase of Br-11-Si$_3$.

On comparing the X-ray pattern presented in figure 3, associated with the mesophase hereafter called Mx that is observed at lower temperatures, with that presented in figure 2, associated with the SmC* mesophase, significant changes can be observed. In the small angle region, four sharp Bragg peaks in the ratio 1 : 2 : 3 : 4 correspond to a lamellar organization with a spacing of about 44 Å. These four harmonics observed for the lamellar stacking are a strong indication of a well developed and well ordered lamellar system. In addition, between the 3rd and 4th orders there is a supplementary peak corresponding to a distance of ~11.6 Å which can be interpreted as resulting from intramolecular interactions, as observed in polymers [9] and as already reported in other similar organosiloxane compounds [4]. As in the SmC* mesophase, the presence of the siloxane part is also detected. In the wide angle region, an additional rather narrow peak which superimposes on the broad band, is observed at 4.1 Å. This supplementary peak, could be associated with strong correlations within the layers, and indicates that the Mx mesophase detected at lower temperatures may be a kind of hexatic phase.

The variation of the lamellar spacing in the different phases is plotted as a function of temperature in figure 4. The layer spacing in the SmC* phase is almost constant. This behaviour is known to be usual in SmC phases which undergo a direct transition into the isotropic phase. It is important to note that the layer spacing of about 38.5 Å is significantly smaller, as expected for a tilted system, than the molecular length, ~49 Å, as determined from molecular modelling. The transition from the SmC* to the Mx mesophases occurs through a sudden jump in the layer spacing. The layer spacing in the Mx phase is also constant as a function of temperature and its value is much closer to the molecular length.

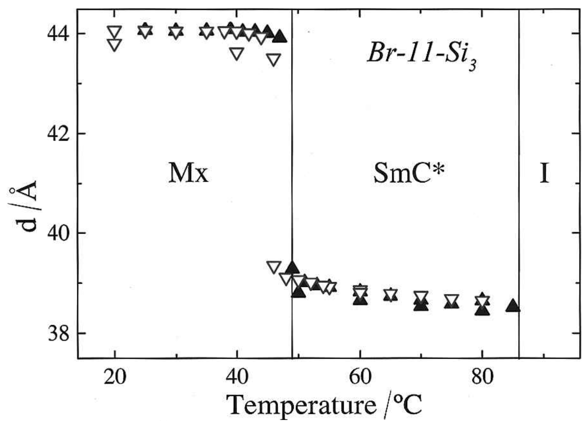


Figure 4. Layer spacing as a function of temperature for Br-11-$Si_3$. Open and filled triangles are for heating and cooling cycles, respectively. SmC*, Mx and I are for smectic C*, the unidentified phase and the isotropic phase, respectively.

### 3.2. *$NO_2$-11-$Si_3$*

This compound was initially studied by POM. Heating the sample from room temperature, a first transition to a mesophase was found at about 41°C. A new transition was then observed at about 58°C and no modification of this texture was detected before the clearing point was observed at about 103.5°C. Trying to understand better the nature of these two mesophases, the sample was cooled from the isotropic phase at a rate of $-0.5^{\circ}\mathrm{C\,min}^{-1}$ in order to obtain well developed textures. A smectic A phase was observed at higher temperatures, characterized by a fan-shaped texture and also homeotropic regions (figure 5). The mesophase found at lower temperatures was a smectic C phase characterized by a broken fan texture and also a schlieren texture in the areas which were homeotropic in the SmA phase (figure 6). Additional observations made with glass substrates treated with silane confirmed the nature of the smectic phases. In this case, a homeotropic texture over the whole sample was observed within the temperature range of the SmA phase, whereas a pale schlieren texture appeared when crossing the transition to the smectic C phase. The DSC traces registered on heating and cooling confirmed the microscopic observations. As a consequence, the polymorphic behaviour of this compound is the following:

$$\mathrm{I} \underset{103\,^{\circ}\mathrm{C}}{\longleftrightarrow} \mathrm{SmA} \underset{58\,^{\circ}\mathrm{C}}{\longleftrightarrow} \mathrm{SmC} \underset{41\,^{\circ}\mathrm{C}}{\longleftarrow} \mathrm{LamellarSolid}$$

