From antiferroelectricity to ferroelectricity in smectic mesophases formed by bent-core molecules

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Abstract. This contribution gives an overview of ferroelectric switching liquid crystalline phases formed by bent-core molecules. First a description of some general principles behind the mesophase formation within bent-core systems will be given, followed by a short review of the mesophase structures formed by such molecules. Then, different classes of ferroelectric switching bent-core mesogens will be described. This type of switching behaviour has been reported for several subtypes of polar smectic phases (B2, B5, B7 and SmC_G) and recently for columnar mesophases. In this discussion particular attention will be made to polyphilic bent-core molecules, composed of three incompatible units, a bent aromatic core, alkyl chains and an oligosiloxane unit. The importance of the decoupling of the layers into microsegregated sublayers for the ferroelectric organisation is discussed. Many of the ferroelectric switching mesophases show dark textures with distinct regions of opposite chirality in their ground states. It is discussed that this might be due to a helical superstructure formed as a result of an escape from macroscopic polar order. Hence, the materials themselves are not ferroelectric in the ground state, but upon alignment within an electric field in the measuring cells the ferroelectric states are stabilised by surface interactions, leading to a ferroelectric switching system. The designing principle was extended to mesogenic dimers with bent-core structural units. For these compounds, depending on the number of dimethylsiloxane units in the spacer either ferroelectric or antiferroelectric switching was observed, whereby the effect of parity is reversed to that observed for conventional calamitic dimesogens. Finally, a carbosilane-based first generation dendrimer is reported. It shows a ferroelectric switching phase, for which a non-correlated organisation of tilted polar smectic layers is proposed ($SmCP_R$).

Keywords. Liquid crystals; ferroelectricity; chirality.

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1. Introduction

Symmetry is one of the basic concepts in physics and chemistry, as numerous properties are symmetry dependent and in chemistry the reduction of the molecular symmetry can lead to complex self-organised structures. In liquid crystal (LC) systems reduction of the phase symmetry can be achieved by segregation, tilting, restriction of the rotational disorder and by reduction of the molecular symmetry. The introduction of chirality into mesogenic molecules is a well-known approach to reduce the phase symmetry [1,2]. A special property which can be realised in tilted chiral smectic phases, like SmC* is polar order, leading to ferroelectric, ferrielectric and antiferroelectric switching behaviour of such mesophases

in electro-optic devices [3]. Several attempts have also been made to reduce the molecular symmetry by appropriate combination of different incompatible segments, leading to polyphilic molecules [4–6]. However, introduction of a bend into the rigid segment of calamitic (rod-like) mesogenic molecules turned out to be one of the most powerful and successful approaches in this direction. Nowadays, such bent-core molecules, often referred to as banana molecules or bow molecules, belong to the most exciting fields of LC research and supramolecular chemistry. First bent-core mesogens have been synthesised by Vorländer and Apel [7] and Matsunaga and Miyamoto [8]. The present rapid development in this field was mainly initiated by the discovery by Niori *et al* [9] who showed that bent-core mesogenic compounds, such as **1** could organise into novel types of LC phases with polar order [10]. The fact that such achiral molecules can give rise to supramolecular chirality in fluid systems also arose significant interest [9].

2. Banana phases, a short overview

There are numerous new mesophases which have been detected with these banana-shaped mesogens. Most of them have no analogues in LC systems formed by conventional calamitic molecules. Initially there were seven phases designated as B1 to B7 according to the sequence of their discovery, where B stands for bent-core, 'banana' or 'bow'. The structures and characteristic features of these phases were summarised in 1999 [11] (see also table 1). In the meanwhile the number of new phases has dramatically risen. It turned out that some of the Bn phases have several subphases, i.e., these phases actually represent families of related phases. Also new phases, which are not covered by this nomenclature system have been reported and finally there are numerous new mesophase structures, which have not been published, because their phase structures are not sufficiently well-characterised at present.

The large diversity of LC phases arises due to the reduced symmetry of these molecules, leading to polar order and supramolecular chirality.

Polar order: The bend in the rigid cores of such liquid crystals leads to a reduction of the rotational disorder of the molecules around their long axes. If segregation of aromatic cores and aliphatic chains is sufficiently strong, the molecular structure facilitates an organisation into layers. Since the molecules are closely packed within the smectic layers and additionally, the rotation about their long axes is strongly hindered, the bent directions align parallel in each layer. As a result of this directed organisation, each layer has a spontaneous polarisation P parallel or antiparallel to the direction of the molecular bend b (figure 4). Many of the mesophases formed by bent-core molecules result from a strong desire to escape from a parallel alignment of the bent directions in adjacent layers, i.e., from the desire to escape macroscopic polar order. As shown in figures 2 and 3 there are at least three distinct ways to achieve this: (1) collapse of the layers, (2) antiparallel alignment of the bent direction in adjacent layers, and (3) formation of helical (= chiral) superstructures.

Often the collapse of the layers leads to the formation of ribbon-like segments of the smectic layers [12,13]. These ribbons organise in such a way that the bent-directions of the molecules in adjacent ribbons is antiparallel, leading to an efficient escape from macroscopic polar order. As shown in figure 2, the collapse can occur in two distinct directions, either perpendicular or parallel to the polar direction P. In the first case the polar direction

Table 1. Summary of the typical feature of B1–B7 banana phases.

Bn	Other symbols	Phase type	Characteristic properties	Switching behaviour
B1	Col$_r$	Columnar mesophases (ribbon phases), different phase structures are possible	X-ray: 2D lattice, mosaic texture (spherulitic textures)	non-switching
B2	SmCP$_A$ C$_{B2}$	Tilted smectic phase, monolayer structure, polar order	X-ray: layer reflections, $L < d > L/2$, diffuse wide angle scattering, Schlieren texture, non-specific broken fan texture	AF
	SmCP$_A$/ SmCP$_F$	Tilted smectic phase, monolayer structure, polar order	X-ray: layer reflections, $L < d > L/2$, diffuse wide angle scattering, dark texture with domains of opposite handedness, sometimes bluish appearance, often high viscosity	AF FE
	SmAP$_A$ C$_{PA}$	Orthogonal smectic phase, monolayer structure, polar order, polar axis parallel to the layer planes	X-ray: layer reflections, $L < d > L/2$, diffuse wide angle scattering on the equator, Schlieren texture, fan texture	AF
B3		Crystalline lamellar mesophase, tilted	X-ray: layer reflections, numerous sharp reflections in the wide angle region	non-switching
B4	SmBlue[a]	Soft crystal, non-tilted, double twisted TGB-like structure?	X-ray: layer reflections, numerous reflections in the wide angle region, but fewer and less sharp reflection compared to the B3 phase, transparent blue colour, regions with opposite chirality, SHG active in the ground state	non-switching
B5		Tilted smectic phase, monolayer structure, polar order, short range 2D lattice within the layers, non-correlated layers	X-ray: layer reflections, $L < d > L/2$, 3 maxima in the wide angle region, Schlieren texture, non-specific broken fan texture	AF FE
B6	Sm$_{int}$ Sm$_c$	Intercalated smectic mesophase	X-ray: layer reflections, $d < L/2$, diffuse scattering in the wide angle region, fan texture and Schlieren texture	non-switching
B7		Modulated layer structure?	Typical textures: screw-like growth, helical superstructures, fibres can be drawn, X-ray: complex diffraction pattern (sometimes layer structure?), diffuse wide angle scattering	non-switching FE (AF)

[a]This assignment should not be used, because it may be mixed up with the smectic blue phases formed by strongly chiral calamitic molecules, which have quite distinct properties and phase structures [2].

is perpendicular to the long axis of the formed ribbons and in the second case it is parallel [14–16]. The resulting ribbons organise with the formation of two-dimensional lattices.
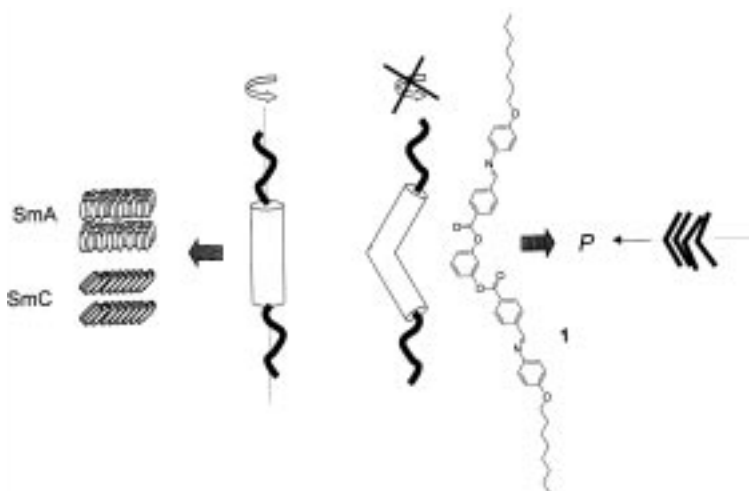
Figure 1. Comparison of calamitic and bent-core molecules and their organisation in smectic layers. SmA and SmC phases are formed by conventional calamitic molecules (left), the directed organisation of bent-core molecules, such as compound **1** in smectic layers gives rise to a spontaneous polarisation *P* parallel to the layer planes (right).
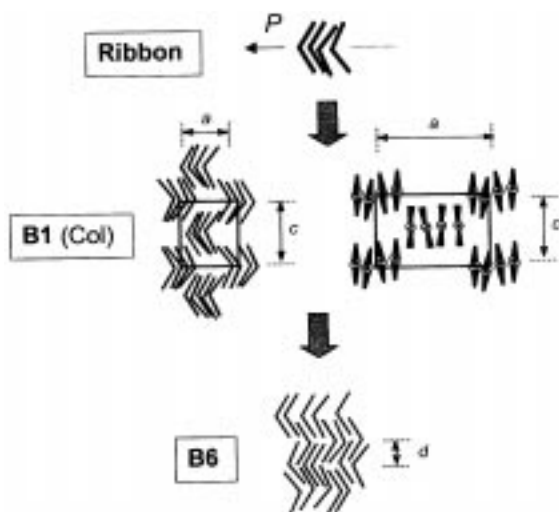

