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Structural characterization of linear dimeric and cyclic tetrameric liquid crystalline siloxane derivatives

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The phase behaviour and the structural characterization of a new series of linear dimeric and cyclic tetrameric molecules which contain three distinct parts, a cyanobiphenyl aromatic core (A), a paraffin chain (P) and a central siloxane group (B) with the A–P–B–P–A sequence, are described. Incompatible with one another, these parts tend to locate themselves in three separate sub-layers superposed in a partially bilayered smectic A structure. Each sub-layer adapts its internal structure in order to be appropriate for superposition, as in the case of organosiloxane molecules with the A–P–B sequence reported previously.

1. Introduction

Side chain polysiloxanes, in particular those containing cyanobiphenyl pendant groups, are well known to produce liquid crystalline phases [1], attracting increasing interest mainly because of the great flexibility of the siloxane backbone which leads to reduced viscosities and lower glass transitions than those for structured polyacrylates or polymethacrylates.

In a recent paper [2], we studied the mesomorphic behaviour of a series of smectogens which may be considered as a repeat chemical unit (monomeric) of such polymers. The advantage of these smectogens is that they constitute an interesting example of smectogenic molecules containing three, instead of only two distinct parts—a cyanobiphenyl aromatic core, a paraffin chain and a siloxane subgroup. We thus found that, incompatible with one another, these parts tend to locate themselves in three separate sub-layers superposed in a partially bilayered smectic A structure. Since the siloxane end groups have an important lateral extension as compared with the other two molecular moieties, the head to head association of the cyano end groups is smaller than usual and the smectic layering of the aromatic cores is closer to a single layer arrangement. This behaviour illustrates the necessity for the sub-layers to adapt their internal structure in order to be appropriate for superposition.

In the field of side chain polymers, one of the areas of great current interest is the study of the mesomorphic behaviour of oligomers, linear [3–19] or cyclic in geometry [20–22]. Fundamentally, it is interesting to understand how the mesomorphic behaviour depends on the molecular weight, and furthermore, and more importantly, how such materials combine the mechanical advantages of polymers with the electro-optical properties of the traditional molecular liquid crystal materials. The present paper is intended to describe the liquid crystal behaviour of further low molar mass organosiloxane mesogens. Herein, we will present comparative studies, based on phase characterization using differential scanning calorimetry, microscopy, molecular modelling and X-ray diffraction of a series of linear dimeric and cyclic tetrameric compounds.

2. Materials

The compounds studied in this work were synthesized by hydrosilylation and characterized as described in a separate paper [23]. The full chemical formula for the dimeric siloxane derivatives (twins) (abbreviated in the

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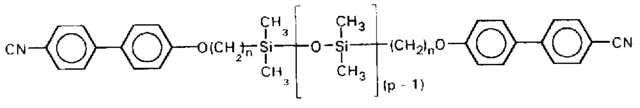
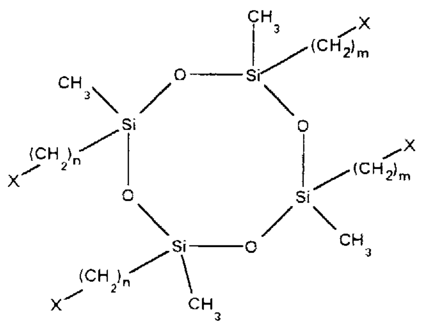
following sections to *n*/*p*/*n*, where *n* denotes the number of the carbon atoms in each paraffin chain and *p* denotes the number of silicon atoms in the siloxane part) is:

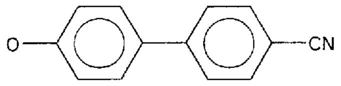


All the *n*/*p*/*n* compounds studied are listed in table 1.

The full chemical formula for the cyclic tetrasiloxanes (abbreviated in the following sections to *n*/*m*) is:



where *m* is the number of carbon atoms in each parraffinic linking group and *X* corresponds to the group



The *n*/*m* compounds studied are listed at the end of table 1.

