A new series of liquid crystalline dimers with exceptionally high apparent tilt \dagger

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A new series of dimeric chiral antiferroelectric materials using a trisiloxane as the central connecting linker and having fluorinated tails has been synthesized together with their corresponding monomers. Spacer lengths of 3-6 and 11 methylene groups were used. As a comparison to see the effect of the siloxane length on the phase behaviour, one dimer with a tetrasiloxane core was also synthesized. Monomers with 3-6 carbons in the spacer showed just orthogonal smeetic phases and only the long 11 carbon spacer 7F4PPB11 showed tilted phases in a very similar way to what was found in the unfluorinated monomers previously studied. All trisiloxanes showed a high temperature antiferroelectric phase and those with a spacer length of 4 or more carbons also showed one or two columnar antiferroelectric phases when decreasing the temperature. The spontaneous polarisation P_s was high, especially in the columnar phases where it ranged from $800-1200 \text{ nC cm}^{-2}$ and upward. The apparent tilt angles were exceptionally high, above 45 degrees for all materials studied. In accordance with the trend described previously, the tetrasiloxane containing dimer showed a ferroelectric phase at high temperature. But in this case the columnar phase was found to be antiferroelectric. Hence, the general idea that trisiloxane cores promote antiferroelectricity and tetrasiloxanes promote the ferroelectric phase is still correct also for these materials in the SmC* phase, but not for the columnar phase. It can also be noted that the phase separation between siloxane, fluorinated tail and mesogenic parts of the molecules was so high that the material became columnar on lowering the temperature.

1. Introduction

Liquid crystals provide a very rich field for research due to the variety of different phases that these materials exhibit as a result of the different molecular structures and interactions between them. Traditionally the greatest emphasis was on the form of the liquid crystal molecule when it came to designing new suitable materials, but also other features like polarity and phase separation effects have also been studied. Lately it has been shown how useful these effects are for providing a complex phase flora.¹ The phase separation has been used to alter the liquid crystalline phase less profoundly but nevertheless in important ways such as for instance in the synthesis of the antiferroelectric materials carried out by Coles *et al.*² That the phase segregation effect of side chain polymer liquid crystals can be used to create smectic phases is also a well established fact.

For low molar mass liquid crystals a favoured way of causing phase segregation is to use a siloxane chain as a part of

the molecule.^{3–10} Siloxane chains as well as fluorinated chains tend to avoid the normally stiff aromatic core of the liquid crystal and create phase separation that can be used to tailor the phase behaviour of the material. Fluorinated chains promote many different types of self assembly of molecules and can be combined with siloxane linking groups in dimers to get a combined effect.^{2,11}

For a more thorough review of how much the complexity of the self organisation of a material can increase due to phase segregation, we recommend to the reader an excellent article by Cheng *et al.*¹² containing many relevant references.

Since their discovery, antiferroelectric liquid crystals (AFLCs)^{13,14} have been considered to be very promising materials for displays. Compared to ferroelectric liquid crystals (FLC), AFLCs can be aligned more easily and their electronic driving is simpler since there is no need for dc compensation. Moreover, AFLCs have potential for generation of a grey scale. In particular AFLC materials with a molecular tilt of 45 degrees, and thus, as described by de Meyere et al.,¹⁵ capable of displaying high contrast images due to the inherent field free dark state of such a material when aligned properly, have been of great interest in the last few years. Several studies of materials with an inherent field free dark state have been performed on both monomer blends,^{2,6,16–19} banana shaped molecules (in this case not having a dark state for the same reason),²⁰ dimeric single compound siloxanes^{2,6,9,10,21,22} and dimers with an alkane as the connecting linker.²³