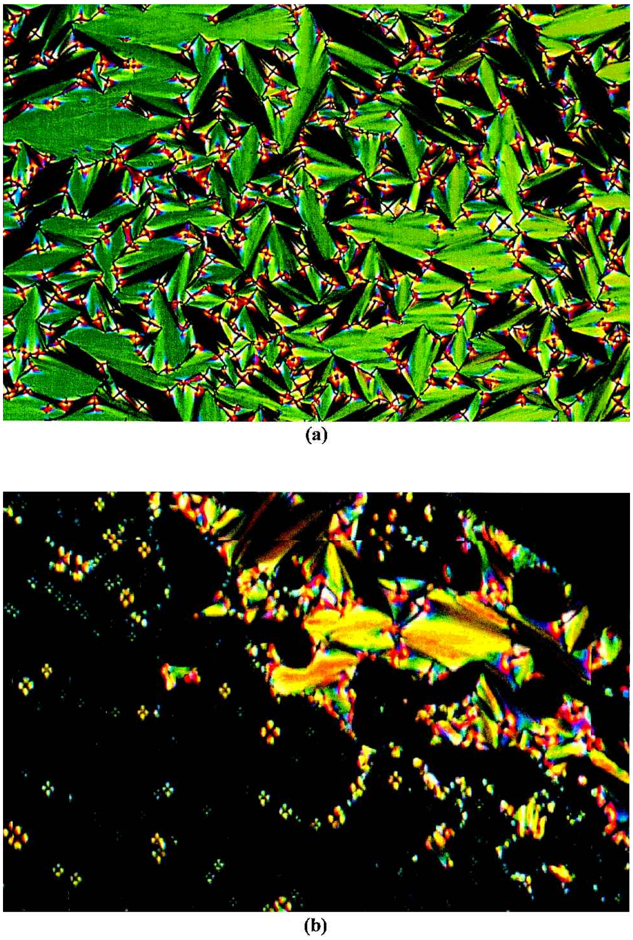
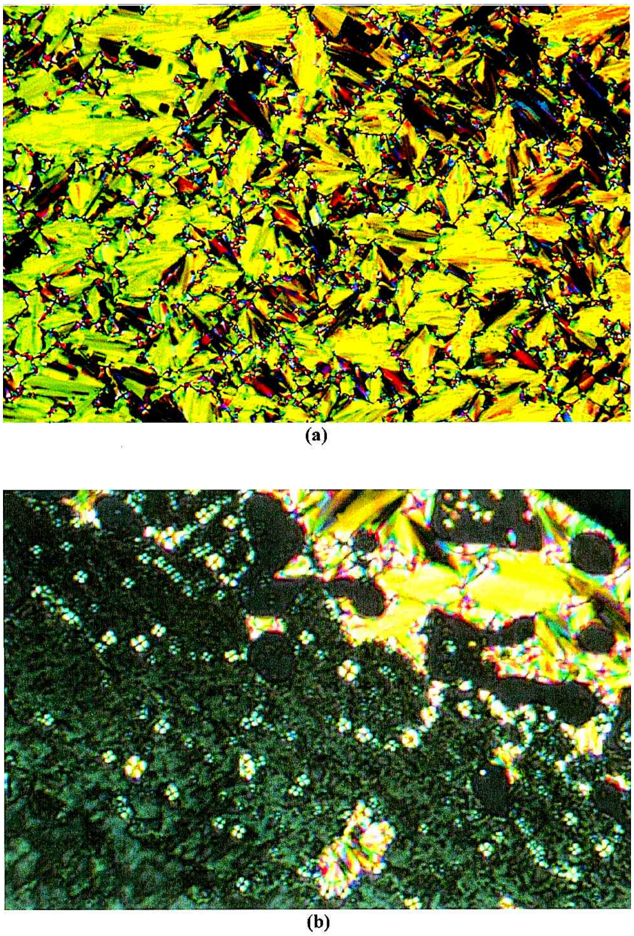


Figure 5. Textures observed for the SmA phase of compound $NO_2$-11-$Si_3$ at $T = 59^{\circ}\mathrm{C}$. (*a*) Fan-shaped texture with focal-conics; (*b*) coexistence of a fan-shaped texture with a large homeotropic domain.

The XRD patterns registered in the SmA and SmC phases are quite similar. In the small angle region, two sharp Bragg reflections in the ratio 1 : 2 correspond to the lamellar stacking. At wide angles, two diffuse bands are observed corresponding to the disordered lateral arrangement of the molecules within the smectic layers: one band arises from combined contributions from the aliphatic spacers in a disordered conformation and the aromatic cores (~4.5 Å); the second, more diffuse, band probably corresponds to the siloxane moieties (~6.5 Å) (figure 7). On cooling to ambient temperature, the compound undergoes a transition into a lamellar solid, characterized also by a lamellar stacking (figure 8). It should be noted that this transition occurs over a wide range of temperature (between 41 and 31°C) where the solid phase being formed coexists with the smectic C phase.