3. Thermotropic mesomorphism

The thermotropic mesomorphism of these compounds was studied by differential scanning calorimetry (Perkin–Elmer DSC7) and polarizing optical microscopy (Leitz). This study revealed for both the dimeric and the cyclic compounds the presence of a smectic A mesophase with a focal conic texture, except for the 3/3 cyclic compound with the shortest paraffinic linking chains, which exhibits a nematic mesophase with a schlieren texture. The transitions from mesophase to crystal on cooling occur below room temperature because of the usual problems associated with nucleation and crystal growth kinetics.

The transition temperatures are affected both by the length of the aliphatic spacer and the siloxane units (see table 1). The increase in the length of the paraffin parts contributes to increase the stability (width of temperature range) of the smectic mesophase and this increase in stability is largest for the longest alkyl spacers (the isotropic clearing temperatures have been increased on average by 30°C). On the other hand, the effect of lengthening the siloxane unit leads to a drastic decrease of

Table 1. Phase transition temperatures (°C) for the dimeric and the cyclic siloxane derivatives.

Compound	Phase transitions
6/2/6	$\mathrm{Cr} \xrightarrow{86} \mathrm{S_A} \xleftrightarrow{91} \mathrm{I}$ $\mathrm{S_A} \xrightarrow{T<0} \mathrm{Cr}$
8/2/8	$\mathrm{Cr} \xrightarrow{89} \mathrm{S_A} \xleftrightarrow{100} \mathrm{I}$ $\mathrm{S_A} \xrightarrow{T<0} \mathrm{Cr}$
10/2/10	$\mathrm{Cr} \xrightarrow{55} \mathrm{S_A} \xleftrightarrow{109} \mathrm{I}$ $\mathrm{S_A} \xrightarrow{T<0} \mathrm{Cr}$
11/2/11	$\mathrm{Cr} \xrightarrow{62} \mathrm{S_A} \xleftrightarrow{112} \mathrm{I}$ $\mathrm{S_A} \xrightarrow{16} \mathrm{Cr}$
3/4/3	$\mathrm{Cr} \xrightarrow{T<0} \mathrm{S_A} \xleftrightarrow{40} \mathrm{I}$ $\mathrm{S_A} \xrightarrow{T<0} \mathrm{Cr}$
3/5/3	$\mathrm{Cr} \xrightarrow{T<0} \mathrm{S_A} \xleftrightarrow{26} \mathrm{I}$ $\mathrm{S_A} \xrightarrow{T<0} \mathrm{Cr}$
3/8/3	$\mathrm{Cr} \xrightarrow{T<0} \mathrm{S_A} \xleftrightarrow{20} \mathrm{I}$ $\mathrm{S_A} \xrightarrow{T<0} \mathrm{Cr}$
6/5/6	$\mathrm{Cr} \xrightarrow{T<0} \mathrm{S_A} \xleftrightarrow{57} \mathrm{I}$ $\mathrm{S_A} \xrightarrow{T<0} \mathrm{Cr}$
10/5/10	$\mathrm{Cr} \xrightarrow{T<0} \mathrm{S_A} \xleftrightarrow{70} \mathrm{I}$ $\mathrm{S_A} \xrightarrow{T<0} \mathrm{Cr}$
3/3	$\mathrm{g} \xrightarrow{54} \mathrm{N} \xleftrightarrow{109} \mathrm{I}$ $\mathrm{N} \xrightarrow{T<0} \mathrm{g}$
3/10	$\mathrm{g} \xrightarrow{T<0} \mathrm{S_A} \xleftrightarrow{96} \mathrm{I}$ $\mathrm{S_A} \xrightarrow{T<0} \mathrm{g}$
6/6	$\mathrm{g} \xrightarrow{57} \mathrm{S_A} \xleftrightarrow{118} \mathrm{I}$ $\mathrm{S_A} \xrightarrow{T<0} \mathrm{g}$
10/10	$\mathrm{Cr} \xrightarrow{55} \mathrm{S_A} \xleftrightarrow{134} \mathrm{I}$ $\mathrm{S_A} \xrightarrow{T<0} \mathrm{Cr}$