Figure 2. Columnar phases (B1) and intercalated smectic phases (B6) resulting from the collapse of the polar smectic layers. In this two-dimensional presentation the ribbons are infinitely extended perpendicular to the projection plane. In the columnar phases the polar direction can be either parallel to the 2D lattice (perpendicular to the long axes of the ribbons, left) or perpendicular to the 2D lattice (parallel to the long axes of the ribbons, right). Only non-tilted arrangements are shown, but tilted organisations are also possible.

These mesophases, often designated as B1 phases, can be regarded as columnar (Col) mesophases. Additionally, the molecules can be tilted or non-tilted within the ribbons, leading to numerous different possible arrangements [15,16]. However, in such columnar mesophases there is an energetic and entropic penalty resulting from the unfavourable overlapping of the rigid aromatic cores and the flexible aliphatic chains at the boundaries between the ribbons. This becomes increasingly important as the length of the chains increases. Therefore, the diameter of the ribbons (i.e. the number of molecules organised side by side in the cross-section of the ribbons) depends on the relative length of the terminal chains with respect to the size of the bent-core [13]. If the chains are relatively short, nematic (N) and intercalated smectic phases (designated as B6) are often observed. Increasing the length of the terminal chains leads to the abovementioned B1 phases. Further elongation of the chains disfavours this collapse and polar smectic phases with monolayer structure (B2) are formed. Hence, the phase sequence B6–B1–B2 is often observed with increasing chain length [17,18]. In the resulting smectic phases the rigid aromatic parts and the flexible lipophilic terminal chains are well-segregated into distinct sublayers. The bent direction in adjacent layers is antiparallel, so that the layer polarisation alternates from layer to layer (figure 3a), leading to a macroscopic apolar antiferroelectric (AF) structure (SmP_A). Within the layers the molecules are in most cases additionally tilted parallel to the polar direction ($SmCP_A$ phases, also designated as B2), however in a few reports a non-tilted $SmAP_A$ structure has also been observed [19].
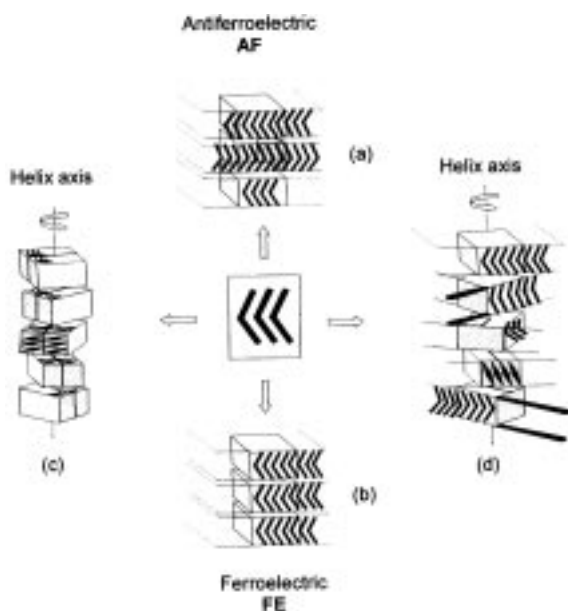

Figure 3. Molecular organisation within polar smectic phases and possible ways to escape from a macroscopic polarisation in mesophases built up by polar layers. (**a**) Antiferroelectric smectic phase, (**b**) ferroelectric smectic phase with macroscopic polar order, (**c**) TGB-like helical structure (helix axis is parallel to the layer planes of the smectic slabs), (**d**) SmC*-like helical structure (helix axis is perpendicular to the smectic layer planes).

The macroscopically polar ferroelectric (FE) states (SmP_F) in which the bent direction and hence the polar direction are parallel (figure 3b) are achieved after applying a sufficiently strong external electric field. These FE states, obtained above a certain threshold voltage are not stable and rapidly relax back to the AF ground state after the electric field is reduced below a certain threshold voltage. This gives rise to a tristable switching process if a triangular wave voltage is applied (see figure 4). There are three distinct stable states, the AF ground state and two FE states (FE1 and FE2). The occurrence of two polarisation peaks in the switching current response in each half period of the applied triangular wave voltage is a characteristic feature of this tristable AF switching behaviour.

Supramolecular chirality: Another possible escape from macroscopic polar order could be the formation of helical (chiral) superstructures, which should occur if for any reason an antiparallel alignment of the molecular bent directions in adjacent layers is energetically disfavoured. In analogy with structures known from some smectic phases of chiral calamitic mesogens [1], the helix axis can be perpendicular to the layer planes (SmC*-like, figure 3d) or parallel to the layer planes (TGB-like, figure 3c) [12,20,21]. In the first case the layer structure is maintained, whereas the latter case requires a collapse of the layers with formation of smectic slabs. Such a TGB-like structure is under discussion for the so-called B4 phase, a soft crystal characterised by the coexistence of chiral domains of opposite handedness [20,22].
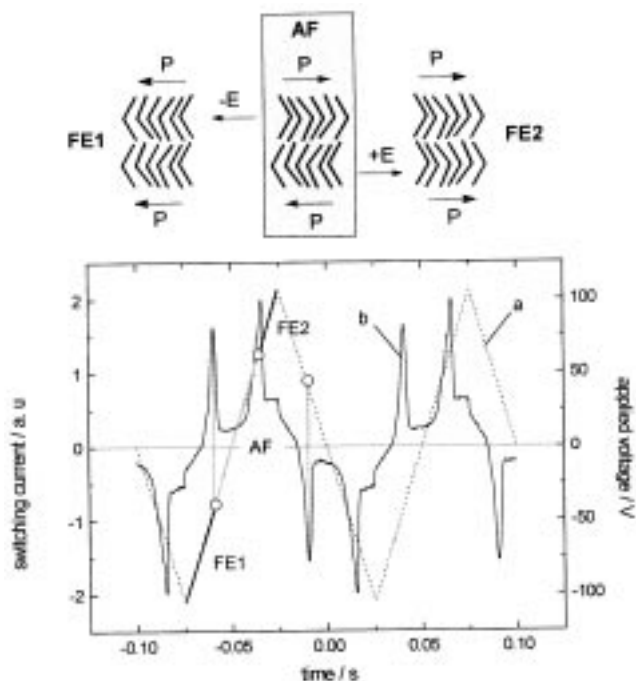

Figure 4. Typical switching current response curve on applying a triangular wave voltage as measured for an antiferroelectric B2-type mesophase. a = triangular wave voltage, b = switching current response curve (6 μm polyimide-coated ITO-coated cell) [13].
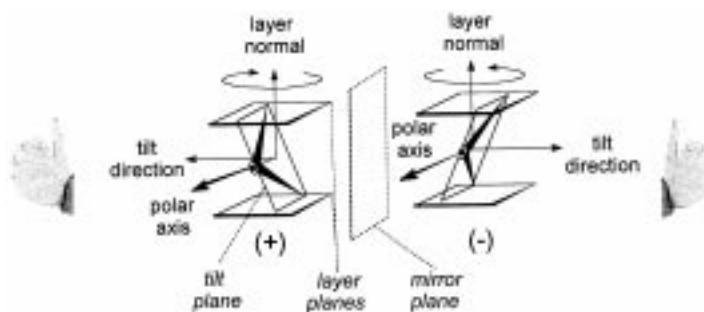
Figure 5. Geometric chirality of polar smectic layers formed by tilted bent-core molecules. Layer normal, tilt direction and polar axis define either a right-handed (+, shown in red) or left-handed (−, shown in blue) coordinate system. Changing either the tilt direction or the polar direction reverses the chirality [27].

Macroscopic helical superstructures were detected in the textures of special mesophases designated as B7 phases [23–25]. These phases are characterised by unique textures, such as spiral germs, ribbons with equally spaced lines, two-dimensional periodic pattern and banana-tree leave textures. However, the X-ray diffraction pattern and also the switching behaviour can be quite distinct for different materials forming these textures. Hence, there is a strong reason to think a B7 group of mesophases rather than the existence of only one single mesophase. Though the B7 phases still represent a mysterious class of banana phases, there are some recent investigations which point to a modulated smectic structure for at least some of these phases [26].

