Polar Orthogonal Smectic Phases Composed of Bent-core Liquid Crystals

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Chapter 1

Introduction

1.1 Liquid Crystals and Their Categories

1.1.1 Discovery and Definition of Liquid Crystals

On the earth, there are three common states of matters, namely solid, liquid and gas. These states of matter, however, are not sufficient to characterize the structures found in all systems. As most substances are heated, they go from a solid (usually crystalline, possessing high order) to an isotropic liquid (highly disordered). Some substances, however, exhibit intermediate states lacking some of the order found in solids, but possessing more order than found in liquids. These ordered fluids are called liquid crystals, which is an intermediate state [1].

This stage of matter was first discovered in the late 19th century by Reinitzer (1888) and Lehmann (1889) [2]. In last century, the science of liquid crystals grew and became flourishing. Up to now, around 40 types of LC phases are founds and more than 100,000 compounds are known to show LC phases [3]. Scientists are still trying to synthesize new liquid crystal materials with interesting properties in recent years.

![Molecular orientation model in crystal, liquid crystals and isotropic liquid states.](image)

**Figure 1.1** Molecular orientation model in crystal, liquid crystals and isotropic liquid states.

(From left to right is under increasing temperature.)
Crystalline solids have positional and orientational order. Conventional liquids have neither and as a result their properties show uniform isotropic. A liquid crystalline, on the other hand, might have no positional order, but some orientational order (with correlations between the direction of neighboring molecules). This ordering usually persists only for a fairly narrow temperature range, and is related to the intrinsic molecular shape (for instance cylinder shape). Liquid crystal (also called mesogens) molecules, are usually highly anisotropic in shape, which gives rise to the preferred orientations of nearby molecules. For illustrative purposes, orientation of rod-like mesogens in three distinct phases is given in Fig. 1.1.

1.1.2 Categories of Liquid Crystals

(1) Lyotropic liquid crystals

A lyotropic liquid crystal consists of two or more components that exhibit liquid-crystalline properties in certain concentration ranges. In the lyotropic phases, solvent molecules fill the space around the compounds to provide fluidity to the system. In contrast to thermotropic liquid crystals, these lyotropics have another degree of freedom of concentration that enables them to induce a variety of different phases.

A compound, which has two immiscible hydrophilic and hydrophobic parts within the same molecule, is called an amphiphilic molecule. Many amphiphilic molecules show lyotropic liquid-crystalline phase sequences depending on the volume balances between the hydrophilic part and hydrophobic part. These structures are formed through the micro-phase segregation of two incompatible components on a nanometer scale. The content of water or other solvent molecules changes the self-assembled structures [4]. Soap is an example of a lyotropic liquid crystal. Cells of living creatures can also be regarded as blocks of lyotropic liquid crystals which are highly ordered organized. Consequently, lyotropic LCs have great potential value for applying in biotechnologies.
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Figure 1.2 Structure of lyotropic liquid crystal. The red heads of surfactant molecules are in contact with water, whereas the tails are immersed in oil (blue): bilayer (left) and micelle (right).

(2) Thermotropic liquid crystals

Thermotropic phases are those that occur in a certain temperature range. If the temperature rise is too high, thermal motion will destroy the delicate cooperative ordering of the LC phase, pushing the material into an isotropic liquid phase. At too low temperature, most LC materials will form a crystal solid. Many thermotropic LCs exhibit a variety of phases as temperature is changed.

In the family of thermotropic LCs, according to the molecular shape, mesogens can be assorted as rod-like (calamitic), discotic, bent-core (banana shaped) as well as polymer liquid crystals (as illustrated in Fig. 1.3).
Based on the orientation order of molecules inside the mesogenic system, liquid crystals are also identified as nematic, smectic, columnar phases, etc. Nematic phase is the simplest phase which has the highest symmetry of all the liquid crystal phases. It exhibits solely orientation order of the long molecular axis, an angular distribution of the long molecular axis around a particular direction, the director. While the mass centers of molecules are isotropically distributed in all three dimensions. Nematic phase does not have layered structure.

In the smectic A phase the director $\mathbf{n}$ and thus the optic axis are perpendicular to the smectic layer plane (parallel to layer normal), as shown in Fig. 1.4(b). So in the homeotropic cell, uniform dark image should be seen when observed under crossed polarizers. But the orientational order is not perfect and in some mixtures or bent shape system, biaxial SmA phase are also reported [8-9]. In the homogeneous sample of smectic A, the focal conic (also called fan-shape) texture is the typical character [10].

The Smectic C (SmC) phase is similar to SmA, also has one dimensional positional
order and shows fan-shape textures in planar cells. But in the SmC phase, the directors are tilted by an angle with respect to the smectic layer normal, namely the tilting angle $\theta$, as shown in Fig. 1.4(c). If chiral carbons are introduced into the SmC molecule, chiral phases such as SmC* or SmC$_A$* which performs ferroelectric/antiferroelectric behavior can be induced [11].

1.2 Bent-core (banana-shaped) liquid crystals

In 1996, Niori et al discovered that molecules incorporating a bent-shaped rigid core instead of a linear one show polar order and chiral superstructures in their LC mesophases [12]. But the constituent molecules of these mesophases are not chiral. This discovery opened a new time of the study of liquid crystals. In the following years, this new way to spontaneous polar order and chirality immediately provoked great interest and became an important topic in soft matters and optical material science.

Figure 1.5 (a) An example of banana-shaped liquid crystal molecule. (b) Bent molecular shape promotes the formation of polar smectic layers, which give rise to polar phases.

The unique feature of the molecules is that the bent shape of the aromatic core restricts the rotation around the long axis which leads to a preferred organization of these molecules with uniform bent direction (Fig. 1.5). This gives rise to a macroscopic polar order within these LC phases providing ferroelectric (FE) and antiferroelectric (AF) switching LC materials being of interest for various potential applications in electro-optical switches, optical phase modulators, or nonlinear optical materials [13].

The bent shape forces molecules to adopt a compact packing arrangement that restricts
their rotational freedom. This lead to novel types of liquid crystalline phases. The structural modes that have been proposed for the different mesophases are characterized by bunch stacking or by lamellar order. The phases can have either tilted or non-tilted arrangements of molecules and the compact packing leads to strong polar order within the layers. However, it should be noticed that macroscopic polarization is unstable in soft systems and the molecules try to rearrange in a way that the net polarity of the system becomes zero.

Several distinct ways of escaping from a macroscopic polar order in mesophases have been found in bent-core compounds:

(1) **Layer modulation.**

In mesophases of bent-core compounds a partial collapse of the layers are observed widely. This leads to layer-broken segments of the smectic layers and the bend directions of the molecules in adjacent segments is antiparallel and helped to avoid macroscopic polar order. The collapse of the layers can occur in two distinct directions, either parallel (B₁ type phase) or perpendicular (B₁<sub>rev</sub> type phase) to the polar direction P (Fig. 1.6). The resulting mesophases are characterised by 2D lattice resulting from the positional ordering of these fragments. These mesophases can be regarded as modulated polar smectic phases or alternatively as columnar phases built up by fragments with an orientational correlation of the molecules in adjacent segments. Within the ribbons the molecules can be either tilted (B₁<sub>revTilted</sub>) or nontilted (B₁ and B₁<sub>rev</sub>) [14].