The variation of the lamellar spacing in the different phases is plotted as a function of temperature in figure 9. Both in the smectic A and C mesophases, the layer spacing is close to 50 Å, which is much larger than the molecular length, 35 Å. As usually observed in smectic A phases, the layer spacing decreases with increasing temperature, this behaviour being due to increased


(a)

(b)

Figure 6. Textures observed for the SmC phase of compound $NO_2$-11-$Si_3$ at $T = 51°C$. (*a*) Broken fan-shaped texture; (*b*) coexistence of a fan-shaped textures with schlieren texture.

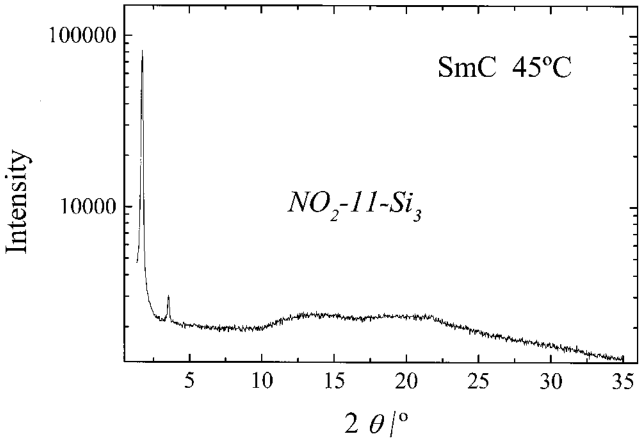


Figure 7. X-ray diffraction pattern registered for the smectic C phase of $NO_2$-11-$Si_3$.

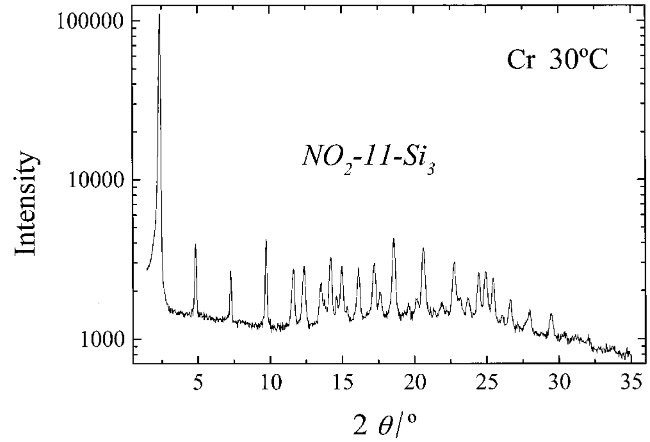


Figure 8. X-ray diffraction pattern registered for the crystalline phase of $NO_2$-11-$Si_3$.

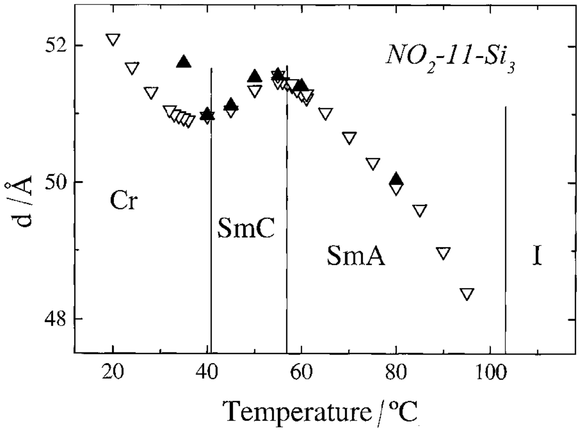


Figure 9. Layer spacing as a function of temperature for $NO_2$-11-$Si_3$. Open and filled triangles are for heating and cooling cycles, respectively. Cr, SmC, SmA and I are for the crystalline, smectic C, smectic A and isotropic phases, respectively. The region separating the imaginary heating and cooling curves between 31°C and 41°C corresponds to the demixing of the crystalline and the smectic C phase as explained in the text.

spreading of the aliphatic chains at the interface between the smectic layers. The behaviour in the smectic C phase is much more surprising since the layer spacing decreases by only 0.5 Å when the temperature decreases by 15°C. Note also the perfect reversibility of the experimental data on both heating and cooling cycles.