Formation of helical superstructures is not the only means by which chirality in bent-core systems can be observed. Supramolecular chirality is a direct consequence of the tilted organisation of bent-core molecules within layers, which leads to a C_2 phase symmetry [27]. In such systems the layer normal, the tilt direction and the polar axis P define either a right-handed or left-handed coordinate system as shown in figure 5. Any reversal of P or tilt direction changes the chirality of the layer. Allowing synclinic (tilt direction in adjacent layers is identical) or anticlinic (tilt direction in adjacent layers is opposite) stacking of tilted polar layers, there are four possible distinct arrangements resulting from polar order (FE or AF) and layer chirality (homochiral or racemic) [27]. Figure 6 gives an overview over the possible structures of polar smectic phases formed by bent-core molecules.

When considering chirality, it should be noted that bent-core mesogens are not flat as the drawing of their chemical formula on paper might suggest. In fact, all mesogenic bent-core molecules reported so far incorporate at least two conformational rather flexible linking units (e.g. COO) and therefore these molecules can adapt many different conformations, among them, numerous helical conformations [20,21]. Indeed, calculations show that a twisted conformation represents the most stable conformer for compound **1** and its homologues [28]. In the liquid state and in solutions the enantiomeric conformers are equally populated and therefore no overall macroscopic chirality could be observed. However, the conformational chirality of the individual molecules and the inherent presence of layer chirality in the tilted banana phases can give rise to diastereomeric relationships between conformational molecular chirality and geometric layer chirality. Therefore the question arises, if this coupling of layer chirality and molecular conformational chirality (in the
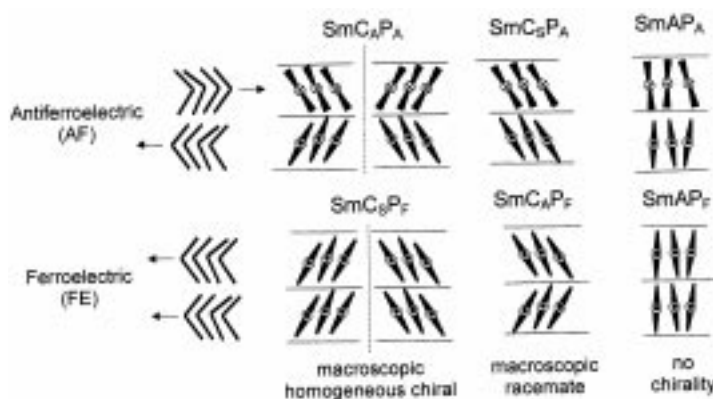
Figure 6. Models of the possible supermolecular isomers of polar tilted smectic SmCP [30] and non-tilted SmAP phases formed by bent-core molecules. At the left, the antiferroelectric (P_A) and ferroelectric organisation (P_F) are shown. All other pictures represent orthogonal views of these arrangements parallel to the polar axis (from the left, parallel to the plane of the paper). The subscripts modifying the tilted SmC phases refer to synclinic (S) or anticlinic (A) tilt, respectively of the molecules in adjacent layers. The colour indicates the layer chirality. There are two possible enantiomers for each of the macroscopic homogeneous chiral states $SmC_A P_A$ and $SmC_S P_F$, which usually occur as conglomerates. The macroscopic racemates $Sm_A P_F$ and $SmC_S P_A$ can be regarded as non-chiral mesostructures and the non-tilted SmAP phases are non-chiral.

confined geometry provided by the dense and directed organisation of the molecules in the layers) could explain the occurrence of macroscopic chiral domains in some mesophases.

Almost all of the bent-core molecules synthesised so far exhibit AF ground state structures (often $SmC_S P_A$). This is easily understandable because of the inherent tendency of fluid systems to escape from a macroscopic polar order. Nevertheless, some reports about ferroelectrically switchable mesophases formed by banana-shaped molecules have recently appeared and immediately attracted significant interest [29]. In the next sections the recent developments in this field will be discussed.

3. First examples of ferroelectric banana phases

Ferroelectric switching is indicated by the occurrence of only one polarisation peak in the current response in each half period of an applied triangular wave voltage (see for example figure 10 and the corresponding explanations in the next section), which means that there is a direct (bistable) switching between the two distinct FE states. However, there are numerous possible artefacts and therefore modified switching experiments (e.g. different frequencies, plateau method [25]), as well as detailed electro-optical investigations, dielectric investigations and SHG experiments are required to unambiguously confirm a FE switching process. Ferroelectric switching with banana mesophases was first confirmed for two types of banana compounds showing typical B7 textures [25,30]. Recent investigations suggest that at least some of these phases represent modulated smectic phases with a frustrated ferroelectric $SmC_S P_F$ structure [26]. Bedel *et al* reported ferroelectric
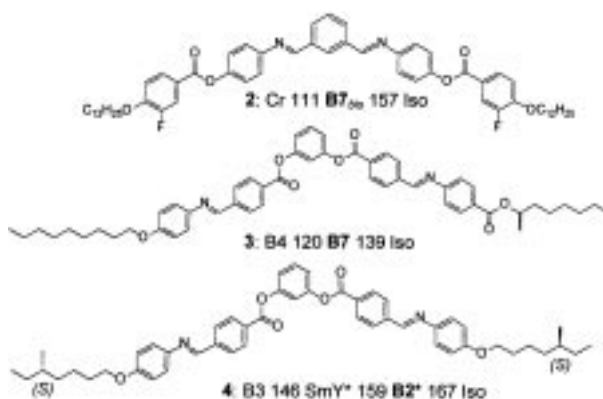
Figure 7. Molecular structures of the first reported examples of bent-core mesogens forming ferroelectric switching mesophases [25,30,34].

switching behaviour for a B7 phase (designated as $B7_{bis}$) formed by the bent-core mesogen **2** substituted by two fluorine atoms in peripheral positions on the aromatic core, *ortho* to each of the two terminal alkoxy chains [25]. This special substitution pattern seems to be a quite useful structural unit for the preparation of FE switchable banana phases, as more recent examples by Nadassi *et al* (B5 phases [31]) Amaranatha Reddy and Sadashiva (B2 and columnar phases [32]) indicate.

Another approach was used by Walba *et al* based on the knowledge that FE structures require an anticlinic interlayer correlation in bent-core systems [30]. Walba used this known property of the 2-octyloxycarbonyl group $[–COO–CH(CH_3)C_6H_{13}]$, either unichiral or racemic, to promote the formation of anticlinic interlayer interfaces [33]. Indeed, the B7 phase of compound **3** was reported to show FE switching behaviour.

The third report uses chiral molecules **4**, which have branches at both ends of the terminal alkoxy chains [34]. Observations of the optical second harmonic generation signal confirms that the ground state of this B2-type mesophase is a bistable ferroelectric ($SmC_AP_F^*$), in which the molecules adapt a twisted orientation from the top to bottom surface (homogenous alignment in book-shelf geometry) in the absence of an electric field. In addition to this, two types of metastable domains, one ferroelectric ($SmC_SP_F^*$) and the other antiferroelectric ($SmC_SP_A^*$) were detected [35]. Binary mixtures of the AF achiral compound **1** (see figure 1) and the ferroelectric $SmC_AP_F^*$ phase of the unichiral compound **4** were also investigated [36]. With increasing concentration of the FE **4** in the AF **1**, a transition from SmC_SP_A via $SmC_SP_F^*$ to $SmC_AP_F^*$ was observed. This indicates a step-wise cross-over from the purely synclinic structure (SmC_SP_A, C_S = synclinic interlayer correlation, but also the AF order has synclinic interfaces) via a mixed synclinic/anticlinic structure ($SmC_SP_F^*$) to the purely anticlinic structure ($SmC_AP_F^*$, the FE order has anticlinic interfaces) of the mesophases. These results show that intermolecular interactions at the interlayer interfaces play an important role in choosing the clinicity and polar order [27].

The occurrence of only one current response peak at low frequencies was also reported for a Schiff's base derived dimesogen. However, because of the high transition temperatures, further investigations were not possible [37].

4. Polyphilic bent-core molecules

Our group more or less incidentally jumped into this area of research as it was tried to further reduce the symmetry of bent-core molecules by making their terminal ends incompatible with each other. For this purpose perflourinated segments [13] as well as oligosiloxane units were used [38]. Three selected examples are compared in figure 8, which shows that the introduction of the third incompatible unit, either RF or oligosiloxane, leads to a significant stabilisation of the liquid crystalline state. However, the mesophase types of the compounds **5** and **7** are completely different. The mesophase of the perfluorinated compound **5** [39] is an AF switchable $SmCP_A$ phase (B2 phase) similar to that observed for the mesophases of the related hydrocarbon analogues with (e.g. compound **6**) or without an olefinic double bond [13].

The mesophase of the oligosiloxane derivative **7** [38] is quite distinct from that of the other two compounds. (Only compound **7** is discussed herein, but same observations were made with related molecules with non-branched oligosiloxane units [40].) Typically, it grows from the isotropic liquid state as fractal nuclei which coalesce to a grainy unspecific texture which appears dark (optically isotropic) between crossed polarisers, showing only very small irregularly distributed bright spots. Shearing leads to completely dark samples. The most remarkable feature is, that in these mesophases domains of opposite handedness can be distinguished. On rotating the analyser by small angles, dark and light domains become visible. If the analyser is rotated in the opposite direction the contrast of the domains is reversed (see figure 9a,b). The area occupied by the distinct regions is on average equal, but addition of a unichiral dopant (ca. 5%) gives rise to the dominance (80%) of one of these regions [39].