![Figure 1.6](image.png)

*Figure 1.6* (a) B₁, (b) B₁<sub>rev</sub>, and (c) B₁<sub>revTilted</sub>. Red arrows indicate the polar direction.
In some other cases, the size of slabs is very small and there is no positional correlation between them (no 2D-lattice), then a smectic phase is formed, in which the bent-core molecules are intercalated. Such intercalated layer structures are characterized by a layer distance comparable or smaller than half the molecular length and such phases were designated as \( B_n \) phase (Fig. 1.3 (c)).

(2) Modified layer correlation

If the layers cannot be fragmented easily, then molecules adopt into smectic layers that the polar direction in adjacent layers is antiparallel to cancel the general polarization. These phases perform antiferroelectric triatable switching and have been reported in either tilted smectic phases (\( B_2 \) phase, SmCP\(_A\)) [15] or in the orthogonal layered structures (SmAP\(_\lambda\)) [16-17].

(3) Helix superstructure

On the other hand, cancellation of the layer polarisation is also possible if the polar direction in adjacent layers changes from layer to layer by a distinct angle, resulting in a helical superstructure if the twist sense is uniform (like TGB or \( B_4 \) phase), or to a random distribution of the polar direction [18]. It is assumed that within the confined geometry of the highly ordered aromatic blocks in the \( B_4 \) phase (the smectic slabs of the TGB-like structure, Fig. 1.7) the stacking of molecules with identical helix sense of their conformation allows a more dense packing than the stacking of conformers with opposite helix sense and therefore layer slabs composed of homogeneously chiral conformers should be more favorable. The correlation between adjacent smectic slabs over macroscopic distances is also expected so that it can realize homogeneously chiral macroscopic domains [19].
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Figure 1.7 Model of the organization of the molecules in the B₄ phase with a TGB helix parallel to the polar axis

Figure 1.7 Model of the organization of the molecules in the B₄ phase with a TGB helix parallel to the polar axis

(4) Polarization splay

If the polar direction in adjacent layers is parallel in smectic phases or in modulated smectic (columnar) phases, then the resulting macroscopic polarization still can be reduced by a splay of the polar directions, leading to splay defects. This type of defects is characteristic for the so called B₇ type phases (Fig. 1.8) [20]. This strategy of escaping from large scale polarization and making the fluid system more stable is also expected in the ferroelectric orthogonal phase.

Figure 1.8 Proposed polarization modulated structure in B₇ phase [21].

1.3 Polar Smectic A Phases

In the family of banana liquid crystals, besides the intensively investigated B₁-B₄ phases, another interesting category of materials are the orthogonal smectic phases. The early study of such nontilted phases was concentrated on the conventional SmA (nonpolar, similar to
rod-like SmA phase as shown in Fig. 1.9(a)), which is uniaxial and emerged between nematic and B₂ phase in the bent core materials [22]. In such SmA phase, molecules freely rotate around the long axis even though the composed molecules have bend shape.

Later, Eremin et al. first reported the uniaxial SmA to biaxial SmA phase transition in a bent-shaped 4-cyano-resorcinol derivative fluorinated on the outer rings [17]. They also showed experimental evidence for a switchable antiferroelectric nontilted biaxial smectic phase with a spontaneous polarization of 1000 nC/cm². Since in X-ray pattern the wide-angle diffuse scattering peaks appear normal to the layer reflection in oriented samples and schlieren texture was observed in contrast to conventional uniaxial homeotropic texture in SmA, the antiferroelectric nontilted biaxial SmA structure was proposed [23].

In sort of the polar smectic A phase, layer net polarization is formed since the bending shape of molecules hindered the rotation around the director (Fig. 1.9 (b)). Depending on the correlation polar order of adjacent layers, both AF and FE SmAP phases are possible to exist. But orthogonal phase with spontaneous macroscopic polarization is very rare to see. Most of the reported SmAP materials do not show net polarization in the absence of electric field except one compound published by Reddy et al [24]. The SmAPF state, which can be induced under the influence of a sufficient electric field is metastable and relaxes back to the nonpolar
The homogeneous aligned SmAP phase show a fan-shaped texture as typical for the rod-like SmA phases and the molecular long axis are mostly parallel to the cell surfaces. In the homeotropic aligned sample, either uniaxial (uniform dark image Fig. 1.10(a)) or biaxial (schlieren texture, Fig 1.10(b)) polar phases have been observed.

![Figure 1.10 The conoscopic results and homeotropic textures obtained from (a) uniaxial SmAPR phase [25] and (b) biaxial SmA_pP phase [26]. (c) 2D X-ray diffraction pattern of homeotropic sample of SmAPA phase [27].](image)

Confirmation for the orthogonal alignment of the molecules within the layers can be obtained from x-ray scattering of aligned samples, where the diffuse wide-angle scattering is centered on the equator and the layer reflections are positioned on the meridian (Fig. 1.9(c)).

1.4 Display Mode Using SmAPR Phase

The exploration of bent core liquid crystals is of enormous meaningful not only because they are interesting from the academic view point, but also since they have great potential for future application.

First, let us shed some light on the traditional LCD devices using nematic phase materials. The history of recently used field-effect LCDs begins in 1970 [3]. As it is known that nematic LC molecules in their natural state are organized with the longitudinal axes almost parallel each other. If microgrooves are carved on a polyimide surface (homogeneous...
alignment layer deposited on the ITO glass substrates), LC molecules lying in the surface will align along the direction of the grooves. Then the LC material sandwiched between two glass plates whose surfaces were grooved in orthogonal directions, molecules near the plates must follow the direction of grooves and, as a consequence, the molecules in the bulk are forced to describe a 90° helical twist, from which the name twisted nematic (TN) for this operating mode is given, as shown in Fig. 1.11.

**Figure 1.11** The Twisted Nematic (TN) effect in a normal white cell: (a) the direction of polarization of the light entering the liquid-crystal region rotates by 90° along the helix arrangement of the LC molecules and the screen appears bright (b) light is blocked by the analyzer and the cell appears black.

Two polarizing filters, which are referred to as the polarizer (light in) and the analyzer (light out), are added to the top and bottom surface of the LC cell, respectively. In an ideal polarizer, 50% of the incident energy of a beam of unpolarized light is absorbed and 50% is transmitted as a beam of polarized light. The transmission axis of the two polarizing filters must be parallel to the direction of the grooves. Hence, only the light with the polarization in axis with that of the polarizer can pass through. The plane of the polarization of light transmitted through the cell will rotate by following the liquid crystal director twist (in a waveguiding fashion) provided bright image on the field-off state (Fig. 1.11(a)).

After applying a voltage across the two plates, the LC molecules tend to align along the
direction of the electric field. In particular, when a voltage greater than the threshold $V_{th}$ is applied, the molecules located at the center of the cell farthest away from the electrodes start to deviate from their quiescent state. With increasing voltage the twist is gradually removed and light polarization is no longer rotated since the LC is not birefringent in this orientation (Fig. 1.11(b)). The light is blocked at the bottom polarizing filter and the screen appears black.

In this mode, two vital disadvantages must be mentions: (1) the bright/dark switching is realized by rotating the rod-like molecule of the LC cell around the transit axis and the response speed is limited by feather of nematic phase (usually the response time of TN mode is around 40ms); (2) this mode calls for defect free homogeneous alignment layer, which require rubbing process in producing and will for sure increase the cost.