the clearing temperature, while the thermal stability range of the mesophases increases (smectic mesophase exists well below room temperature). Concerning the cyclic siloxane derivatives, the transition temperatures are higher than in the case of the corresponding monomeric or dimeric siloxane derivatives. On cooling, three of the four cyclic siloxanes (see table 1) form a glassy phase and not a crystalline phase.

4. Structural model of the dimeric siloxane derivatives

X-ray diffraction studies were carried out using a set-up described elsewhere [2] and the X-ray patterns recorded are similar to those of monomeric siloxane derivatives (see figure 1 in [2]). The S_A nature of the mesophase identified by optical microscopy was confirmed by X-ray diffraction. The X-ray patterns recorded contain two sharp equidistant Bragg reflections in the small angle region due to the smectic layering. In the wide angle region they contain one diffuse band located at $\cong 4{\cdot}6$ Å, corresponding to the liquid-like conformation of the paraffin chains and the disordered lateral arrangement of the aromatic cores in the smectic layers, together with one much more diffuse band at about 6·3 Å, corresponding to the liquid-like arrangement of the siloxane moieties [24, 25].

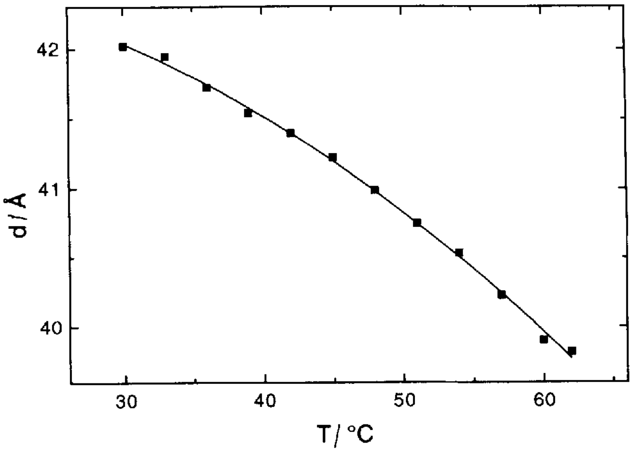


Figure 1. Typical variation of the smectic period of 6/5/6 with temperature.

Table 2. Smectic period, d, at 30°C, and molecular length (measured by molecular simulation using Sybyl software from Tripos), L, of the dimeric siloxane derivatives.

$n/p/n$	d/Å	L/Å	$2d/L$
6/2/6	30·6	41·7	1·47
8/2/8	35·3	45·1	1·56
10/2/10	39·6	49·6	1·60
11/2/11	42·4	53·0	1·60
3/4/3	33·4	38·4	1·70
3/5/3	35·7	43·0	1·58
3/8/3	liquid	48·1	—
6/5/6	42·0	51·7	1·62
10/5/10	52·4	61·6	1·70

The smectic periods measured at 30°C for all the dimeric compounds are given in table 2, along with the corresponding molecular lengths L ($L = 2L'$, where L' is the length of the corresponding monomer, estimated from molecular modelling: Sybyl software from Tripos). The smectic period increases with the molecular length as expected and, as we will show, the value of d/L' which is equal to 1·5–1·7 indicates a partially bilayered arrangement (A_d) for the smectic layers and, therefore, a certain degree of head to head association of the molecules through their cyano end groups [26]. Figure 1 illustrates the typical variation of the smectic period of compound 6/5/6 with temperature: the smectic layer thickness clearly decreases as a function of increasing temperature; this behaviour is similar to that observed for the monomeric siloxane derivatives, showing the tendency of the head to head association of the molecules to decrease.