X-ray investigations confirmed a well-defined layer structure. The diffuse wide angle scattering has two maxima, one at 0.45 nm that corresponds to the mean distance between the fluid alkyl chains and a second one with a maximum at about 0.7 nm corresponding to the mean distance between the disordered siloxane units [38]. This is an indication
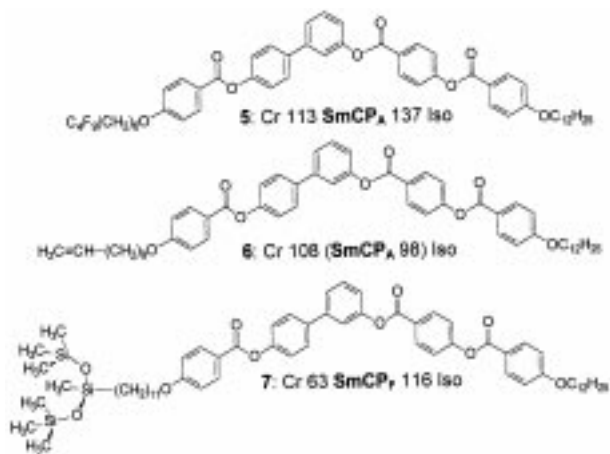

Figure 8. Comparison of the liquid crystalline properties of the polyphilic bent-core mesogens **5** and **7** with the conventional bent-core molecule **6**.

of nanosegregation of the oligosiloxane sublayers from the rest of the molecules. As the cross-sectional area of the siloxane units is much larger than that of the other parts of the molecules, the molecules adapt an average antiparallel end-to-end packing within the layers. In this way the siloxane units build up their own sublayers, leading to a micro-segregated triple layer structure in which the molecules are additionally tilted with respect to the layer normal.

Electro-optical investigations show only one peak in the switching current curve for each half period of the applied triangular voltage, as is typical for a FE switching (figure 10). Even at very low frequencies (0.02 Hz) and also by using the plateau method [25] only one very sharp current response peak was found. Another remarkable feature is the significantly lower threshold voltage for this FE switching process (ca. 0.7 V μm^{-1}), in comparison to the threshold voltage of the AF switching process (10–11 V μm^{-1}, see figure 4).

The bistable FE switching behaviour was also confirmed by optical observations of the switching process [38]. Applying a voltage to the optically isotropic texture of compound **7** induces a birefringence and a fan-like texture develops. This indicates that the organisation of the molecules significantly changes under the influence of the applied field. If the isotropic liquid of **7** is slowly cooled down under an applied DC electric field (10 V μm^{-1}) a texture with circular domains appears (figure 11). In these domains the smectic layers are arranged circularly around the centres of the domains. The characteristic feature of these domains are extinction crosses, wherein the direction of the extinction brushes corresponds to the direction of the optical axes of the smectic layers. In these bright birefringent field-induced circular domains the extinction crosses are rotated by 70–80° either clockwise or anti-clockwise depending upon the sign of the applied electric field. However, the position of the extinction crosses remain unchanged if the field is switched off. This bistable switching confirms a FE switching process. It also indicates that in the FE ground state obtained after alignment in a DC field the correlation between adjacent smectic layers is synclinic (SmC$_S$P$_F$). This means, that the mesophase structure is homochiral, composed of domains of opposite handedness (indicated by the opposing directions of the rotation of the extinction brushes in different regions).
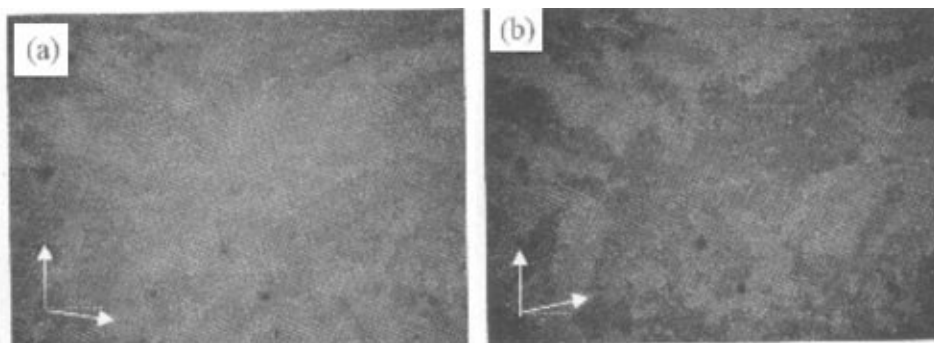

Figure 9. Texture of the mesophase of compound **7** obtained on cooling from the isotropic liquid without applied field. The photographs were taken with polariser and analyser slightly uncrossed to distinguish domains of opposite chirality. Changing the direction of the analyser [(**a**) and (**b**)] reverses the brightness of the domains [38].
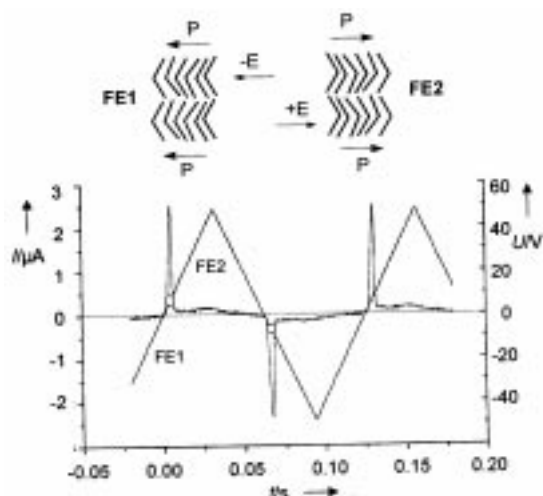
Figure 10. Typical switching current response on applying a triangular wave voltage as recorded for the ferroelectric switching banana mesophase of compound **7** (10 μm non-coated ITO cell) [38].
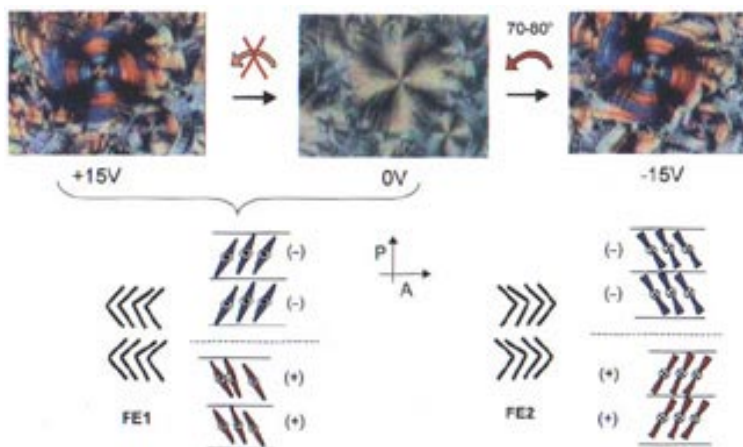

Figure 11. Switching behaviour of compound **7** as observed between crossed polarisers. The texture was obtained upon cooling from the isotropic liquid under an applied electric DC field of 10 V μm^{-1}. The extinction crosses of the circular domains do not coincide with the crossed polarisers. By switching the electric field between $U = +15$ V (left) and $U = -15$ V (right) the extinction cross rotates by an angle of 70–80°. There is no relaxation of the extinction crosses if the voltage is switched off ($U = 0$ V). Below the textures the proposed organisation of the molecules in the different switched states are shown [38].

If an alternating field (AC, 10 V μm^{-1}, 200 Hz) is applied during cooling of the isotropic liquid, then weakly birefringent circular domains are formed (figure 12) [38]. In these domains the extinction crosses have different directions to those obtained by the alignment of the sample in a DC field. Here, the extinction crosses coincide with the direction of
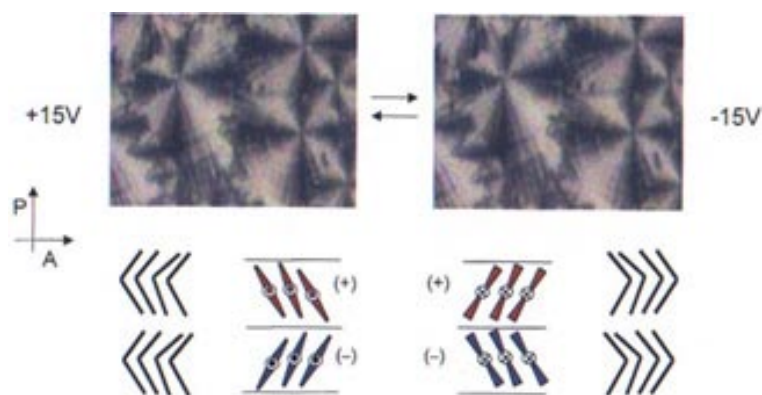
Figure 12. Switching behaviour of compound **7** as observed between crossed polarisers. The texture was obtained upon cooling from the isotropic liquid under an applied electric AC field of 50 V μm^{-1} (200 Hz). The extinction crosses coincide with the crossed polarisers and do not rotate when an electric field is applied. Below the textures the proposed organisation of the molecules in the different switched states are shown [38].

the polariser and analyser. On applying an electric field the extinction crosses do not rotate, although a switching process is clearly visible. In this case the FE ground state can be explained by an anticlinic packing of the molecules in adjacent layers (SmC$_A$P$_F$), which corresponds to a macroscopic racemic structure. Hence in these mesophases, the type of applied external field determines the interlayer clinicity and thus, which of the diastereomeric supramolecular organisations is actually formed. Related effects were also observed by applying triangular (SmC$_A$P$_F$) and square wave fields (SmC$_S$P$_F$) [41]. The influence of distinct fields on the supermolecular organisation of AF switching B2 phases was recently investigated by Heppke *et al* [42]. Comparison of these results with our own observations indicates, that the influence of the external field on the domain type (homogeneous chiral vs. racemic) is identical for FE and AF banana mesophases, i.e., a triangular wave field leads to the racemic structure, whereas a square field leads to a homogeneous chiral structure in both cases. However, with respect to the interfaces the effect is opposite for FE and AF phases as shown in figure 13. This means that, for example, a triangular wave field in the case of a FE switching phase leads to an anticlinic organisation whereas in an AF switching phase it induces a synclinic interlayer correlation.