In the year of 2006, a novel display mode utilizing banana liquid crystal was published by Shimbo et al [28-29]. The principle of this display mode is given in Figs. 1.12. The red arrows stands for dipole moment of local polar domains, and the new moon shape represent the local polar domains made of bent core LC molecules. In the absence of an electric field, the homeotropically aligned sample show a complete dark view, that’s because the dipoles are randomly distributed, as shown in left side of Figs. 1.12. By applying an in-plane electric field, the dipoles gradually orient toward the field direction. Because of the bent molecules, the orientational change induces birefringence (bright patterns in Fig. 1.12 (c)). Hence, dark and bright views can be displayed under crossed polarizers.

![Figure 1.12](image)

**Figure 1.12** Homoetropically aligned SmAP$_{b}$ cell: (a) top view (b) side view of and (c) microscopic photography at field-off (left side) and field-on (right side) state,
respectively. (dark patterns are in c are the metal electrode which are untransparent.)

This new display mode has a number of advantages:

(1) **Continuous gray level**: a gradual transmittance change was observed both for positive and negative pulses;

(2) **High contrast ration**: since the field off stage is defect free and uniform dark, it is confirmed that a contrast ratio 3000:1 can be realized;

(3) **Wide viewing angle**: the in-plane switching and together with self compensation of anisotropy due to the molecular bend guarantees a wide viewing angle;

(4) **High respond speed**: very fast switching under electric field was recorded. Except for a low field strength region, the response time upon field termination is almost constant, 40 µs. The response time upon field application is slightly electric field dependent, from 240 to 130 µs. Thus, field-insensitive fast response can be achieved and it is around 100 times faster than the nematic displays.

In addition, rubbing-free surfaces for homeotropic alignment which gives high contrast ratio also cost less than the rubbed homogeneous alignment surface. As a result, such bent-core SmAP phases become a promising candidate for the new generation fast response display devises.

### 1.5 Motivation for This Work

Although several work have been published on smectic A phases with polar order, the layer structures and the performance are still not clearly understood, especially for the potential display material, SmAP\(_R\) phase. In order to use it in industry, we have to expend the temperature range down to room temperature and reducing the operating voltage. In this dissertation, the new compounds exhibiting SmAP\(_R\) phase with distinct molecular construction and optimized performance is going to be investigated into details. Moreover, new orthogonal bent core smectic phases with various polarizing behavior (SmAP\(_A\), SmAP\(_F\), etc.) will also be characterized through various experimental methods.
References of chapter 1


1. Introduction


"Distinct Ferroelectric Smectic Liquid Crystals Consisting of Banana Shaped Achiral Molecules"


"Bent-Core Liquid Crystals in the Route to Functional Materials"


"Dynamics of Electro-Optical Switching in the Antiferroelectric B2 Phase of an Achiral Bent-Core Shape Compound"


"Polar Switching in the Smectic- A_3P_\lambda Phase Composed of Asymmetric Bent-Core Molecules"


"Experimental Evidence for an Achiral Orthogonal Biaxial Smectic Phase without in-Plane Order Exhibiting Antiferroelectric Switching Behavior"


"Chirality and Macroscopic Polar Order in a Ferroelectric Smectic Liquid-Crystalline Phase Formed by Achiral Polyphilic Bent-Core Molecules"


"On the Nature of the B4 Banana Phase: Crystal or Not a Crystal?"
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"Bistable Linear Electro-Optical Switching in the B7 Phase of Novel Bent-Core Molecules"


"Bent-Core Liquid Crystals: Their Mysterious and Attractive World"


"New Variants of Polymorphism in Banana-Shaped Mesogens with Cyano-Substituted Central Core"


"Paraelectric-Antiferroelectric Transitions in the Bent-Core Liquid-Crystalline Materials"


"Spontaneous Ferroelectric Order in a Bent-Core Smectic Liquid Crystal of Fluid Orthorhombic Layers"


"Ferroelectric Mesophase with Randomized Interlayer Structure"


"Biaxial Smectic a Phase in Homologous Series of Compounds Composed of Highly Polar Unsymmetrically Substituted Bent-Core Molecules"


"Bent-Core Liquid Crystals: Polar Order, Superstructural Chirality and Spontaneous Desymmetrisation in Soft Matter Systems"

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1. Introduction


"Electric-Field-Induced Polar Biaxial Order in a Nontilted Smectic Phase of an Asymmetric Bent-Core Liquid Crystal"


"Ideal Liquid Crystal Display Mode Using Achiral Banana-Shaped Liquid Crystals"
Chapter 2

Experimental Section - Techniques and Methods

The basic principles and detailed experimental procedures of investigating distinct mesogenic materials are described in this chapter. Compounds showing the SmAP phases are mainly characterized through DSC, X-ray diffraction, microscope observation, electro-optical study, second-harmonic generation (SHG) as well as dielectric permittivity measurements. For some specific compounds with unique structure, such as hydrogen bonding, FT-IR spectroscopy is also utilized for detecting the physical property.

2.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature [1]. Therefore, it is a useful and basic technique to identify phase transition temperature and related enthalpies of thermotropic liquid crystals. The instrument measures the energy necessary to establish a nearly zero temperature difference between a target material and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

In this dissertation, phase transition temperatures and associated enthalpies of various compounds were determined by Pyris Diamond Perkin-Elmer 7 DSC [2] at various rates of 1–20 °C/min under both cooling and heating runs. The instrument is designed
using the unique power compensation approach, which yields true heat flow measurements. Usually small amount of target material (2-6 mg) was taken for DSC measurement. Before starting measurement, we repeatedly heat and cool the sample on heating stage to avoid any moisture or solvent.

![DSC result of bent-shaped compound KBS-C18 taken by Pyris Diamond Perkin-Elmer 7 DSC at 10°C/min.](image)

**Figure 2.1** DSC result of bent-shaped compound KBS-C18 taken by Pyris Diamond Perkin-Elmer 7 DSC at 10°C/min.

As shown in Fig. 2.1, three peaks appeared both in heating and cooling runs indicating three clear phase transitions occurred. Take cooling process for example. The location of peak marks the transition temperature. Considering the enthalpy value (Delta H) and combining with microscope observation, we could confirm that there are two mesogenic phases appeared in sequence. The temperature range between the adjacent peaks is the range for the related mesophase. The hysteresis in heating and cooling may caused by the behavior of the material itself or could also be an artificial effect of too fast heating/cooling. Usually we use the rate of 10°C/min, but if the peak
is too small to be recognized, higher rate is recommended since higher heating/cooling speed leads to increasing of peak height. However, if two peaks are very close to each other, lower rate should be used so that the two peaked could be separated.

2.2 Cell Fabrication and Alignment

In the identification of liquid crystal behaviors, several distinct types of cells with various electrodes and substance are fabricated.

(1) Cells for vertical electric field

In the measurements of switching current, dielectric permittivity etc., cells coated with electrodes are used. For texture observation cells, substrates with transparent Indium Tin Oxide (ITO) electrode are required (Fig. 2.2 (a)). But in some materials, the relaxation of ITO electrode may have essential effect on dielectric relaxation at the frequency around 10MHz [3], as a result cells with metal (aluminum or gold) electrode will be necessary (Fig. 2.2 (b)) for dielectric measurements. The fabrication method is the same as described in Ref. [4].

![Figure 2.2](image)

**Figure 2.2** Glass substrates (a) with rectangular transparent ITO electrode in the center; (b) with metal electrode obtained by thermal evaporation. The length unit is millimeter.
(2) Cells for in-plane electric field

We also have several choices with in-plane electrodes cells. Fig. 2.3 gives three types of homeotropic cells with in-plane electrodes. In the Al cell (Fig. 2.3 (a)), aluminum foil worked as both spacer and electrodes. The advantage of the thick Al electrodes is uniform and straight external electric field. But this type of cells cannot be used for display devices because of the narrow appearance.