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The goal of the present work has been to make very stable antiferroelectric materials by increasing the phase segregation of some dimers, previously synthesized by us,⁹ by fluorinating the tails of the mesogenic groups. The syntheses and liquid crystalline properties of 1,5-di(4'-alkyloxy)biphenyl-4-carboxylic acid 4-[1-(2,2,3,3,4,4,4-heptafluorobutoxycarbonyl)-1-(*R*)-ethoxy]phenyl ester) 1,1,3,3,5,5-hexamethyltrisiloxanes with spacer lengths of 3-6 and 11 carbons, and the corresponding monomers are reported. We synthesized one tetrasiloxane dimer in order to differentiate between the siloxane effect and the effect from the dimeric structure as shown in Scheme 1. The chiral centres of these liquid crystalline dimers are located near the periphery of the molecule to allow the chiral group great freedom of movement. Characterisations using microscopic observation, powder and oriented X-ray diffraction, calorimetric and electro-optical methods were applied to deduce the phase behaviour and physical characteristics of the substances. All dimers proved to be antiferroelectric with very high apparent tilt angles, above 45 degrees, as well as showing columnar phases. These dimers are, to the best of our knowledge, the first dimers with a siloxane central connector that have an apparent tilt that exceeds 45 degrees.

2. Experimental

The proposed structures of all the dimers and their intermediates were verified using 300 MHz ¹H NMR spectra obtained using a Varian VXR300 spectrometer. All spectra were run in CDCl₃ or DMSO- d_6 solutions. Infrared spectra were recorded on a Perkin-Elmer 1000 FT-IR spectrophotometer using a BaF₂ cell for liquid phase IR and toluene as the solvent.

Materials and reagents were of commercial grade quality and used without further purification unless otherwise noted. Dry toluene and methylene chloride were obtained by passing the solvents through a bed of aluminium oxide (ICN Alumina N-Super I). (+)-2-(4-Hydroxyphenoxy)propionic acid was generously provided by BASF. The 4-(2-alkenoxy)biphenyl-4-carboxylic acids (**2a**–e) were previously prepared by us to make the analogous non-fluorinated compounds.⁹

2.1. Synthesis

The synthesis of monomers 3a-3e and dimers 4a-f was carried out according to the reactions in Scheme 1. All structures were verified with ¹H NMR spectroscopy and NMR data were in accordance with the structures in all cases.



Scheme 1 Reagents and conditions: (i) heptafluorobutanol, 1,2-diethoxyethane, cyclohexane, PTSA; (ii) C_6H_6 , EtOH; (iii) acetone, alkyl bromide, K_2CO_3 , followed by EtOH + NaOH; (iv) DCC/DMAP, CH₂Cl₂; (v) toluene, Pt catalyst, dihydrosiloxane.

The monomers and dimers described are all based on the central mesogenic unit derived from the phenoxy propanoic ester of biphenyl carboxylic acid (PPB) and after the synthetic part we will use the abbreviated name based on the PPB unit with numbers depending on the number of carbons in the tail and spacer, number of fluorine atoms in the tail, and the number of silicon atoms in the siloxanes used.

Preparation of 2-(R)-(4-hydroxyphenoxy)propionic acid 2,2,3,3,4,4,4-heptafluorobutyl ester (1). A solution of 2-(R)-(4-hydroxyphenoxy)propionic acid (27 mmol, 5 g) and 1,1,1,2,2,3,3-heptafluorobutanol (6.5 g) in 1,2-diethoxyethane (75 ml) and cyclohexane (80 ml) was refluxed in a Dean Stark apparatus with sulfuric acid (2 g) for 7 days, periodically following the reaction progress with TLC. The product was dissolved in diethyl ether and washed with water. The ether phase was evaporated and the dry product was purified by column chromatography on silica gel with petrol ether–ethyl acetate 2 : 1 as an eluent. Yield 4.7 g (48%).

¹H NMR in CDCl₃: δ 1.63 (d, 3 H), 4.65 (m, 2 H), 4.76 (d, 1 H), 5.65 (s broad, 1 H), 6.76 (m, 4 H).

Preparation of 4'-allyloxybiphenyl-4-carboxylic acid 4-[1-(2,2,3,3,4,4,4-heptafluorobutoxycarbonyl)-1-(R)-ethoxy]phenyl ester (3a) 7F4PPB3. 360 mg (1.35 mmol) of the acid 4'-allyloxybiphenyl-4-carboxylic acid (2a), 493 mg (1.35 mmol) of 1 and 10 mg dimethylaminopyridine (DMAP) in dry methylene chloride was treated with 280 mg (1.35 mmol) dicyclohexylcarbodiimide (DCC) at 0 °C. The temperature was allowed to rise to room temperature and stirring was continued overnight. Dry glassware was used. Column chromatography on silica gel with a gradient of toluene and 0–5% ethyl acetate eluent gave 420 mg of pure product. Yield 51%.