## 4. Discussion and conclusions

Let us emphasize that both compounds have been designed to have similar chemical architectures in order to favour complete mixing of the different molecules. In particular they have the same terminal siloxane group, which promotes mutual solubility through the siloxane–siloxane interactions, and the same aliphatic spacer containing 11 methylene groups. The only difference lies in the aromatic core. In Br-11-$Si_3$ this moiety is mainly characterized by a lateral dipole moment and a short terminal branched aliphatic chain to induce the ferroelectric properties; whereas in $NO_2$-11-$Si_3$ the aromatic core is shorter and characterized by a relatively strong longitudinal dipole moment due to the nitro group (3.6 D) [10]. From the structural point of view, Br-11-$Si_3$ exhibits a smectic C* phase and $NO_2$-11-$Si_3$ exhibits smectic A and smectic C phases. But the most striking feature is the difference in the values of the smectic layer spacings, *d*, for the two compounds. Whereas *d* is significantly shorter than the molecular length in the case of Br-11-$Si_3$, *d* is much larger than the molecular length for $NO_2$-11-$Si_3$. Indeed, the ratio $d/l$ is equal to 0.79 in the smectic C* phase of Br-11-$Si_3$ and 1.47 in the smectic C phase of $NO_2$-11-$Si_3$.

For Br-11-$Si_3$, the molecular organization within the smectic C* layers has already been described [4]. It corresponds to monolayers of aromatic groups tilted at an angle of about 40–45° and a partially interdigitated siloxane bilayer. For $NO_2$-11-$Si_3$, the situation seems completely different. First, the layer spacing in the smectic C phase has an almost constant value, practically equal to the maximum value in the smectic A phase at the transition between these two phases. This behaviour seems to indicate that the molecules are only slightly tilted in the smectic C phase. Second, the presence of a relatively strong dipole at one end of the molecule favours longitudinal interactions with the possible formation of pairs of molecules, as already observed in the smectic A phase of cyano compounds of the same type [11].

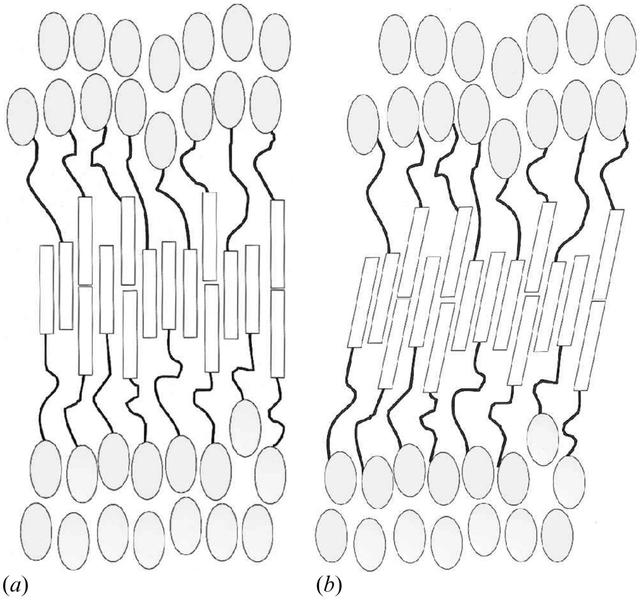

(*a*) (*b*)

Figure 10. Schematic representation of the smectic A (*a*) and C (*b*) layers of $NO_2$-11-$Si_3$. 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 partial bilayered structure. The siloxane moieties (ellipses) are located in a double layered arrangement at the interface of the smectic layers. The disordered aliphatic chains (wavy lines) are between the aromatic and siloxane sublayers.