In order to describe the detailed molecular structure of these S_A phases, it is useful to calculate, not only the smectic period, but also the molecular coverage of the smectic layers [26] by using the molar volume of the molecules. The limited amount of the samples prevented us from carrying out dilatometric measurements to determine directly the molar volume of the molecules. However, with the usual assumption of additivity of the partial molar volumes of the constituent parts of the molecules, it is possible to estimate (see [27]) the molar volume using the available volume data for the compounds $C_nH_{2n+1}(C_6H_4)_2CN$ (nCB) [28] and the monomeric siloxane derivatives: $(CH_3)_3SiOSi(CH_3)_2(CH_2)_nO(C_6H_4)_2CN$ (nAPB) [2].

Table 3 summarizes the estimated molar volumes and the calculated molecular areas $S = V/d$ at 30°C. As in the case of the A–P–B siloxanes [2], the values of S found are between σ_{ar} ($\cong 22$ Å^2) and $2\sigma_{ar}$, σ_{ar} being the surface area of one aromatic core; they clearly indicate a partially bilayered arrangement of the aromatic cores with a fraction of cores dimerized ($\tau \cong 2 - S/\sigma_{ar}$) in the range

Table 3. Values of the molar volume at 30°C (V) and the molecular area (S) of the dimeric siloxane derivatives.

$n/p/n$	V/Å^3	S/Å^2	τ
6/2/6	1120	36·6	0·34
8/2/8	1126	34·8	0·42
10/2/10	1333	33·6	0·47
11/2/11	1386	32·7	0·51
3/4/3	1198	35·9	0·34
3/5/3	1315	36·8	0·33
6/5/6	1474	35·1	0·40
10/5/10	1687	32·2	0·54

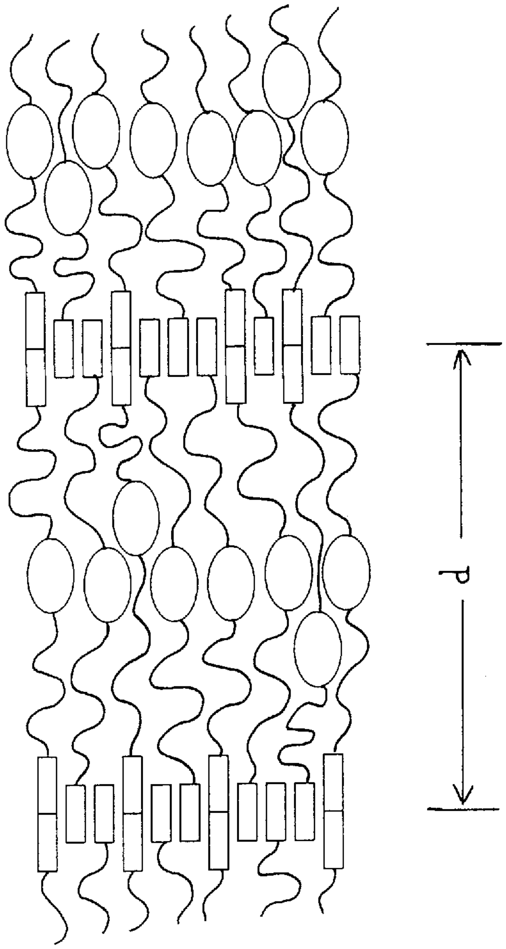


Figure 2. Schematic representation of the smectic A layers of the dimesogenic siloxanes. The central part of the smectic layers is arbitrarily chosen to be formed of the siloxane sub-layers, with the aromatic cores (rectangles) arranged in a partially bilayered structure. The disordered paraffin chains (wavy lines) are arranged in single layers. The central siloxane moieties (ellipses) are located within distinct sub-layers in a partially bilayered arrangement.

from 0·3 to 0·5 (see figure 2) [26]. The three constituent parts of the molecules tend to segregate in separated sub-layers. As a result of their location in the centre of the molecules, both the siloxane and the paraffin parts can only arrange themselves in discrete layers. For the paraffin chains, the S values are consistent with a single layered arrangement. For the siloxane sub-layers, the S values, significantly smaller than the lateral size (~ 43 Å^2) of a polydimethylsiloxane, suggest that for them a partially bilayered arrangement exists.