In the absence of an external electric field no birefringence was observed upon the formation of the smectic phase, i.e., this phase seems to be optically uniaxial or isotropic. However, these molecules have both, polar order and tilt organisation within the layers which would produce optical biaxiality in this phase and birefringence would be expected. Another characteristic feature of this texture is the existence of domains with opposite chirality (see above). These findings could be explained by a helical arrangement of the molecules with the helix axis perpendicular to the substrate surfaces. Within this structure the pitch is outside the wavelength of visible light, and the helix-sense differs in regions of opposing chirality. The helix axis can either occur perpendicular to the layer planes (SmC*-like, see figure 3d) or parallel to the layer planes (TGB-like, see figure 3c). Both helical superstructures would give rise to optical uniaxiality of the phases and would allow
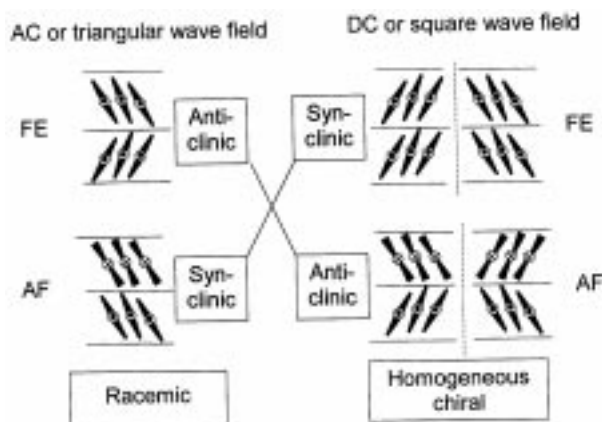
Figure 13. Influence of external electric fields on the organisation of FE and AF switching mesophases of bent-core molecules. DC or square wave fields lead to homogeneous chiral structures (synclinic interfaces for FE phases, but anticlinic interfaces for AF phases). AC or triangular wave fields lead to racemic structures (anticlinic interfaces for FE phases, but synclinic interfaces for AF phases).

a compensation of the layer polarity on a macroscopic scale by simultaneously retaining a nearly parallel alignment of the bend directions of the molecules in adjacent layers. In order to distinguish between these two possible arrangements, X-ray scattering and AFM investigations were carried out. X-ray scattering indicates a correlation length for the layer reflections of ca. 90 nm [43]. This is of the same order of magnitude as that observed for the fine structure at the surface of a glassy sample of **7** by AFM [44]. This fine structure indicates a rather complex mesophase structure and might possibly be due to an organisation based upon a TGB-like helical structure. Because of the tilted arrangement within the slabs, quite complex superstructures related to the TGBC or TGBC* phases [45,46] are possible. In addition to this, the twist can occur in one direction (as in conventional TGB phases), in two directions (as proposed for the B4 phases [20]) or even three directions, leading to a variety of different possible phase structures. Although a TGB-like helical superstructure seems to be a likely possibility for the organisation of compound **7** in the ground state mesophase structure, further investigations are necessary to determine the precise phase structure.

5. The importance of layer coupling for ferroelectricity

The most important result obtained from these studies is, that it clearly confirms the importance of the interlayer interfaces for the FE/AF organisation of the bent-core molecules. Usually, the AF state of banana phases is stabilised by the escape from a macroscopic polar order and also by the synclinic nature of the interlayer interfaces within this arrangement (see figure 14). Such interfaces easily allow out-of-plane interlayer fluctuations and are therefore entropically favourable. In the FE state, the parallel molecular bend directions within adjacent layers lead to anticlinic interlayer interfaces. Such interfaces are entropically disfavoured because they suppress the interlayer fluctuations [3]. Decoupling of the
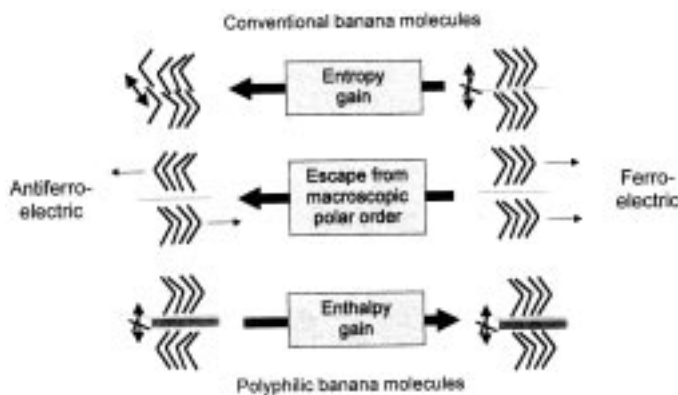
Figure 14. The driving forces behind the FE and AF organisation of bent-core molecules. The AF structure is stabilised by the escape from a macroscopic polar order and the entropy gain due to out-of-plane interlayer fluctuations. If the layers are decoupled the importance of the entropy gain is reduced and intermolecular interactions (enthalpy gain) can give rise to a stabilisation of the FE structure.

layer interfaces by the siloxane sublayers reduces or inhibits these interlayer penetrations and therefore their role in molecular organisation is reduced, allowing a FE structure more easily. However, this alone cannot explain the preference for a FE correlation and another driving force behind the stabilisation of the anticlinic interlayer correlation must be present. This stabilisation might be due to increased van der Waals interactions at the ends of the terminal chains [47] or due to dipole (electrostatic) interactions at the interlayer interfaces [33].

The FE correlation leads to a macroscopic polar order. In order to escape from this unfavourable interaction a slight deviation from the FE correlation must occur. This would give rise to a helical superstructure, and the materials themselves would not be ferroelectric in the ground state. However, upon alignment with an electrical field in the measuring cells the FE states are stabilised by surface interactions, leading to a FE switching.

The idea of decoupling the layers to obtain FE switching banana phases could also be applied to other reported bent-core systems, where ferroelectricity was found (see figures 7 and 15). For example, it is now rather well-known that the 2-octyloxycarbonyl group (as used in compound **3** [30]) favours an anticlinic interlayer correlation [3,48]. In such compounds only one of the branches (either the methyl group or the alkyl chain) aligns almost parallel to the molecular long axis, whereas the other must adapt an orientation almost parallel to the layers [49]. This gives rise to increased disorder in the aliphatic region and hence decouples the smectic layers, making interlayer fluctuations difficult. A related effect can be expected for molecules with branchings at other positions of the terminal chains (e.g. compound **4** [34]).

Ferroelectric switching was also reported for several mesophases formed by bent-core molecules with F-substituents at the periphery of the aromatic core and rather long terminal chains (compounds **2, 8–11**). In this case it is important that the F atoms are located next to the alkoxy chains. When two F atoms are located at each of the peripheral benzene ring, as in compound **8** [50], FE switching phases are also observed. In an isomer of compound **2** however, in which the F atoms are shifted to more central positions, the
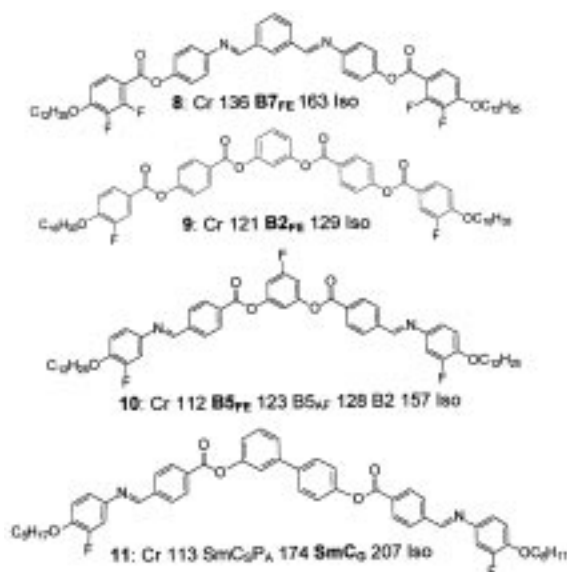
Figure 15. Molecular structures of recently reported bent-core mesogens with ferro-electric switching mesophases [31,32,50,51].