¹H NMR in CDCl₃: δ 1.68 (d, 3H), 2.09 (q, 2 H),4.61 (m, 2 H), 4.66 (d, 2 H), 4.87 (q, 1 H), 5.32 (d, 1 H), 5.48 (d, 1 H), 6.09 (m, 1 H),6.93 (d, 2 H), 7.03 (d, 2 H), 7.15 (d, 2 H), 7.60 (d, 2 H), 7.68 (d, 2 H), 8.22 (d, 2 H).

Preparation of 3b-3e followed the same general principle and is outlined in the ESI.[†]

Preparation of 1,5-di(4'-allyloxybiphenyl-4-carboxylic acid 4-[1-(2,2,3,3,4,4,4-heptafluorobutoxycarbonyl)-1-(R)-ethoxy]phenyl ester) 1,1,3,3,5,5-hexamethyltrisiloxane (4a) di(7F4PPB3)3Si. 94 mg (0.154 mmol) of 3a, 14.5 mg (0.0695 mmol) dihydro-1,1,3,3,5,5-hexamethyltrisiloxane and 0.1% platinum divinyltetramethyldisiloxane as catalyst were dissolved in 5 ml of dry toluene in a flask fitted with a calcium carbonate drying tube and was stirred at room temperature overnight. Using IR spectroscopy the completion of the reaction was checked by monitoring the disappearance of the Si–H stretch at 2160 cm^{-1} . The product was purified by column chromatography on silica gel with toluene-ethyl acetate gradient as an eluent followed by precipitation in petrol ether from a minimal amount of toluene and collected with centrifugation. Dust was removed by dissolving in dichloromethane and passing the solution through a 0.2 µm Teflon filter. Drying in vacuum at 50 C yielded 90 mg of pure product. Yield 90%.

¹H NMR in CDCl₃: δ 0.1 (m, 18 H), 0.63 (m, 2 H), 1.68 (d, 3H), 1.87 (m, 2 H), 3.98 (m, 2 H), 4.69 (t, 2 H), 4.90 (q, 1 H),

6.92 (d, 2 H),6.99 (d, 2 H), 7.15 (d, 2 H), 7.56 (d, 2 H), 7.66 (d, 2 H), 8.21 (d, 2 H).

Preparation of **4b–4f** follows the same general principle as the preparation of **4a** and is outlined in detail in the ESI.†

2.2. Characterisation

Phase characterisation techniques. The phase behaviour of the different materials under study was identified by a combination of optical microscopy, differential scanning calorimetry (DSC), electrical and electro-optical measurements. DSC measurements were carried out with a Perkin-Elmer DSC 7 differential scanning calorimeter.

X-Ray diffraction patterns were recorded using a Guinier film camera or a Guinier goniometer on non-oriented samples; X-ray investigations on oriented samples were carried out with a two-dimensional detector (HI-Star, Siemens AG).

Optical microscopy studies were carried out on standard E.H.C. cells with gaps of 2, 4 and 6 µm, respectively. The cells were filled with the liquid crystal material in the isotropic phase by capillary forces. The inner substrates surfaces of the cells, precoated with ITO transparent electrodes, were covered by a thin polyimide alignment layer unidirectionally rubbed. An alignment layer of this type usually imposes a planar alignment on most liquid crystals. The electro-optic studies were carried out in a set-up consisting of a polarising microscope connected to a camera and photo-detector, oscilloscope, function generator with an amplifier and thermo stage with temperature control within ± 0.1 °C. The apparent tilt angle, θ_{app} , of the molecules was determined from the electro-optical studies as half of the switching cone angle in the field-induced ferroelectric state with $\pm 1^{\circ}$ accuracy as described previously by us.⁸ Spontaneous polarisation, P_s , of the field-induced ferroelectric state was measured using the Diamant-Bridge method.24

3. Results and discussion

3.1. Monomers and their liquid crystal properties

As the monomers, with the phase transitions shown in Table 1, were not in the focus of this study we made only a cursory characterisation of their behaviour. Only the monomers with spacer lengths of 4, 6 and 11 had the phase sequence verified with Guinier film X-ray measurements but the similarities between their textures and the respective textures of the other monomers were convincing enough to assign the phase sequences given in Table 1.