Let us consider now in detail the molecular organization in the smectic A phase. Because of the mutual incompatability of their constituent parts, these three-block molecules pile up in layers, pointing alternately up and down. 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: $S = 2V_m/Nd$, where *N* is Avogadro's number, $V_m$ the molecular volume and *d* the layer spacing. From molecular simulations and values already reported in the literature for aliphatic chains and siloxane moieties in liquid crystals, the molecular volume can be estimated to be 956 and 977 Å$^3$ at 55 and 80°C, respectively. The *S* value is then deduced to be 37.1 and 39 Å$^2$ for the corresponding temperatures. These values are similar to those found in the smectic A phase of siloxane compounds carrying a terminal cyano group in place of the nitro group in the present work. Thus, the molecular packing in each of the three sublayers of the smectic structure is the following. For the paraffin sublayers, the *S* values are in perfect agreement with what is known of the lateral expansion of aliphatic chains in a disordered conformation and are therefore consistent with the single layered arrangement represented in figure 10. However, for the aromatic sublayers, the *S* values are between one and two times their usual lateral bulk ($\sigma_{ar} \sim 22$ Å$^2$), and indicate a partially bilayered arrangement. This partial bilayer is composed of a mixture of aromatic cores of individual molecules and of dimers of molecules formed through longitudinal interactions of the terminal nitro groups. The fraction, $\tau$, of aromatic cores (as calculated from the relation: $S \sim (2 - \tau)/\sigma_{ar}$ [12]) implied in this arrangement is in the range 0.16 to 0.11 on going from 50 to 80°C. As for the siloxane sublayers, the *S* values are smaller than the size ($\sim$43 Å$^2$) of the siloxane end groups, suggesting a double layered arrangement, with some of them squeezed out into the neighbouring aliphatic sublayers. Here, the small values of the head to head association are worth noting compared with those found in the case of similar cyano compounds (from about 0.3 to 0.5). This behaviour is in complete agreement with that already observed in the case of classical polar disymmetric mesogens (i.e. non-siloxane-based systems) where it has been found that the head to head association of nitro compounds is much less than that of cyano compounds. This behaviour has been attributed to the bulkiness of the nitro group compared with cyano, leading to more difficult interdigitation of the longitudinal dipoles. The decrease in the degree of association with increasing temperature is also worth noting, in agreement with previous observations on alkoxycyanobiphenyls [12]. Apparently, there exists a strong competition between the tendency of the nitro end groups to associate pairwise, and thus to decrease *S*, and the tendency of the siloxane end groups to segregate into distinct layers, and thus to bring about the opposite effect.

Now, it is interesting to know what happens in the smectic C phase. Two possible molecular packings may be encountered. Taking into account the very small variation of *d* within the smectic C phase and also the intrinsic value of *d* which does not change significantly (less than 0.5 Å) when going from the smectic A at 54°C down to the smectic C phase at 40°C, it is very tempting to conclude that the molecular packing within the smectic C layers stays roughly the same as that at higher temperatures, with a very small tilt of the aromatic cores with respect to the layers. However, a more dramatic change in the molecular packing occurring at the smectic A to smectic C transition on cooling cannot be excluded *a priori*, such a change being related to a modification of the degree of the head to head association of the molecules. Let us assume the extreme situation where the degree of association is 1, i.e. only pairs of molecules exist in the smectic layers. In such a case, the sublayer thickness, $d_{\mathrm{ar}}$, formed by the aromatic cores can be deduced from the relation:

$$d_{\mathrm{ar}} = d(V_{\mathrm{ar}}/V_{\mathrm{m}})$$

where $V_{\mathrm{ar}}$ is the volume of the aromatic cores and $V_{\mathrm{m}}$ is the molecular volume, $d$ being the total smectic layer thickness. $d_{\mathrm{ar}}$ is thus found to be about 12.5 Å, which has to be compared with twice the total molecular length of the aromatic stilbene core. In such a configuration, the cores would be tilted with an angle of about 60°.

Both situations or any intermediate one are possible. However, let us recall that the homeotropic regions observed in the smectic A phase, when using glass plates treated to obtain homeotropic alignment, transform into grey textures of low intensity in the smectic C phase. This behaviour seems to be more in favour of a small tilt angle, and thus of a molecular packing similar to that described in detail above for the smectic A phase. In recent electro-optic measurements on mixtures of these two siloxane based systems [7], the electro-optic tilt angle is negligible up to a concentration of about 30 wt % of Br-11-$Si_3$ in $NO_2$-11-$Si_3$ with no observation of spontaneous polarization in this concentration range. Since Br-11-$Si_3$ is essentially a chiral additive and as such should allow the molecular tilt angle in $NO_2$-11-$Si_3$ to be observed, this strongly suggests that the tilt angle in the SmC phase of the achiral $NO_2$-11-$Si_3$ compound is indeed very small. Only XRD on well oriented samples or a systematic study of several similar siloxane compounds exhibiting both smectic C and A phases may bring some additional useful information to describe more precisely the molecular organization within the smectic C layers.

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