FE switching B7 phase is replaced by an AF switching B2 phase [50]. Observations made with compounds **9** and its homologues ($n = 12, 14$) [32] are similar to those reported for the siloxane terminated bent-core molecule **7** [38]. For these materials a FE switching was observed and the mesophase appears dark between crossed polarisers, but it is not mentioned whether domains of opposite chirality were observed [32]. One major difference between the mesophases of the F-substituted compounds **9** and the siloxanes **7** is that the viscosity of the isotropic appearing mesophase of compounds **9** is higher than observed for the related phases in the siloxanes **7**.

In the phase sequence of compound **10**, a transition from AF to FE switching was observed for the B5 phase [31]. The B5 phase is related to the B2 phase, but instead of having only one diffuse wide angle reflection, three reflections are observed in the powder diffraction pattern, which indicates an additional 2D positional order within the non-correlated layers. Upon decreasing the temperature, the phase sequence B2–B5$_{AF}$–B5$_{FE}$ was observed. The appearance of the ferroelectric B5$_{FE}$ phase below the antiferroelectric B5$_{AF}$ phase is due to a decrease in the interlayer fluctuations on reducing the temperature. This shows that reduction of the temperature has the same effect as decoupling the layers by microsegregated sublayers, i.e., it sharpens the interlayer interfaces and thus reduces out-of-plane interlayer fluctuations, and this diminishes the entropic penalty for FE organisation.

Although most FE switching banana mesophases have been reported for this type of bent-core molecules with F atoms adjacent to the alkyl chains, the reasons for this behaviour are still under discussion. A possible explanation for this phenomenon could be that the F atoms have an impact upon the preferred conformation or the conformational mobility of the linear alkoxy chains. This can lead to an increased disorder within the aliphatic regions, which decouples the layers. Another proposal is, that the strong dipole moment of
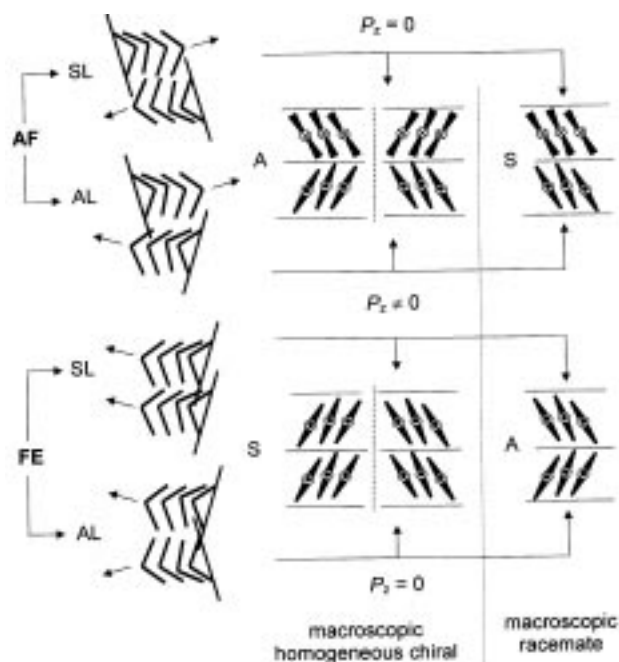
Figure 16. Views of the eight possible supermolecular isomers of polar double-tilted SmC_G phases [55]. At the left AF and FE organisations are shown. For each isomer a synleaning (SL) and antileaning (AL) correlation is possible. All pictures at the right represent orthogonal views upon these arrangements; P_Z = out-of-plane polarisation component [55].

the C–F bond close to the interlayer interfaces may give rise to strong polar interactions. This could contribute to the enthalpic stabilisation of the anticlinic (FE) organisation [33].

The F-substituted unsymmetrical compound **11** was investigated by Rauch *et al* [51] who reported a transition from an AF switching phase (racemic SmC_SP_A) to a FE switching phase at higher temperature. This phase sequence is contrary to the case of the B5 phases and also to the theoretically expected phase sequence. It has been suggested that this FE phase is a SmC_G phase which has a chiral triclinic structure with an out-of-plane polarisation component [51]. This phase has a polar double-tilted smectic structure, where both the molecular plane and the long molecular axis (referred to as 'leaning') are tilted with respect to the layer normal, giving rise to eight possible arrangements (figure 16). Such a phase structure was first proposed by de Gennes [52] and the macroscopic properties of this phase were discussed by Brand *et al* [53]. The first experimental evidence for this phase was reported by Jakli *et al* [54] and the Boulder group [55].

Another interesting observation was reported by Huang *et al* for compound **12** which has an AF switching B2 phase ($SmCP_A$). In mixtures with *n*-hexadecane, a solvent which dissolves specifically in the sublayers of the alkyl chains, an optically isotropic LC phase appears and with increasing solvent concentration the switching becomes more and more FE-like [56]. It seems that in this case the solvent molecules contribute to the decoupling of the layers.
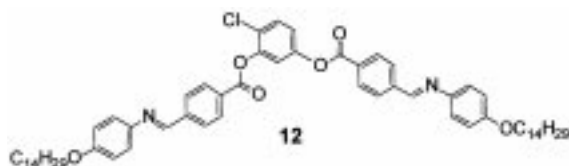
6. Oligosiloxane-based dimesogens

From conventional calamitic LC molecules, it is known that the interlayer correlation can alternatively be engineered by covalently fixing two molecules at their terminal ends, leading to dimesogens [57,58]. In this case the shape of the connecting unit determines the arrangement of the molecules in adjacent layers. Linear spacers prefer a synclinic interlayer correlation, favouring conventional SmC phases whereas bent spacers could give rise to an anticlinic organisation (SmC$_A$) [57,59]. In the case of chiral molecules this produces FE and AF switching behaviour, respectively. Similar results were also obtained with mesogenic dimers containing oligosiloxane spacers [60,61]. Calamitic dimesogens with an odd number of SiO units exhibit AF phases, whereas FE phases were found for dimesogens with an even number of SiO units. At first it was assumed that this was due to different conformations of the oligo(dimethylsiloxane) chains giving rise to different average shapes depending on the number of SiO units: a nearly linear shape for an even number of dimethylsiloxane units and a bent shape for an odd number [60]. However, there was no energy difference found between linear and bent conformations, independent of the number of SiO units [61]. It has been concluded that the dimesogens prefer to adapt a non-linear shape due to a free energy difference between the synclinic and anticlinic phases (for details, see ref. [61]).

13a (n = 1): Cr 64 SmCP$_F$ 132 Iso
13b (n = 2): Cr 92 SmCP$_A$ 132 Iso
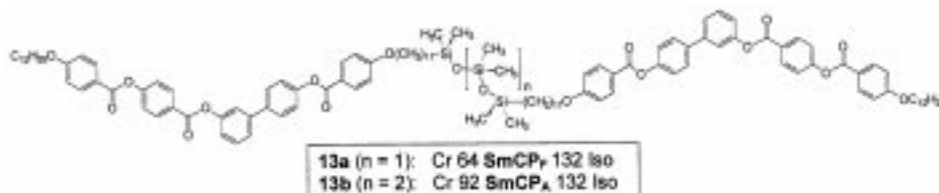
Having the effect of the number of SiO units on the phase structure in mind, our group has synthesised two liquid crystalline dimers consisting of two identical bent-core mesogenic units, connected by spacers containing three or four SiO units [62]. The textures and the switching behaviour of the mesophases observed for these two compounds are completely different. Compound **13a** with an odd number of SiO units has the same textural features as the oligosiloxane-substituted molecule **7**, characterised by domains of opposite chirality and FE switching behaviour. However, compound **13b** with an even number of SiO units shows a typical AF switching behaviour. Upon slow cooling (0.1 K min^{-1}) of compound **13b**, a Schlieren texture with domains of disturbed focal conics was observed. This is typical for antiferroelectric B2 (SmCP$_A$) phases, hence, the effect of the parity is opposite to that found for conventional rod-like dimesogens.

Similar to the effect seen for oligosiloxane-substituted single mesogens, a segregation of the oligosiloxane units from the hydrocarbon segments leads to a decoupling of the layers,
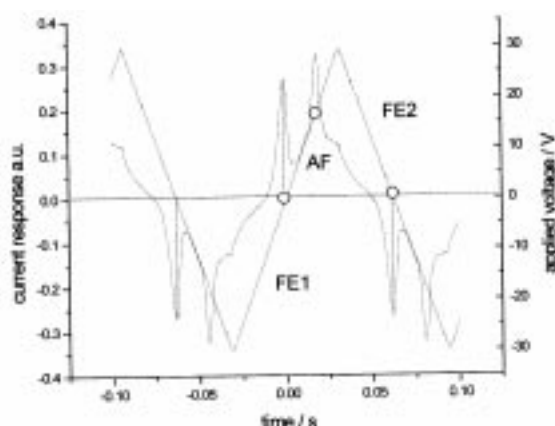
Figure 17. Switching current response on applying a triangular wave voltage as recorded for the antiferroelectric switching banana mesophase of compound **13b** (6 μm polyimide-coated ITO cell) [62].

which allows the formation of anticlinic interfaces and this leads to a FE arrangement. The inclusion of an odd numbered SiO spacer is in good agreement with this anticlinic organisation and also gives rise to additional stabilisation of this phase structure. The even numbered SiO spacer unit on the other hand favours a synclinic correlation between adjacent layers. This effect is in competition with the anticlinic organisation favoured by microsegregation and seems to be the more dominant effect. Therefore, an AF switching behaviour was observed for compound **13b**.