7F4PPB3 (3a). The monomer with the shortest spacer showed the highest transition temperatures with an isotropic to SmA* transition at 223 °C and crystallisation at 100–105 °C. This monomer is very easily supercooled. Slow cooling in the DSC below 1 °C min⁻¹ gave primarily a very ordered/crystal phase below 100 °C while faster cooling produced a monotropic phase, the range of which increased with increasing cooling rate as crystallization was suppressed. In the thin E.H.C. cells the more ordered/crystal phase formed very slowly as the cell surfaces stabilised the monotropic phase in comparison to the crystal phase. The monotropic phase

	$ \begin{array}{c} & & \\ & & $						
Label		<i>n</i> + 2	Transition temperature	es/°C			
7F4PPB3 7F4PPB4 7F4PPB5 7F4PPB6 7F4PPB11	heating heating heating heating heating	3 4 5 6 11	Cr 105 SmE 96 Cr1 102 Cr2 108 Cr 110 Cr 73 SmF 84	SmA* 223 SmB 117 SmE 115 SmB 125 SmB 116 SmC* 132	Iso SmA* 207 SmA* 203 SmA* 190 SmA* 146	Iso Iso Iso Iso	

Table 1 Transition temperatures ($^{\circ}$ C) of the monomers taken at heating, n + 2 equals the number of carbons in the spacer

showed the characteristic banded focal conic texture where the bands stayed clearly visible down to room temperature in the E.H.C. cell and is believed to be the SmE phase.

7F4PPB4 (3b). The second shortest monomer behaved in a way very similar to **7F4PPB3** but at lower transition temperatures. The SmA* focal conic texture is seen between 117 °C and 207 °C and below that range the banded SmB* or SmE focal conic texture appeared. Guinier-film measurements showed that the top banded texture belong to an SmB phase at 96 °C–117 °C while the low temperature phase is an SmE phase.

7F4PPB5 (3c). On cooling this monomer showed a transition from isotropic to SmA* at 201 °C with focal conic texture that showed transition bars at lower temperatures. The similar behaviour to **7F4PPB4** makes us believe that we have a transition to an SmB phase at 123 °C and to SmE at 113 °C.

In the DSC measurements we got crystallisation at low temperatures that showed as two extra melting points before the SmE phase forms but these crystal phases could not be seen in the E.H.C. cells.

7F4PPB6 (3d). The second longest monomer showed a transition from isotropic to SmA^* at 190 °C with focal conic texture patterned by transition bars at lower temperatures

when it transforms into the SmB phase at 116 $^{\circ}C$ and crystallized at 110 $^{\circ}C$ as was shown by Guiner-film X-ray measurements.

7F4PPB11 (3e). The longest monomer in this study is the first one with tilted smectic phases coming from the larger rotational volume of the side chain compared to the volume of the mesogenic core.

It showed a SmA phase from 132–146 °C and a broad SmC* phase in the temperature interval 84–132 °C with a tilt angle at 117 °C of about 35 degrees exhibiting spontaneous polarisation $P_{\rm s}$ of 220 nC cm⁻² at 85 °C, followed by what was shown to be a SmF phase at 73–84 °C. In an E.H.C. cell the SmF phase was found to be monotropic down to room temperature.

The general feature of the monomers with six or fewer carbons in the alkylene spacer is the formation of orthogonal phases while the monomer with 11 carbons in the spacer forms a broad tilted phase below a SmA* phase. It is important to note that only **7F4PPB11** showed a tilted phase and that none of these materials are antiferroelectric.