Figure 2.3 In-plane electrode cells with different electrode geometry. (a) Al electrode cell: aluminum plays the role of electrode and spacer. (b) Wide gap ITO cell: two parallel transparent electrodes are coated on the bottom glass substrate and they give one fixed width gap (50 µm); (c) narrow gap Cr electrode cell: comb-pattern electrodes are printed on bottom substate, the gap can be controlled to as thin as ~4 µm.

The wide gap ITO cell is broadly used in the evaluation of SmAP$_b$ performance (Fig. 2.3(b)). Through the transparent electrode, the reorientation process of molecules can be seen clearly. But the wide gap requires high operating voltage for switching and the single response gap (small switching area) is not a good candidate for industrial application as well. The third type has narrow electrodes and narrow gaps, which can offer both low operating voltage and large scale switching area (Fig. 2.3(c)). Nevertheless, every coin has two sides. Since electrodes are printed on only one substrate, the bending of electric field is unavoidable, especially in the narrow gap cells (Fig. 2.3 (b) and (c)). Related discussion will be given in chapter 3.
(3) Homogeneous alignment

When we refer to homogeneous or planar alignment, it means that the long axes of LC molecules are parallel to the substrate (Fig. 2.3(a)). In the homogeneous cells, we used polyimide AL1254 (JSR) as alignment layer. The AL1254 solution is spin coated on glass substrates and then heated at 80 °C for 30 min to remove the solvent. After that, substrates are cured at 180 °C for 60-90 min. The top and bottom plates with cured polyimide layer were rubbed antiparallely to each other (Fig. 2.4(b)). In my experiments, I set the gap between roller and stage as 6.5 mm which is the recommended value of our laboratory. While, in some specific cases in order to get defect free alignment result, I reduce the gap to 6.35 mm, which means rubbed very hard.

![Figure 2.4](image.png)

**Figure 2.4** (a) Geometry of homogeneously aligned liquid crystal molecules.[5] (b) Instrument to rub the glass plates [6].

(4) Homeotropic alignment

In contrast to planar cells, as we can seen in Fig. 2.5(a) homeotropic alignment means that the LC molecules are “standing up” (long axis are perpendicular to the substrate).
2. Experiment

Figure 2.5 (a) Geometry of homeotropically aligned liquid crystal molecules. (b) Molecular structure of silane coupling agent AY43-021.

In the homeotropically aligned cells, either silane coupling agent (Fig.2.4 (b)) or polyimide SE1211 (Nissan Chemical) were utilized. In the case of silane coupling agent, after treated by ultrasonic in silane coupling agent solution (100 μm/L) for more than 15 min, the glass substrates should be washed by clean water for more than 5 times and dry at 80 °C for 30 min. While, if polyimide SE1211 is used. It should be noted that SE1211 is very sensitive to humidity, so in rainy season the cell should be stored carefully.

For all handmade cells, UV curable adhesive mixed with spacer was used to make cells of typical thickness. The liquid crystal sample was filled in empty cells in isotropic phase by capillary effect.

2.3 Electro-optical Study

(1) Texture observation

The textures of liquid crystals were observed through polarized light microscope (POM) Nikon, Optiphot-pol equipped with a hot stage and temperature controller (Mettler Toledo FP 82). POM is a contrast-enhancing technique that can improve the quality of the image obtained with birefringent materials compare to other techniques such as darkfield and brightfield illumination etc. It has a high degree of sensitivity and
can be utilized for both quantitative and qualitative studies targeted at a wide range of anisotropic specimens, for example mesogenic materials.

**Figure 2.6** Configuration of polarized light microscope and the polarizing light principle is given on left [7].

Image contrast arises from the interaction of plane-polarized light with a birefringent (or doubly refracting) specimen to produce two individual wave components that are polarized in mutually perpendicular planes (as explained in Fig. 2.6). The velocities of these components are different and vary with the propagation direction through the sample. After penetrating the specimen, the light components become out of phase with each other, but are recombined with constructive and destructive interference when they pass through the analyzer [8]. In the birefringence measurement based on microscope, a Berek compensator Nichika No.10547 was used.

**2) Spontaneous polarization \((P_S)\)**

A molecule that has an electric dipole moment in the absence of an external electric field is called a polar (or dipolar) molecule, for instance bent-core liquid crystal
molecules. Such molecules will tend to orient itself in an external electric field when they form polar clusters (or polar domains). Usually, liquid crystal compounds contain a large number of ions and are fairly conductive. When electric field is applied to the sample, the current induced in the liquid crystal contains three parts [9].

\[ I_{LC} = I_c + I_p + I_i \]

\[ I_c = C \frac{dV}{dt} \quad \text{Charge accumulation to the capacitor} \]

\[ I_p = \frac{dP}{dt} \quad \text{Polarization realignment} \]

\[ I_i = \frac{V}{R} \quad \text{Ionic flow} \]

Within them, \( I_p \) is the current generated by polar switching of material which we are searching for. Usually triangular wave field is applied to the planar cell. In ferroelectric material which has bistable stage of molecules, only a single switching current peak could be detected in each half cycle. While, in antiferroelectric materials since tristable switching occurred, as a result, double peak will be observed in the current curve.

![Measurement system of reversal current](image)

**Figure 2.7** Measurement system of reversal current (the system must connect to common ground to avoid noise.)

In this dissertation, the switching behavior is obtained using a function generator
2. Experiment

(HP 3245A) connected with a high voltage amplifier (NF 4005) as shown in Fig.2.7. The switching current was measured across a 1 MΩ resistance (I-V converter). The spontaneous polarization value was obtained by integrating the area under the peak in each half cycle of the current curve.

2.4 X-ray Diffraction

X-ray diffraction is based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization. X-rays primarily interact with electrons in atoms. When X-ray photons collide with electrons, some photons from the incident beam will be deflected away from the direction where they originally travel, much like billiard balls bouncing off one another. If the wavelength of these scattered X-rays did not change (meaning that X-ray photons did not lose any energy), the process is called elastic scattering (Thompson Scattering) in that only momentum has been transferred in the scattering process. These are the X-rays that we measure in diffraction experiments, as the scattered X-rays carry information about the electron distribution in materials. On the other hand, in the inelastic scattering process (Compton Scattering), X-rays transfer some of their energy to the electrons and the scattered X-rays will have different wavelength than the incident X-rays [10].

Figure 2.8 Bragg diffraction and Bragg Law. Two beams with identical wavelength and
phase approach a crystalline solid and are scattered off two different atoms within it. In the equation, \( \lambda \) is the wavelength of the X-ray, \( \theta \) is the scattering angle, and \( n \) an integer representing the order of the diffraction peak.

Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows us to deduce the distribution of atoms in a material. For a given set of lattice planes with an inter-plane distance of \( d \), the condition for a diffraction (peak) to occur can be simply written as the following equation in Fig. 2.8, which is known as the Bragg’s law. It should be noted that Bragg’s Law applies to scattering centers consisting of any periodic distribution of electron density. In other words, the law holds true if the atoms are replaced by molecules or collections of molecules, such as colloids, polymers, proteins and virus particles. The Bragg’s Law is one of most important laws used for interpreting X-ray diffraction data [10].

\[
\sin \theta = \frac{n \lambda}{d}
\]

\( d \) is the inter-planar distance, \( n \) is the order of the diffraction peak, \( \lambda \) is the wavelength of the X-ray, and \( \theta \) is the scattering angle.