The molecular area S decreases with increasing number of methylene groups in the aliphatic parts (see figure 3). The extrapolation of S, in the case of the $n/2/n$ dimers, to $n = 0$ at 40°C, shows the molecular area to reach a value of about 41 Å^2, which is approximately that expected for the lateral packing of the siloxane parts when arranged in discrete layers. In the case of the $n/5/n$ dimers, the extrapolation to $n = 0$ gives an almost identical value of 42 Å^2. 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 end groups. The siloxane groups play an important steric role which, with a tendency to segregate into distinct sub-layers as required by their amphiphilic character, contributes to the lateral expansion of the layers and consequently to an increase of the molecular coverage S. Table 3 illustrates this effect, showing the strong dependence of τ upon the length of the paraffin chains. Indeed, the thinner the paraffin sublayers, the less room there is for the siloxane groups to 'dissolve' therein (see [2]), and the more the siloxane end groups are located into their nominal sub-layers.

5. Structural model of the cyclic siloxane derivatives

The smectic period measured at 30°C for all the cyclic compounds is given in table 4, together with the corresponding lengths of the molecules in their cylindrical conformation as measured by molecular modelling (Sybyl software from Tripos). The smectic period increases with the molecular length ($n + m$) as expected and the value of $2d/L$, which is equal to 1·5–1·6, indicates a partially bilayered arrangement (A_d) for the smectic layers.

The existence of the smectic structure is due to the 'cylindrical' conformation of the molecule found to be the most probable (Sybyl from Tripos/Mopac 5·0). A recent molecular simulation study of a cyclic siloxane macromolecule based on a pentamethylcyclosiloxane core and biphenylyl 4-alkyloxybenzoate mesogenic groups showed the cylindrical conformation to be the most probable; the molecular interactions were found to be optimized for the

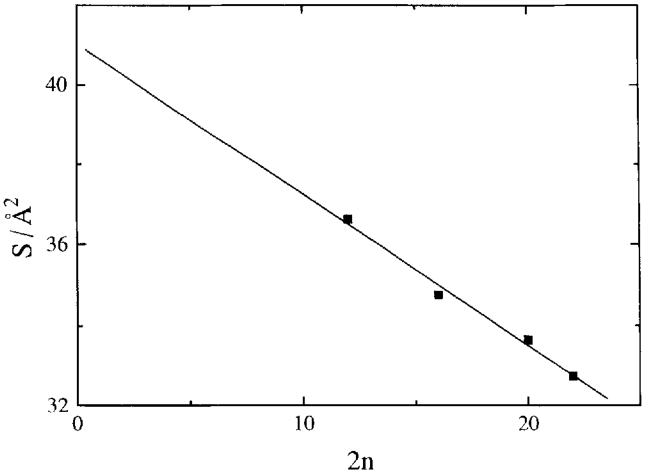


Figure 3. Evolution of the molecular area S of $n/2/n$ with the number of carbon atoms ($2n$) at 30°C.

Table 4. Smectic period, d, at 30°C, and molecular length (measured by molecular simulation using Sybyl software from Tripos), L, of the cyclic siloxane derivatives.

n/m	d/Å	L/Å	$2d/L$
6/6	30·3	41·0	1·48
3/3	33·8	43·0	1·57
10/10	36·7	49·0	1·50

Table 5. Values of the molar volume at 30°C (V) and the molecular area (S) of cyclic siloxane derivatives.