3.2. Dimers and their liquid crystal properties (Table 2)

di(7F4PPB3)3Si (4a). The dimer with the shortest spacer has the most narrow liquid crystalline temperature range. On





Label	n	Transition temperat	Transition temperatures/°C				
di(7F4PPB3)3Si	3	Cr 79 Cr2	134 SmC _A	140 Iso			
di(7F4PPB4)3Si	4	X 85 X2	97 Col	106 SmC _A	138 Iso		
di(7F4PPB5)3Si	5	X 98 X2	106 Col	120 SmC_{A}	143 Iso		
di(7F4PPB6)3Si	6	CR 81 X2	88 Col	120 SmC_{A}	140 Iso		
di(7F4PPB11)3Si	11	79 Col1 102	Col2 133.5 SmC _A	145 SmA*	150 Iso		
di(7F4PPB6)4Si	6	X 76	Col 111	SmC*	128 Iso		
a <i>n</i> stands for the num	ber of carbons in	the spacer di(7F4PPB6) 4	Si has a tetrasiloxane central	unit while the other com	nounds have a		

" *n* stands for the number of carbons in the spacer. **di**(7F4PPB6)4Si has a tetrasiloxane central unit while the other compounds have a trisiloxane centre.

heating it shows just a typical SmC_A phase between 134 °C to 140 °C. On cooling the material is easily supercooled and what seems to be a columnar phase like in the longer members of this series appears between 118–122 °C when cooling at 5 °C min⁻¹ in the DSC and just below the SmC_A phase in the E.H.C. cell. Only a limited study was performed with this material due to its monotropic behaviour.

di(7F4PPB4)3Si (4b). The dimer with four carbons in the spacer exhibited a rectangular columnar phase between 97–108 °C and a SmC_A up to 138 °C where it underwent a transition to the isotropic phase. The field-induced ferroelectric phase had a very large apparent tilt angle in the entire temperature range 97–138 °C, between 44–46 degrees. The slow vibration axis changes direction with 90 degrees at 106 °C which indicates that the tilt angle reaches 45 degrees at 106 °C.⁸

Below 97 $^{\circ}$ C the material was still switchable in the E.H.C. cell, but it was very difficult to measure the apparent tilt due to the changes in texture taking place under the application of an electric field.

di(7F4PPB5)3Si (4c). As the spacer is extended to five carbons the properties stay similar to those of the material with a four carbon spacer. di(7F4PPB5)3Si exhibited a rectangular antiferroelectric columnar phase between 106-120 °C and an antiferroelectric SmCA phase up to 143 °C, after that transforming to the isotropic phase. The tilt angle is very large in the entire antiferroelectric phase and varied between $44-47^{\circ}$ in the field-induced ferroelectric phase. The 90 degree switch of the slow axis that indicates the field-off state with 45° molecular tilt was measured with a λ first-order red plate in the same way as in the study of di(7F4PPB11)3Si.⁸ In that way the tilt angle was found to go above 45° at 124 °C and back below 45° at approximately 100 °C. At 124 °C this matches the measured induced tilt angles well (at 100 °C the induced tilt angle could not be measured). It should be noted that in the columnar phase we could not apply enough field strength to switch the sample without destroying the cell and the switch is also to a very large extent a continuous transition without a clear switching threshold.

di(7F4PPB6)3Si (4d). When the spacer has six carbon atoms the properties stay very much the same. The material exhibits an antiferroelectric columnar phase between 88–120 °C and antiferroelectric SmC_A phase up to 140 °C becoming isotropic at higher temperatures. Also in this material the apparent tilt in the field-induced ferroelectric phase is very large and above 45° in the entire columnar phase. By using a λ first-order red plate, a switch in the vibration axis at 119 °C was shown. In this case, in contrast to the others, it was easier to measure the induced tilt angle in the columnar phase than in the SmC_A phase as there seemed to be a rotation of the texture in the antiferroelectric top phase when an electric field was applied, which made measurements of tilt angles uncertain.

di(7F4PPB11)3Si (4e). The material with the longest spacer was extensively studied earlier,⁸ the highlights are that it has two different columnar phases at 79–103 °C and 103–133 °C as well as a SmC_A phase at 133–145 °C. At 145–150 °C there was

a SmA phase which means that the material had a much greater temperature dependence of the tilt angle then the previously described substances. The molecular tilt also exceeds 45° in the columnar phase.