**Figure 2.9** Two types of geometry used in recording powder X-ray diffraction results: (a) transmission mode, (b) reflection mode [10].

X-ray diffraction data can be collected using either transmission or reflection geometry (Fig. 2.9) In this dissertation, The X-ray diffraction patterns were recorded through transmission mode for samples with homeotropic alignment obtained by slowly
cooling a drop of the isotropic liquid below the clearing temperature. The x-ray beam was directed almost parallel to the substrate surface. The Bruker D8 Discover and GADDS system were used.

2.5 Dielectric Permittivity Measurements

Permittivity is a physical quantity that describes how an electric field affects, and how it is affected by, a dielectric medium. Dielectric permittivity is determined by the ability of a material to polarize in response to the field, and thereby reduce the total electric field inside the material. The dielectric permittivity is a *macroscopic* quantity and therefore it is a very useful tool to investigate the dielectric materials. It connects the external field which people can measure and the macroscopic polarization which we are trying to understand.

The relationship can be briefly summarized as follow:

\[
D = \varepsilon E = \varepsilon_0 E + P = \varepsilon_0 E + \varepsilon_0 \chi E = \varepsilon_0 E(1 + \chi)
\]

\[
\varepsilon^* = \varepsilon' - j\varepsilon'' = \frac{\varepsilon'}{\varepsilon_0} - j\frac{\varepsilon''}{\varepsilon_0}
\]

- \(P\): the polarization of the medium;
- \(\chi\): the electric susceptibility;
- \(\varepsilon^*\): complex dielectric permittivity;
- \(\varepsilon'\): real part of permittivity;
- \(\varepsilon''\): imaginary part of permittivity

The dielectric constant of a material can be found by a variety of static electrical measurements. The complex permittivity is evaluated over a wide range of frequencies by using different variants of dielectric spectroscopy [11]. Also, by using heaters the dielectric properties of a medium can be characterized over an array of temperatures. In the characterization of liquid crystals, dielectric measurements are performed to identify both individual and
cooperative motion of the polar molecules [12].

In the dielectric study of this dissertation, materials were tested in planar aligned cells with indium tin oxide coated electrode. A frequency response analyzer (Solatron 1255B) and a dielectric interface Solartron (1296) were used. The samples were heated by a heater connected to Mettler temperature controller (Mettler Toledo FP 82).

2.6 Second-harmonic Generation

Second-harmonic generation (SHG) is a nonlinear optical process, in which photons interacting with a nonlinear material are effectively "combined" to form new photons with twice the energy, and therefore twice the frequency and half the wavelength of the initial photons. In the study of liquid crystals, SHG is usually carried out to investigate the polarization of the LC systems [13]. Polar order of materials is equivalent to a noncentro-symmetric arrangement of molecules, therefore non-linear optical study especially SHG is vital for investigating ferroelectric and antiferroelectric behavior [14].

![Figure 2.10](image-url) Optical setup for SHG measurement [15]. (ND: neutral density filter; BS: beam splitter; P1, P2: polarizers; λ/2: half wave plate; VIS: VIS-cut filter; IR: IR-cut)
In my experiments, the SHG signal was recorded using the optical setup in Fig. 2.8. The fundamental beam was Nd:YAG laser (1064 nm, 8 ns duration, 10 Hz repetition). The laser with strength of 7 mJ/mm$^2$ was incident at 45° for the homogeneously aligned cells. Linear polarizations parallel to the optic plane including the applied field direction were used for the fundamental and SHG light. The SHG signal was detected in the transmission direction by a photomultiplier tube (R955: Hamamatsu) after blocking the fundamental light by IR cut and interference filters. The signal was accumulated for 30 s with a boxcar integrator (SR-250: Stanford Research Systems).

2.7 FT-IR Spectroscopy

Infrared spectroscopy ("IR spectroscopy") is a technique used to identify chemical compounds based on how infrared radiation is absorbed by the compounds' chemical bonds. Fig. 2.11 gives IR absorption bands of common types of atomic bonds and functional groups. Note that this information is unreferenced, and may not be accurate.

![Absorption bands of various atomic bonds in molecules. The unite of wavenumber is cm$^{-1}$.](image)

Figure 2.11 Absorption bands of various atomic bonds in molecules. The unite of wavenumber is cm$^{-1}$.

An FT-IR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. FT-IR has made dispersive infrared spectrometers all but obsolete (except sometimes in the near
infrared), opening up new applications of infrared spectroscopy [16]. In organic chemistry, FT-IR is an important technique. It is an easy way to identify the presence of certain functional groups in a molecule. Also, people can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities.

In our experiment, we used the transmittance mode. When the tested sample is placed into an FT-IR spectrometer, the light source will pass different wavelengths of light through the sample. On the other side of the sample is a detector which detects the light that is transmitted through the sample. Fourier algorithms are used to transform the absorbance and transmittance information into a spectrum. These algorithms are complicated and a computer program is used for the calculations. Each peak on the infrared spectrum will correspond to a chemical bond. By comparing the percent transmittance for each wavelength and comparing them with known chemical transmittance it is possible to determine the structure of unknown compounds.

In this dissertation, FT-IR spectroscopy was used to identify the existence and the strength of intermolecular hydrogen bonding of liquid crystal systems. The FT-IR results were obtained through a JASCO FT-IR-460 PLUS spectrometer. The LC materials were injected in the isotropic phase to CaF₂ cells with the thickness around 5 μm through capillary effect.
Reference of chapter 2


"屈曲構造を有する液晶分子の電場誘起極性構造解析とディスプレイモード"

"学位論文 液晶における反強誘電性の出現と分子配列構造"


"Chirality and Polarity in Bent-Core Liquid Crystals"


"Phase Charactorization of Polar Liquid Crystals Using Dielectric Spectroscopy"


"屈曲分子液晶系における非線形光学効果"

Chapter 3

Randomized Polarization Smectic A Phase

As explained in chapter 1, a promising novel display mode can be realized in the SmAP$_R$ phase. Since this mode has a number of advantages of such as the fast response time (~400µs), continuous gray level, high contrast ratio (3000:1) and the wide viewing angle, further study is worthy [1-2]. In order to understand the relationship between the molecular structure and the mesomorphic properties in such systems and also seek for large variety of SmAP$_R$ candidates, our colleague have designed and synthesized several different series of bent-core mesogens with diverse modification of the molecular structure. In this chapter, I chose three major types of compounds which exhibit the target SmAP$_R$ phase to present.

3.1 Methylbenzene Core SmAP$_R$ Compounds

3.1.1 Background and Materials

The very first SmAP$_R$ compound reported by Pociecha et al has a methylbenzene central and the bent-core has five rings. Therefore the modification is first based on the methylbenzene core molecules. In this part I would present the property of new bent-core asymmetric compounds developed from five ring methylbenzene core. As the matter of fact, two series of modified compounds were synthesized [3] in which the lack of symmetry is derived from different lateral substituent and differences in the terminal alkoxy chain lengths. In some compounds, asymmetry was also induced through introducing carbon-carbon double bonds in one or both of the terminal chains. It is expected that, the introduction of above structural modifications may result in decrease of transition temperature and widen the range of the SmAP$_R$ phase.
The name of each compound was given according to the following rule: m and n stand for the carbon number in terminal chains; N and Cl symbolize NO\textsubscript{2} and Cl, respectively; d in the second series represents double bond at the end.

In the first series, both arms have saturated carbon chains. The lack of symmetry was derived from different lateral substituents or differences in the terminal alkyl chain lengths. The molecular structure and phase sequence are shown in Table 3.1.