n/m	V/Å^3	S/Å^2
6/6	2187	72
10/10	2614	71
3/10	2240	66

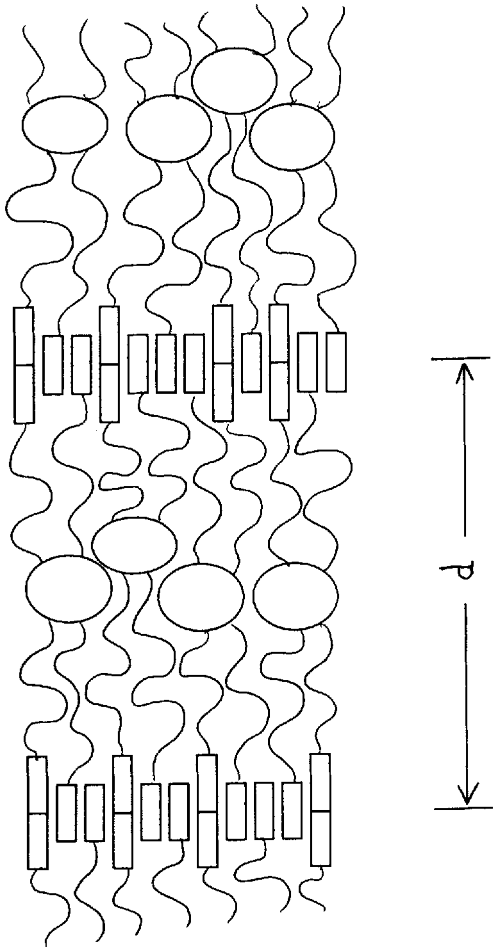


Figure 4. Schematic representation of the smectic A layers of the cyclic siloxane derivatives. The central siloxane moieties (ellipses) are located within distinct sub-layers in a partially bilayered arrangement. The aromatic cores (rectangles) are arranged in a partially bilayered structure. The disordered paraffin chains (wavy lines) are arranged in single layers.

case where the mesogenic units were planar and parallel to each other.

In order to determine the molecular structure of the smectic A mesophase formed by the cyclic siloxane derivatives we will use, as for the dimeric compounds, the additivity of the partial molar volumes of the different parts of the molecules.

Table 5 summarizes the calculated molar volumes and areas $S = V/d$ of the molecules at 30°C. The values of S range between $2\sigma_{ar}$ (44 Å^2) and $4\sigma_{ar}$ and, as in the previous section concerning the dimeric compounds, clearly indicate a partially bilayered arrangement of the aromatic cores with a fraction of the cores dimerized ($\tau \cong 2 - S/2\sigma$) in the range from 0·3 to 0·5 as in the case of the monomeric and dimeric siloxane derivatives (see figure 4).

In the case of the n/m cyclic siloxane derivatives, a very crude extrapolation of S to $n = 0$ shows that the molecular coverage reaches a value of about 82 Å^2, which is very close to the expected value for the lateral packing area of the siloxane rings when they are forced to occupy their specific sub-layers.

6. Conclusions

The main conclusion of this work is that, regardless of the way the mesogenic units are linked to produce multi-mesogenic compounds (in linear dimesogens or in cyclic tetramesogens), the spatial arrangement of the resulting mesophase is identical. Clearly, the mesomorphic behaviour is primarily governed by the intramolecular segregation of the constituent parts of the molecules, that is, the cyanobiphenyl aromatic cores, the paraffin chains and the siloxane groups. The structural parameters of the mesophases are controlled by the lateral packing area of each constituent part of the molecules.

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[27] The three constituent parts of dimeric siloxane derivatives are the aromatic cores (A), the siloxane parts (B) and the paraffin chains (P) with the A–P–B–P–A sequence. Their molar volume may be deduced from the combination of the molar volume of $C_nH_{2n+1}(C_6H_4)_2CN$ [28] ($V(n\mathrm{CB})/\text{Å}^3 \cong 281{\cdot}5 + 26{\cdot}67n$) and the molar volume of A–B–S siloxanes [2] ($V(n\mathrm{AB})/\text{Å}^3 \cong 544{\cdot}6 + 26{\cdot}68n$).

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