di(7F4PPB6)4Si (4f). This dimer has four siloxane units instead of the three that di(7F4PPB6)3Si contains and this change proved to alter the characteristics more then the variation of the carbon spacers had done. It has an antiferroelectric columnar phase at 76-111 °C and a SmC* phase between 111–126 °C. Notice that in this case the phase is a ferroelectric SmC* and not an antiferroelectric one as in the previous compounds. This is in agreement with what Coles et al. described as the effect of 3 and 4 silicons in the bridging group of the dimers.^{6,10,11} The columnar phase still has antiferroelectric behaviour, however, and this can be explained by the fact that the columnar phases are non-interdigitating phases, the siloxane parts are assumed to be in the middle of each layer and the fluorinated end tails are phase separating. Thus the layer-layer interaction is governed by the fluorinated tails in all the columnar phases and the siloxane bridging group in the dimer structure is not as much of an issue. The siloxane group, however, still has an influence on the switching process. Although the antiferroelectric phase of the di(7F4PPB6)4Si is a columnar phase, it is very easy to switch from the antiferroelectric to the ferroelectric state. The fieldinduced antiferro- to ferroelectric transition is of first order manifested by generation and propagation of field induced solitary waves invading the anticlinic liquid crystal phase along the smectic layers. The time for relaxation back to the antiferroelectric state in the lower temperature region, when the applied electric field is switched off, is on the order of minutes. This means that the antiferroelectric structure in this compound is greatly destabilized compared to the corresponding phase in the analogous dimer with 3 siloxane units. Due to the very long relaxation time, the double current peak, typical characteristic of the antiferro- to ferroelectric switching, was not observed and the X-ray measurements only showed that the phase of this compound in the temperature range at 76-111 °C is a tilted columnar phase, which could be either ferro- or antiferro-electric. However, the generation and propagation of the quasi-one dimensional finger-like solitary waves observed in di(7F4PPB6)4Si under an applied electric field is an indication of the antiferroelectric character of the columnar phase.

X-Ray characterisation. X-Ray studies were performed using the Guinier method and a small angle camera for powder-like samples as well as a 2-D detector for oriented samples. The alignment was achieved by slowly cooling a drop on a clean glass plate from the isotropic state. It can be summarised that the patterns of the different compounds in the corresponding phases exhibit a very similar feature. Therefore the general structural properties from a X-ray viewpoint, that gives the phase diagram shown in Fig. 1, shall be discussed for the example of the compound **di(7F4PPB11)3Si**.

Cooling the sample from the isotropic phase a layer structure without order in the layers appears. This is indicated by sharp reflections in the low angle region as well as by a



Fig. 1 Phase diagram of the dimers as deduced from just the X-ray measurements.

diffuse scattering in the wide angle region of the pattern. In the high temperature phase (145–150 °C) the outer diffuse scattering is more or less smeared out on an arc (Fig. 2a), this means that a tilt of the molecules within the layer cannot be ruled out definitely. But in the next phase (133–145 °C), following with decreased temperature, the diffuse scattering is concentrated more and more out of the equator of the pattern (Fig. 2b), from which an increasing tilt with decreasing temperature can be deduced. This is in agreement with the temperature dependence of the *d*-values (Fig. 3). Together with information about the textures (homeotropic texture in the



Fig. 3 Temperature dependence of the *d*-value of di(7F4PPB11)3Si.

high temperature phase; schlieren texture in the following phase) and switching behaviour a SmA*–SmC_A polymorphism is proved. At further cooling the pattern is changed at about 133 °C (Fig. 2c). In the small angle region of a pattern of a well oriented sample (Fig. 2d) several reflections can be seen and they can be indexed on the basis of a rectangular centred cell with a *c2mm* symmetry (only reflections with h + k = 2n are observed). The pattern is changed once more at about 104 °C (Fig. 2e). The reflections exhibit a different extinction, which ruled out a centred cell. Reflections with h + k = 2n + 1 are observed, too, where the 0k reflections were found only with k = 2n. Since h0 reflections (on the equator of the pattern)





Fig. 2 X-Ray diffraction pictures of di(7F4PPB11)3Si as described in the text

Table 3 Smectic layer thickness of the dimers near the centre of the ${\rm SmC}_A$ temperature region

Label	d-Value/nm	<i>n</i> + 2
7F4PPB4	2.76	4
7F4PPB5	2.85	5
7F4PPB6	2.94	6
7F4PPB11	3.41	11

could not be detected, a difference between the possible plane groups p2mg and p2gg can not be distinguished.