**Table 3.1** Phase transition temperatures (°C) and corresponding enthalpies [J/g] for compounds of series I.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>B\textsubscript{1RevTilted}</th>
<th>SmAP\textsubscript{R}</th>
<th>Iso</th>
<th>ΔT (SmAP\textsubscript{R})</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-NCl-5</td>
<td>104.36 [18.06]</td>
<td>113.03 [10.92]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12-NCl-7</td>
<td>92.45 [13.68]</td>
<td>125.93 [12.95]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12-NCl-16\textsuperscript{a}</td>
<td>123.24 [24.70]</td>
<td>128.30 [0.40]</td>
<td>134.60 [9.72]</td>
<td>16.30</td>
</tr>
<tr>
<td>12-NCl-14</td>
<td>100.72 [45.50]</td>
<td>125.02 [0.55]</td>
<td>135.45 [10.59]</td>
<td>10.45</td>
</tr>
<tr>
<td>12-NCl-11</td>
<td>121.00 [15.70]</td>
<td>125.90 [0.61]</td>
<td>136.80 [10.89]</td>
<td>10.90</td>
</tr>
<tr>
<td>12-NCl-15\textsuperscript{b}</td>
<td>103.30 [45.90]</td>
<td>123.30 [0.20]</td>
<td>136.30 [6.80]</td>
<td>13.00</td>
</tr>
<tr>
<td>12-NCl-14\textsuperscript{b}</td>
<td>107.00 [51.72]</td>
<td>124.92 [0.66]</td>
<td>137.96 [10.53]</td>
<td>13.04</td>
</tr>
<tr>
<td>12-NCl-16\textsuperscript{c}</td>
<td>118.00 [23.12]</td>
<td>125.97 [0.99]</td>
<td>140.06 [9.77]</td>
<td>14.09</td>
</tr>
<tr>
<td>12-NCl-18\textsuperscript{c}</td>
<td>113.71 [20.89]</td>
<td>121.39 [0.20]</td>
<td>134.72 [8.40]</td>
<td>13.33</td>
</tr>
<tr>
<td>14-NCl-13\textsuperscript{c}</td>
<td>102.77 [38.59]</td>
<td>126.81 [0.85]</td>
<td>139.24 [9.04]</td>
<td>12.43</td>
</tr>
<tr>
<td>14-NCl-14\textsuperscript{c}</td>
<td>116.53 [22.06]</td>
<td>127.72 [1.00]</td>
<td>141.27 [9.08]</td>
<td>13.55</td>
</tr>
<tr>
<td>14-NCl-15\textsuperscript{c}</td>
<td>117.70 [21.27]</td>
<td>126.70 [0.86]</td>
<td>140.93 [8.70]</td>
<td>14.23</td>
</tr>
<tr>
<td>14-NCl-16\textsuperscript{c}</td>
<td>116.40 [22.47]</td>
<td>125.31 [0.85]</td>
<td>140.88 [8.55]</td>
<td>15.57</td>
</tr>
</tbody>
</table>

In this series, compounds with middle and long terminal chains show two enantiotropy mesophases such as lower temperature B\textsubscript{1RevTilted} and higher temperature SmAP\textsubscript{R}. But the short-tailed homologues 12-NCl-5 and 12-NCl-7 only form B\textsubscript{1RevTilted}. This phase is the tilted columnar phase with broken layers and 2D density modulation in the plane perpendicular to the polarization direction [4]. conoscopic measurements confirmed that the SmAP\textsubscript{A} phase is uniaxial [5]. Introduction of tetradecyloxy group as a constant part of the structure in series 14-NCl-m compounds resulted in only slightly increased isotropization temperature and did not influence the range of SmAP\textsubscript{R}.
mesophase during the variations of length of the second tail.

In the second series of compounds there are different carbon-carbon double bonds in one or both of the terminal chains. The structures and phase sequences of this series is given in Table 3.2

**Table 3.2** Phase transition temperatures (°C) and corresponding enthalpies [J/g] for compounds of series II.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>X</th>
<th>Y</th>
<th>Cr</th>
<th>B_{RevsTiled}</th>
<th>SmAP$_R$</th>
<th>Iso</th>
<th>ΔT (SmAP$_R$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11d-NCl-11d</td>
<td>NO$_2$</td>
<td>Cl</td>
<td>120.76 [10.95]</td>
<td>119.37 [0.61]</td>
<td>123.03 [9.36]</td>
<td>•</td>
<td>—</td>
</tr>
<tr>
<td>12d-NCl-11d</td>
<td>NO$_2$</td>
<td>Cl</td>
<td></td>
<td>118.50 [0.90]</td>
<td>125.76 [10.41]</td>
<td>•</td>
<td>3.66</td>
</tr>
<tr>
<td>14d-NCl-11d</td>
<td>NO$_2$</td>
<td>Cl</td>
<td></td>
<td>118.50 [0.95]</td>
<td>127.97 [9.79]</td>
<td>•</td>
<td>6.39</td>
</tr>
<tr>
<td>16d-NCl-11d</td>
<td>NO$_2$</td>
<td>Cl</td>
<td></td>
<td>117.10 [0.99]</td>
<td>129.77 [9.16]</td>
<td>•</td>
<td>9.47</td>
</tr>
<tr>
<td>18d-NCl-11d</td>
<td>NO$_2$</td>
<td>Cl</td>
<td></td>
<td>115.83 [0.85]</td>
<td>125.36 [9.92]</td>
<td>•</td>
<td>12.67</td>
</tr>
<tr>
<td>11d-NCl-14d</td>
<td>NO$_2$</td>
<td>Cl</td>
<td>105.97 [7.78]</td>
<td></td>
<td></td>
<td>•</td>
<td>9.53</td>
</tr>
<tr>
<td>11d-ClCl-11d</td>
<td>Cl</td>
<td>Cl</td>
<td>108.10 [12.04]</td>
<td></td>
<td></td>
<td>•</td>
<td>—</td>
</tr>
<tr>
<td>11d-NN-11d</td>
<td>NO$_2$</td>
<td>NO$_2$</td>
<td>149.77 [50.31]</td>
<td></td>
<td></td>
<td>•</td>
<td>—</td>
</tr>
</tbody>
</table>

In series II which have unsaturated terminal chains in the molecules, compound 11d-NCl-11 and those with two double bonds in terminal chains do not show mesophases. All the rest materials exhibit SmAP$_R$ phase and monotropic B$_{RevsTiled}$. Introduction of a vinyl group at the end of a terminal chain decreases the clear point of SmAP$_R$, but did not widen the range of mesophase as was expected. Also at room temperature the transition from the B$_{RevsTiled}$ to crystal was not observed. Compound 11d-NCl-14 (laboratory name is KGJ29) was selected as a representative for those two series of materials to study into details.

### 3.1.2 Results

(1) Texture Observation
11d-NC1-14 (KGJ29) is a typical asymmetry compound with double bond on one end chain. It exhibits SmAP$_R$ phase in higher temperature and after that shows B$_1$RevTiled phase down to room temperature. Fig. 3.1 gives the homeotropic and homogeneous texture of this compound of SmAP$_R$ and B$_1$RevTiled phase, respectively.

![Figure 3.1](image)

**Figure 3.1** Photomicrograph of textures of KGJ29 in (a) homogeneous and (b) homeotropic cell at 123 °C (SmAP$_R$ phase); textures of B$_1$RevTiled phase in (c) homogeneous and (d) homeotropic cell at 101 °C. Cell thickness was 5 µm.