However, it was also found that the textures of compound **13b** depend on the cooling rate used. Upon slow cooling the typical birefringent Schlieren texture of an antiferroelectric B2 phase was observed. On faster cooling (3 K min^{-1}), a dark texture similar to that obtained for the ferroelectric switchable dimer **13a** was observed. The switching curves of **13b** are identical, regardless of the cooling rate and are characterised by two peaks in each half cycle, as typical for AF switching (see figure 17). However, when the switching curves of **13b** are compared with those of other antiferroelectric B2 materials (compare figure 4), then a lower threshold voltage for the switching into the FE state (2.8 V μm^{-1}, instead of 10–11 V μm^{-1}) was observed and the switching back to the AF state occurs close to zero voltage (ca. 0.1 V μm^{-1}, instead of 7 V μm^{-1}). This indicates that the FE states can be achieved more easily than in conventional antiferroelectric B2 phases. Although the AF state is the more stable state (in the confined geometry of the measuring cells), the energy, necessary to switch into the FE state is greatly reduced, due to the presence of siloxane sublayers, which easily allow the anticlinic interlayer correlation within the FE arrangement.

As mentioned above, the appearance of a dark mesophase in the ground state was observed for the AF switching compound **13b** as well as for the ground states of the ferroelectric switching compounds **7** and **13a**. This shows that this kind of mesophases can occur in FE switching as well as in AF switching materials. A number of other banana mesophases show related textures and these materials will be discussed in the next section.
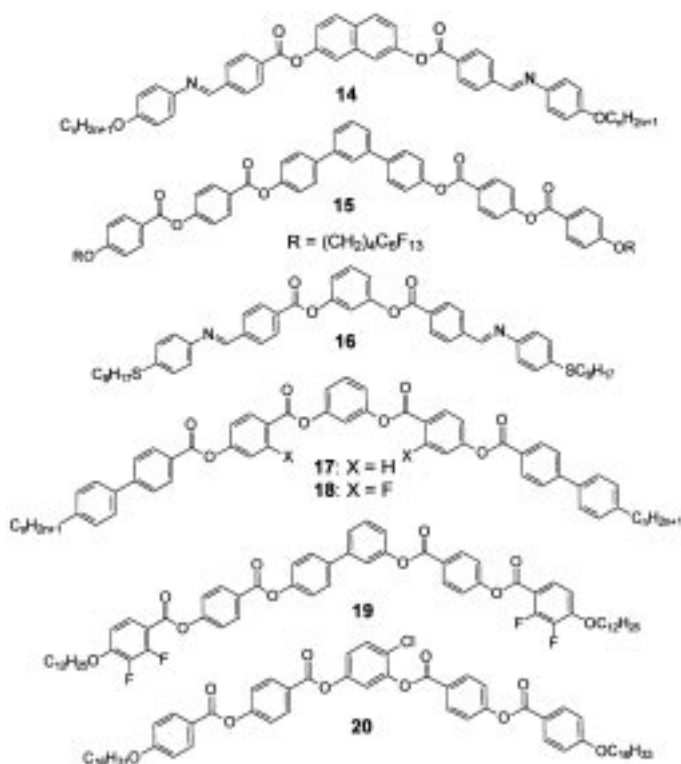
Figure 18. Molecular structures of bent-core mesogens showing liquid crystalline phases with textures composed of regions of opposite chirality.

7. Mesophases with regions of opposite chirality

Mesophases composed of domains of opposite handedness (compounds showing such phases are shown in figure 18) were at first reported for the B4 phase [20,22], but this mesophase is actually a soft crystal whereas the mesophases discussed in this section represent layer structures with no additional long-range in-plane order.

Such a chiral mesophase was found for some naphthalene derivatives **14** initially designated as 'Sm1'-phase [21]. In these mesophases only a simple layer structure without in-plane order was determined by X-ray scattering. Unlike the FE switching phases of the siloxane derivatives **7** and **13a**, a transparent blue colour was additionally observed in these mesophases. Upon reinvestigation of a terphenyl derivative (compound **15**) [13] a similar bluish texture composed of domains of opposite handedness was observed (figure 19a) upon cooling from the liquid state. However, upon heating from the crystalline state a Schlieren texture of the B2 phase (SmCP$_A$) develops (see figure 19b). The type of switching could not be determined for compounds **14** and **15** due to the high transition temperatures. Furthermore, these bluish mesophases are highly viscous, similar to cubic phases.
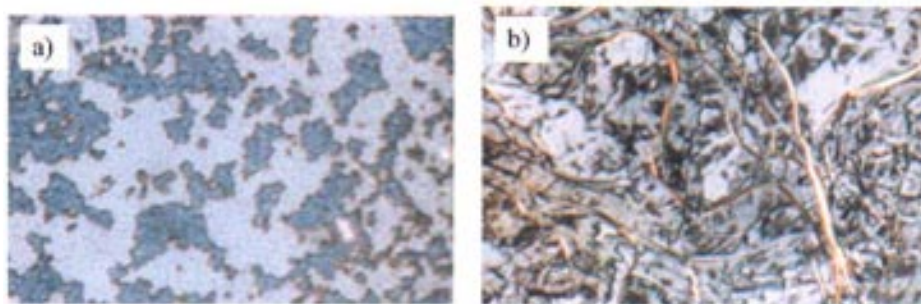
Figure 19. Textures of the mesophase of compound **15**. (**a**) Texture composed of regions with opposite chirality as obtained upon cooling from the isotropic liquid state (the photograph was taken with polariser and analyser slightly uncrossed to distinguish domains of opposite chirality, upon changing the direction of the analyser the brightness of the domains is reversed) and (**b**) Schlieren texture as obtained upon heating from the crystalline solid state.

Other mesophases do not exhibit this blue colour. Such a mesophase was observed for the AF switching material **16** upon cooling in an electric field, whereas in the absence of an applied field, spiral domains were observed, similar to those of B7 phases [63].

Highly viscous non-birefringent mesophases comprising distinct domains of opposite chirality were also reported for the AF mesophases of long chain compounds of the homologous series **17** and **18** ($n = 14–18$) [64]. For the shorter homologues of the series **17** and **18** ($n = 11, 12$) however, the typical highly birefringent B2 textures were observed. This means that upon increasing the chain length in these homologous series a transition from the B2 phase to this isotropic mesophase takes place. The switching behaviour does not change and the transition temperatures, the transition enthalpies and the layer distances change continuously at this transition and therefore, this phase has also been classified as B2 [64]. Our group has observed the same textures for AF phases of some peripherally F-substituted bent-core molecules, such as compound **19** [39]. The textures of these mesophases are very similar to those observed for the FE switching compounds **7** and **13a**. The main difference is the significantly lower viscosity of the FE switching mesophases of the oligosiloxane derivatives in comparison to the highly viscous LC phases of the core-fluorinated molecules. Furthermore, the AF switching of compound **19** and related materials is characterised by low threshold voltages for the switching into the FE states as has also been seen for the dimesogen **13b**. It appear that these dark mesophases occur for FE switching phases, as well as for AF switching phases in which a low energy difference occurs between the AF and FE states. Therefore, one possible explanation could be that the occurrence of this special type of mesophases might be an indication of a FE arrangement within the polar layers in the ground state. In this case the escape from a macroscopic polar order could be achieved by a slight regular deviation from the ferroelectric correlation, leading to a helical superstructure. If a strong FE correlation exists within the mesophase, then the FE organisation would be unaffected by surface interactions in the measuring cell and ferroelectric switching is observed. However, if only a weak FE correlation exists, then in the measuring cell the FE state may adapt a helical structure in the absence of a field. After alignment into a book-shelf geometry (the layers are perpendicular to the surfaces)

using an external electric field the AF state might be stabilised by surface interactions. Here, the molecules are enclosed in a confined geometry which may disrupt the formation of a helix. This could lead to an energetic penalty in the formation of the FE arrangement (the macroscopic polarity is less efficiently cancelled) and the non-polar AF organisation becomes more stable. This system can then be easily switched to a FE state, which would relax back to the surface-stabilised AF organisation at zero voltage [65]. However, a number of questions still remain unanswered and therefore, significantly more experimental data is required before a clearer picture of these unusual mesophases can be drawn.

The situation became even more confusing as it was recently reported that a dark texture can be induced in a FE switching smectic mesophase of compound **20** (the ground state has a fan texture) upon applying an electric field. In this mesophase a bistable (FE) switching of the chirality within the domains of different handedness was observed [66]. As a possible explanation, a SmC_G structure [52,53], which has polarisation component perpendicular to the layer planes has been suggested. However, a full explanation of all experimental facts was not possible.

Finally, it should be pointed out that not all ferroelectric switching banana phases have these dark textures with chiral domains as their ground state structures. For example, B7 phases have been observed for compounds **2**, **8** [25,50] and **3** [30]. The formation of such B7 phases might represent an alternative way to escape from macroscopic polar order within the ground state. A birefringent mesophase was also observed for the optically active molecules **4** [34], where the molecular chirality might have an additional impact on the phase structure and the texture.