If we speculate about a molecular model, then the length of the molecules (L was estimated by CPK models) has to be compared with the layer thickness (d-value). In Table 3, the d-values as a function of the spacer length are shown. The function displays a linear behaviour, but the increase per methylene group is much smaller than expected for an elongated molecular form (0.05 nm instead of 0.125 nm). It suggests a large tilt and/or a deviation of the alkyl spacers from the all-trans conformation. Despite this deviation the comparison of the *d*-value with the length of the molecule (L)shows a great difference. For example, for compound di(7F4PPB11)3Si: $L \approx 8.5$ nm, d = 3.41 nm; for compound di(7F4PPB4)3Si: $L \approx 7.0$ nm, d = 2.74 nm. Such a difference demands additional assumptions about the conformation and the packing of the molecules. It is known from the literature that the siloxane spacer (especially with 3 siloxane groups 25) favours a bent conformation leading to an antiferroelectric structure. We also see from the apparent tilt measurements (Fig. 4) that the tilt of the mesogenic part varies between $0-53^{\circ}$. However, even if a bending angle average of about 120° is assumed it leads to a length L of 7.5 nm. That is greater than twice the d-value in the SmC_A phase (=3.41 nm) and demands an intercalation of the molecules by one leg. This packing (Fig. 5) in connection with the measured tilt angle results in a very good agreement between the measured and calculated values and proves the existence of an interdigitated SmCA phase.

The lattice parameters for compound di(7F4PPB11)3Si in the Col_{rect} phase amount to a long side of 8.5 \pm 0.3 nm and short of 6.5 \pm 0.2 nm. These parameters remain unchanged at



Fig. 4 Apparent tilt angle θ_{app} of the dimers as a function of temperature. **di(7F4PPB4)3Si** (\blacklozenge); **di(7F4PPB5)3Si** (\square); **di(7F4PPB6)3Si** (\bigstar); **di(7F4PPB11)3Si** (\times).

the transition into the low-temperature Col_{rect} phase at 104 °C. This transition is connected with a change of the symmetry. In the high temperature phase the symmetry demands identical building groups at the positions 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$ of the lattice. Therefore it is assumed that in the high-temperature Col_{rect} phase the bent direction of the molecules within a column (perpendicular to the drawing plane) is statistically distributed from left to right. At cooling into the low temperature Col_{rect} phase the bent direction is more ordered, which results in a primitive lattice with the symmetry p2gg.

The cooling process described above can be illustrated by Fig. 5 and 6. The highest temperature liquid crystal phase is a SmA phase which experiments indicate is a de Vries type of SmA phase. The similar materials studied previously^{9,21} have been shown to have such a SmA phase. Each layer in a de Vries SmA is tilted as shown in Fig. 5b but the orientation of the tilt angle changes randomly from one layer to another. Upon cooling the tilt angle increases and the molecular order transforms into anticlinic, *i.e.* SmCA, with alternating tilt direction in every layer (Fig. 5a). The anticlinic molecular order in SmCA could be changed to synclinic, *i.e.* SmC (Fig. 5b), by applying an electric field. The energy required to rotate the very flexible siloxane/alkane chains in the middle of



Fig. 5 The interdigitated nature of the dimer ordering with the fluorinated outer parts and the siloxane centre being mixed in the SmCA phase (a) and in the induced ferroelectric phase (b); d represents the smectic layer thickness, θ represents the tilt angle.



Fig. 6 Possible ordering of the molecules that produces a columnar phase. The box depicts the column with the long and short lattice parameters a and b.

the dimers is very low, and therefore will not greatly influence the energy needed to switch the molecules from anticlinic to synclinic order. At lower temperatures an additional increase of the molecular order takes place, which results in the formation of two different columnar phases, with structure schematically depicted in Fig. 6. However, the exact models of these phases are still not known. Upon very high electric fields, close to the dielectric breakdown of conventional cells, a ferroelectric state can be induced. Due to the high field that is needed considerable changes in the phase structure may take place during the switching process.