In homogeneously aligned cells, typical focal conic texture was observed. With cooling down, the birefringence increased gradually. When it turned to B$_1$RevTiled phase, the boundary of fan-shape fainted indicating a layer-break structure. When this compound was sandwiched in a cell treated for homeotropic alignment and cooled from the isotropic phase, a uniform dark view indicating the uniaxial SmA phase was observed as shown in Fig. 3.2(b) and in B$_1$RevTiled phase biaxial gray texture showed up.
When external electric field was applied to the sample, switching behavior was observed in both of the two phases. While in B1RevTilted phase, the operating voltage was much higher than that of in SmAPR phase. Texture change of 11d-NCl-14 measured at in the SmAPR phase is shown in Fig. 3.2. Rectangular wave 280 V_{pp} was applied to the cell. It is noticed that the focal conic texture does not change except for slight increase of birefringence. It has confirmed the non-tilted structure of SmAPR.

(2) Spontaneous Polarization

We recorded switching current of 11d-NCl-14 using a triangular wave electric field. In homogeneous cell at 120°C, one broad polarization current peak for each half cycle was obtained at the voltage of 280 V_{pp}, as shown in Fig. 3.3(a). The broadness of the peak indicates field-induced alignment of dipoles from a random orientation through the Langevin process [5]. The switching current of B1RevTilted phase is also given. It is noted that in the current curve, two peaks partially overlapped each other could be observed. That is because of the antiferroelectric-like behavior of this tilted columnar phase.
3. SmAP\textsubscript{R} Phase

Figure 3.3 Switching current of 11d-NCl-14 (a) in SmAP\textsubscript{R} phase at 120\textdegree{}C and (b) in B\textsubscript{1RevTilted} phase at 106\textdegree{}C. Cell thickness is 8.4 \textmu{}m.

The variation of the polarization as a function of temperature is shown in Fig. 3.4. The polarization value was about 40 nC/cm\textsuperscript{2} at 124 \textdegree{}C, increased up to 160 nC/cm\textsuperscript{2} at 115 \textdegree{}C and then reduced sharply in the B\textsubscript{1RevTilted} phase.

Figure 3.4 The variation of the polarization as a function of temperature.

(3) Dielectric permittivity

The dielectric measurements of 11d-NCl-14 were conducted in a planar cell. Since
there is a strong contribution of ions below 10Hz in the SmAPR phase, we conducted the dielectric measurements in a frequency range from 10 Hz to 1 MHz. The real part of dielectric permittivity ($\varepsilon'$) of compound KGJ29 is shown in Fig. 3.5 as a function of frequency at various temperatures. Only a single relaxation mode was observed in the whole temperature range of liquid crystal phases. (The high frequency mode is an artifact due to the limited conductivity of ITO electrodes; this mode also exists in the SmAPR phase.)

Figure 3.5 Real part of the dielectric permittivity in the SmAPR and B1RevTilted phases of 11d-NCl-14 as a function of frequency at various temperatures. Solid symbols correspond to the data in the SmAPR phase (left vertical scale) and the open symbols correspond to the data in the B1RevTilted phase (right vertical scale). The continuous lines are the fits to the Cole–Cole formula.

At each temperature the relaxation frequency and mode strength could be obtained
by fitting experimental points to the Cole–Cole formula.

\[
\varepsilon^* (\omega) = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1 + (i\omega\tau_2)^{1-\alpha_2}}
\]  

(1)

Where \(\varepsilon_i (i=1, 2)\) is the low and high frequency limits of the dielectric constant; \(\omega = 2\pi f\) and \(f\) is frequency; \(\tau\) is the relaxation times and \(\alpha_i\) are Cole-Cole distribution parameters.

The parameter \(\alpha\) which indicates the distribution of relaxation frequencies for the dielectric mode was close to 0 except for in temperature range near the phase transition where it increases to 0.4.

In the SmAP\(_R\) phase the dielectric relaxation frequency increases from 70 to 440 Hz (Fig. 3.6) and the value of dielectric permittivity decreases from 60 to 20, with rising temperature. The high dielectric response with low relaxation frequency indicates the presence of a strong positive dipolar correlation and dipole cooperative motions in the SmAP\(_R\) phase, which can be considered as local ferroelectric order in this phase. As indicated by dielectric measurement results this ferroelectric order of dipoles becomes weaker with increasing temperature.
Figure 3.6 Variation of relaxation frequency in the SmAP$_R$ phase of 11d-NCl-14 as a function of temperature. The effect of DC bias voltage measured at 115°C is shown in the inset. Cell thickness was 8.4 µm. The continuous lines are drawn as a guide to the eyes.

The effect of DC bias on the relaxation mode was also examined (Fig 3.6, inset). In the SmAP$_R$ phase it is noted that the relaxation frequency begins to rise keeping the dielectric strength the same in the field beyond 3 V/µm. This might be expected, as under DC bias the collective motion of the dipoles is faster due to the external electric field limited the rotation angle of molecules along their long axis, as a result the relaxation frequency is increased. At still higher bias field the relaxation mode strength should be completely suppressed. However, full suppression was not observed due to the insufficient bias voltage, limited by the equipment used in the experiment. Similar field dependent behavior in the kHz frequency range was previously described [6].

In the B$_{1\text{RevTilted}}$ phase the dielectric permittivity is one order of magnitude weaker and the dielectric relaxation frequency much higher than in the SmAP$_R$ phase. The
relatively small value of the dielectric constant in the B1RevTilted phase indicates the antiferroelectric nature of this phase (Fig. 3.6).

In the B1RevTilted phase which is built of layer fragments, molecules are tilted from the layer normal and polar ordered, the relaxation mode can be ascribed to fluctuation in the azimuthal orientation of the molecules in the layer fragments. Hence this mode can be considered as an analogue of the antiphase azimuthal mode[7] in the antiferroelectric SmCA* phase made of calamitic or bent-core molecules [8]. Observation of such a mode in a broken-layer columnar phase has already been reported by Gorecka et al [9].

![Figure 3.7](image)

**Figure 3.7** (a) Real part and (b) imaginary part of dielectric permittivity of B1RevTilted phase under DC bias field.

Since the dielectric response in the B1RevTilted phase is much weaker than in the antiferroelectric lamellar B2 phase [8], we can assume that azimuthal fluctuation of molecules must be strongly suppressed, most probably due to some anchoring of the director at boundaries of the layer fragments. The dielectric response is suppressed by the DC bias voltage in the B1RevTilted phase (Fig 3.7). But because of the limitation of the instrument on the DC voltage (maximum 40 V), the relaxation was not completely suppressed.
5) X-ray diffraction

We performed X-ray diffraction measurements in the SmAP<sub>R</sub> phase as well as in the B<sub>1RevTilted</sub> phase on unoriented samples.

![Figure 3.8](image)

**Figure 3.8** Variation of layer spacing \(d\) in the SmAP<sub>R</sub> phase of 11d-NCl-14 compound (solid circles) and parameters of 2D primitive unit cell in the B<sub>1RevTilted</sub> phase: \(a\) (open squares), \(c\) (open circles) and angle \(\beta\) (open triangles).