8. Ferroelectric switching columnar mesophases

21: Cr 141 Col$_{ob}$ 171 Iso
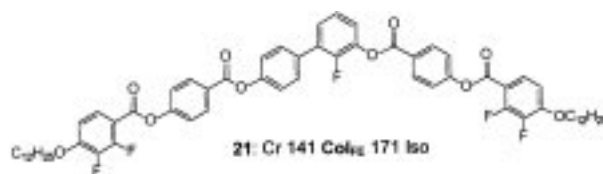
Recently a ferroelectric switching mesophase with a two-dimensional lattice was reported for a compound of type **9** with two *n*-octadecyloxy terminal chains [32]. Our group has observed a ferroelectric switching columnar phase for compound **21** [39]. In the series of compounds **9** the columnar mesophase occurs on increasing the chain length. Therefore, in the columnar mesophase discussed here a modulated layer structure or ribbon structure (figure 20), caused by an unequal space filling of aromatic and aliphatic molecular parts seems likely. For this reason, this class of columnar phases should not be confused with those described in §2 (B1-type phases), which are due to an escape from macroscopic polar order. In the ribbon phases discussed here, ferroelectric correlation would still exist between adjacent ribbons and ferroelectric switching behaviour is observed. No chiral domains were observed in the ground state of these FE switching columnar phases and therefore the question arises as to whether the 2D-lattice would suppress the formation of a helical superstructure.
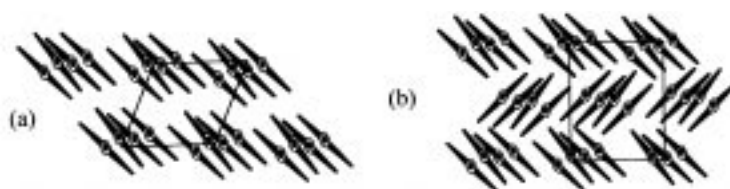
Figure 20. Models of possible organisations of bent-core molecules in ferroelectric switching columnar mesophases. (**a**) Synclinic correlation between adjacent ribbons may lead to an oblique 2D lattice and (**b**) a possible 2D organisation of ribbons with anticlinic correlation.

9. A dendritic oligomesogen with carbosilane core

Ferroelectric switching has also been observed for the carbosilane dendrimer **22** [67]. However, the texture of this mesophase is quite different from that of the related monomeric compound **7** and the dimesogen **13a**. Polarising microscopy investigations showed a fan-like texture which can be homeotropically aligned producing pseudoisotropic textures with birefringent oily streaks, which is very typical for SmA phases. Polar order within the layers was confirmed by dielectric measurements, and also by electro-optical investigations which showed a FE switching process with a very high value of the spontaneous polarisation ($P_S = 1400$ nC cm^{-2}). X-ray investigations of aligned samples show that the diffuse outer scattering has four crescent-like diffuse maxima located out of the equator which confirm a tilted arrangement of the molecules. Hence, according to microscopic investigations the ground state represents an optically uniaxial mesophase, but the polar order and the tilted organisation of the molecules within the layers would require optical biaxiality. Unlike the monomeric compounds **7** and the dimesogen **13a**, no chiral superstructure could be detected in the mesophase of the carbosilane **22**. Therefore, compound **22** might form a random tilted SmCP phase, i.e., a smectic LC phase without long range orientational correlation between the layers (see figure 21) [68,69]. This means that the molecules are tilted and adapt a polar order within the layers, but the polar direction and the tilt direction change randomly (SmCP$_R$) from layer to layer as shown in figure 21. This gives rise to an optical uniaxial non-polar ground state structure. Upon applying a sufficiently strong electric field, however, the polar directors of the layers align parallel to the field and a FE state was observed (SmCP$_F$). Once formed, this phase is additionally stabilised by the interactions with the surfaces of the measuring cell and therefore a FE switching process can be observed.

Hence, there seems to be different ways to escape from macroscopic polar order in bent-core materials with ferroelectric organisation, either by helix formation or by randomisation.

10. Conclusions

In the past two years significant progress has been made in designing bent-core mesogenic materials with ferroelectric switching mesophases. Two basic principles, known from calamitic systems, namely decoupling of the adjacent layers by microsegregated
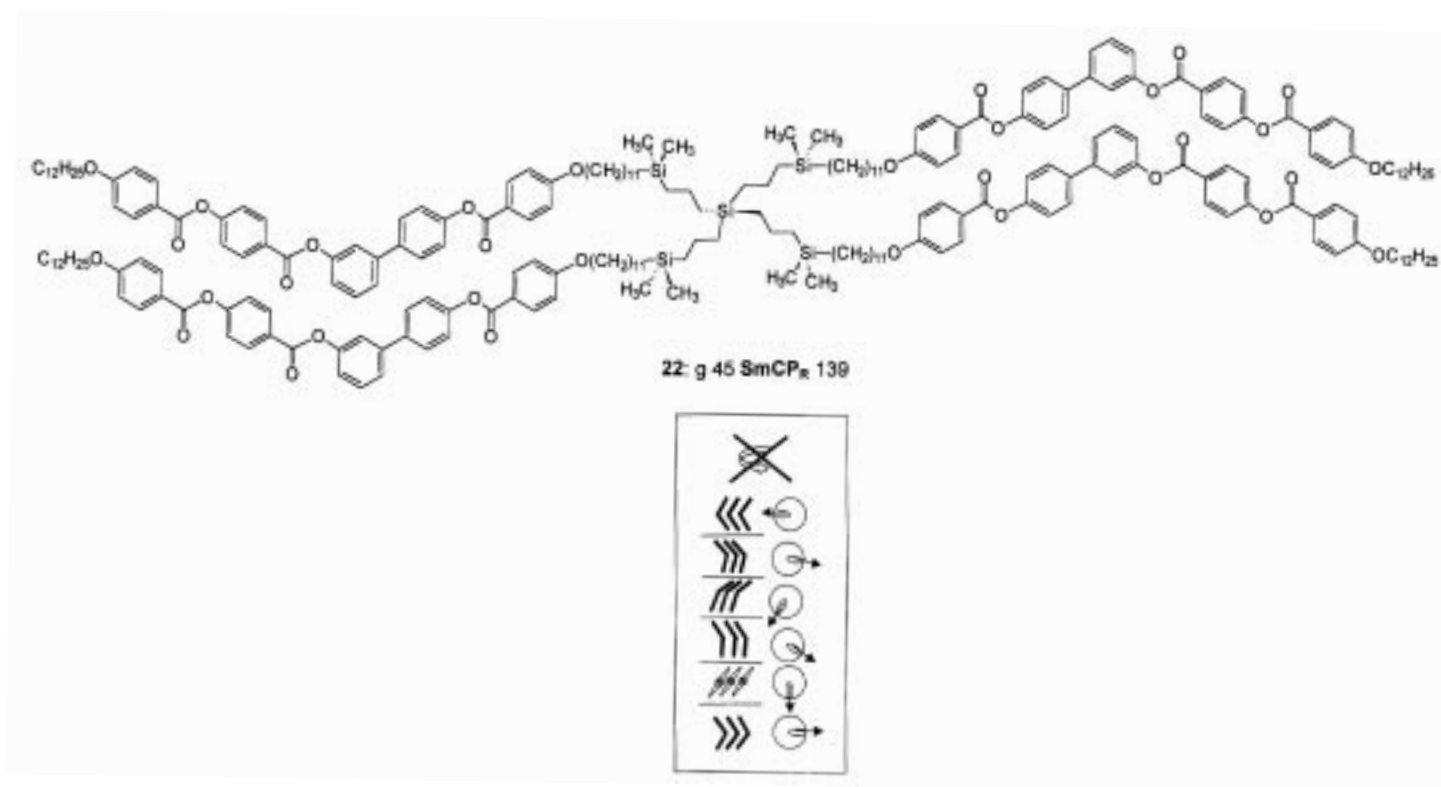
Figure 21. Molecular structure of the first generation carbosilane dendrimer **22** and proposed model for the organisation of this molecule in the SmCP$_R$ mesophase (the tilt direction and the polar direction change randomly from layer to layer) [67].

sublayers and also coupling of the molecules by appropriate spacer units have proven important in designing such mesogens. It has been found that the effects of structural changes are opposite to those found in calamitic materials. For example, decoupling of the layers leads to AF phases in calamitic systems, whereas in bent-core materials it gives rise to FE switching phases. Similarly, AF phases of calamitic dimesogens are stabilised by odd numbered SiO spacer, whereas AF organisation in bent-core dimesogens is stabilised by spacers with an even number of SiO units. This is due to the differences in clinicity of the interfaces of FE switching phases in calamitic systems (synclinic) and in bent-core systems (anticlinic).

Although significant progress has been made in this field, there are still many open questions that remain to be answered. The first concerns the precise structure of these dark mesophases with chiral domains, and the second relates to the origin of the energetic preference of the FE (= anticlinic) interlayer correlation. Nevertheless, the investigation of bent-core LC systems is one of the most fascinating and stimulating fields of LC research and supramolecular chemistry, which can provide deeper insights into the fundamental principles of molecular self-organisation.

Acknowledgements

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