3.3. Comparison of liquid crystal properties

In this study all the dimers show complex phase behaviour in comparison to the non-fluorinated counterparts that only had the SmA* and SmC*/SmCA* phases.9 It is well known that fluorination induces greater phase separation and we believe that in this case we get three different layers, siloxane rich, fluorine rich and mesogen rich, at temperatures below the SmC_A phase. However, due to the different size of the three different parts the final structure is not a simple smectic structure and instead we get alternating columnar blocks to make up for the size incompatibility of the different layers. All the dimers also show high apparent tilt angles that exceed 45 degrees (Fig. 4) and very high polarisation in the columnar phase (Fig. 7). The smectic layer thickness, shown in Table 3, are consistent with each layer being formed by one tilted mesogen, being less then half the calculated length of the total dimer and thus V-shaped and probably interdigitated as suggested by Coles et al.^{2,3,10,25}

All in all a new series of dimeric chiral antiferroelectric materials using a trisiloxane as the central connecting linker and fluorinated tails has been synthesized together with their corresponding monomers. Spacer lengths of 3–6 and 11 methylene groups were used. As a comparison to evaluate the



Fig. 7 The spontaneous polarisation of the dimers as a function of temperature. di(7F4PPB4)3Si (\blacklozenge); di(7F4PPB5)3Si (\square); di(7F4PPB6)3Si (\blacktriangle); di(7F4PPB11)3Si (\times).

effect of the siloxane length, one dimer with a tetrasiloxane core was also made and studied. Monomers with 3-6 carbons in the spacer showed orthogonal smectic phases and only the long 11 carbon spacer 7F4PPB11 showed tilted phases in a very similar way to what we obtained in the unfluorinated monomers previously studied.⁹ All trisiloxanes showed a high temperature antiferroelectric phase followed by one or two columnar antiferroelectric phases when decreasing the temperature. The polarisation was high especially in the columnar phases where it ranged from 800–1200 nC cm⁻² (Fig. 7) but was also difficult to study as very high fields was required to induce a transition to the ferroelectric state. The apparent tilt angles were also very high, above 45 degrees for all materials studied (Fig. 4). In comparison, the tetrasiloxane containing dimer showed a ferroelectric phase at high temperature, in accordance with the trend described by Coles et al. 3,6,10,11 for tetrasiloxanes. But also in this compound the columnar phase was found to be antiferroelectric even though it was much easier to switch into a ferroelectric state. It relaxed, however, very slowly back to the antiferroelectric state. Hence, the general idea that trisiloxane cores promote antiferroelectricity is still correct also for this material. It can also be noted that the phase separation between siloxane, fluorinated and mesogenic parts of the molecules and the difference in size of these parts in the series of molecules studied here have a similar effect as in some fluorinated dimers previously studied¹¹ and in this case with an even greater effect as the phases became columnar when lowering the temperature while in the earlier study it was found that the separation gave rise to modulated tilted smectic phases. It is of interest to note that these dimers do show columnar phases with some resemblance to banana phases, but it has to be kept in mind that although without an electric field the molecules resemble bananas the siloxane and alkane spacers ensure that the freedom of movement for each mesogen is very high. The fact that the mesogens can move relatively independently of each other under an electric field means that the switching characteristics to a large degree resembles those found in normal monomeric liquid crystals, especially in the SmCA and SmA* phases

4. Conclusions

The main goal of this work was to study the effects of increased phase separation in siloxane dimeric liquid crystals with fluorinated tails. New dimeric materials of this kind were synthesized and characterized. These compounds possess higher polarisation and tilt angles than their unfluorinated counterpart previously made.9 One goal in making these new materials was to study the properties of antiferroelectric liquid crystal materials with very high tilt close to 45 degrees. This goal was achieved and the optical ramifications of passing 45 degrees tilt angle in antiferroelectric materials were studied by us in detail⁸ on di(7F4PPB11)3Si, while the present work contains all other structure-property relationships studied as well as their synthesis. For practical use further work on design and mixing of several fluorinated and unfluorinated compounds is needed to obtain AFLC materials possessing a large molecular tilt, preferable with 45 degrees molecular tilt over a broad temperature range centred at room temperature, as is required for display applications.

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