For the compound 11d-NCl-14 in the SmAP<sub>R</sub> phase, two commensurate reflections could be seen in the small angle region indicating a smectic ordering of the mesophase. The layer spacing \(d\) gradually increases as the temperature is lowered in the SmAP<sub>R</sub> phase. The X-ray pattern for B<sub>1RevTilted</sub> is consistent with a 2-D oblique lattice: one of the lattice parameters, \(c\), is close to the \(d\) (layer spacing of SmAP<sub>R</sub>) value. The lattice parameter \(a\), that is related to the length of the layer fragment, increases on cooling, whereas the unit cell inclination angle, \(\beta\) slightly larger than 90 degree, is almost temperature independent (Fig. 3.8).
3.1.3 Discussion

In order to confirm that the identity of the two mesophases observed in these compounds, we carried out miscibility studies between compound 11d-NCI-14 and the well studied 14-NCI-14. This reference compound has the following sequence of transitions Cr.114 B_{1Rev Tilted} 123 °C SmAP_R 138.6 °C Iso. The binary phase diagram obtained for these two compounds is shown in Fig. 3.9.

Figure 3.9 Binary phase diagram obtained for a mixture of compound 14-NCI-14 (original SmAP_R phase material, also named 2315 in Ref. [1]) and 11d-NCI-14. The continuous line is drawn as a guide to the eyes.

It can be noticed that the two phases of compound 11d-NCI-14 are completely miscible with the mesophases of the standard material over the entire composition range, indicating that the two mesophases are exactly the same. It also provides a method to expand the temperature range of SmAP_R other than synthesizing new compound but by properly mixing.

3.1.4 Summary

The mesomorphic behavior of asymmetric bent-core compounds derived from
2-methylresorcinol, containing a lateral chloro/nitro group and saturated or unsaturated terminal alkoxy chain/s, has been investigated. The mesophases exhibited by these compounds have been characterized as the lamellar uniaxial polar SmA phase (SmAP\textsubscript{R}) and the brokenlayer type columnar B\textsubscript{1RevTilted} phase. Introduction of a double bond in the terminal chain can lower the isotropization temperatures but also slightly destabilizes the smectic phase. The dielectric relaxation in the SmAP\textsubscript{R} phase is much stronger than in the B\textsubscript{1RevTilted} phase due to the cooperative dipolar relaxation. In the B\textsubscript{1RevTilted} phase which has antiferroelectric segregation, the dielectric response arises from weak anti-phase fluctuation of the polarization vector in neighbouring layer fragments.
3.2 Acetophenone Core SmAP\textsubscript{R} Compounds

3.2.1 Background and Materials

The methylbenzene core series add a number of new compounds to the SmAP\textsubscript{R} phase family. Nevertheless, the narrow temperature range ($\Delta T$ in methylbenzene core compounds is less than 20°C) of the random polarized (SmAP\textsubscript{R}) phase is still a vital problem for application in the industry. In this part of work, I would introduce a new series of bent shaped mesogens which have 1,3-dihydroxyacetophenone as a central unit. Stilbene arms were used bearing NO\textsubscript{2} or Cl substituents at the lateral position. This series also contains the first reported symmetric BC molecules showing the SmAP\textsubscript{R} mesophase [10].

The mesophases and transition temperatures of the synthesized compounds are summarized in Table 3.3. All the compounds exhibited LC phases, and the mesophase stability increased with elongation of terminal chains except for AP-20-NN-20. We should note that the transition enthalpy at the SmAP\textsubscript{R}-SmAP\textsubscript{A} transition was quite small and was even hard to be detected particularly in AP-20-NN-20. The introduction of an asymmetric substituent leads to broader mesophase ranges at lower temperatures, as noticed by comparing AP-14-NN-14 with asymmetric analogue AP-14-NCl-14.

**Table 3.3** Phase transition temperatures (°C) and corresponding enthalpies [J/g] for compounds of AP-\textit{n}-NN-\textit{n}; AP-14-NCl-14 and AP-14-ClCl-14. Numbers at the both sides of the sample names stand for the numbers of carbons in both end chains. AP stand for central unit – acetophenone. N and Cl stand for substituents NO\textsubscript{2} and Cl at the left and right wings, respectively.
3. SmAP\textsubscript{R} Phase

(n is the number of carbon in the flexible terminal chains.)

<table>
<thead>
<tr>
<th>Code</th>
<th>X</th>
<th>n</th>
<th>Cry</th>
<th>SmAP\textsubscript{A}</th>
<th>SmAP\textsubscript{R}</th>
<th>Iso</th>
<th>(\Delta T) (SmAP\textsubscript{R})</th>
</tr>
</thead>
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<tr>
<td>AP-14-NN-14</td>
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<td>105.23</td>
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<td></td>
<td></td>
<td></td>
<td>[0.03]</td>
<td>[5.70]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AP-16-NN-16</td>
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<td>−</td>
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<td>130.10</td>
<td>●</td>
<td>36.00</td>
</tr>
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<td></td>
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<td></td>
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<td>136.03</td>
<td>●</td>
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<tr>
<td>AP-20-NN-20</td>
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<td>20</td>
<td>−</td>
<td>95*</td>
<td>134.70</td>
<td>●</td>
<td>39.70</td>
</tr>
<tr>
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<tr>
<td>AP-14-NCI-14</td>
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<td>−</td>
<td>97*</td>
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<td></td>
<td>[3.78]</td>
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</tr>
<tr>
<td>AP-14-ClCl-14</td>
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<td>●</td>
<td>79.10</td>
<td>●</td>
<td>−</td>
<td></td>
</tr>
</tbody>
</table>

* Determined by texture observation, since corresponding DSC peaks are so small.

3.2.2 Results

(1) X-ray Diffraction Results

The 2-dimentional X-ray diffraction patterns of homeotropically aligned sample of AP-20-NN-20 in both SmAP\textsubscript{R} and SmAP\textsubscript{A} phases are shown in Fig.3.10 (a) and (b). It is quite obvious that although both have liquid like order inside the layer, the layers are much better defined for the SmAP\textsubscript{A} phase, as indicated by larger number of harmonics of the main signal. The diffuse character of wide-angle scattering, found even at ambient temperature, signifies a liquid-like disorder within layers. But it should be noticed that in the low temperature phase SmAP\textsubscript{A}, the wide angle signal is slightly sharper than in the SmAP\textsubscript{R} phase, indicating larger correlation length of in-plane molecular ordering (Fig.3.10 (c)). The in-plane correlation lengths, obtained by fitting wide angle signal to Lorentz formula, in SmAP\textsubscript{R} and SmAP\textsubscript{A} are 2.4A and 4.8A, respectively.
3. SmAP<sub>R</sub> Phase

**Figure 3.10** Two dimensional x-ray patterns for compound AP-20-NN-20: (a) in the SmAP<sub>R</sub> phase at 130°C, (b) in the SmAP<sub>A</sub> phase at 25°C. Slight up/down asymmetry in the pattern is due to shadowing by sample heating stage. (c) Intensity vs. 2θ obtained by integration of 2D patterns over azimuthal angle at 130°C and 25°C, respectively.

(2) Texture Observation

Figure 3.11 reveals optical photomicrographs of homeotropic and homogeneous cells in SmAP<sub>R</sub> and SmAP<sub>A</sub> phases in the absence of an electric field. In homeotropically aligned samples of **AP-18-NN-18**, the high temperature phase exhibited a uniform dark image with some minor defects, indicating optical uniaxiality of the phase (Fig.3.11( a)) and this is the same as observed in the methylbenzene core materials. Then the transition to the low temperature phase was recognized as the appearance of grain-like textures with weak birefringence, as shown in Fig. 3.11 (b). Under microscope, the transition occurs gradually indicating that the related enthalpy is small which is consisting with the DSC result.
Figure 3.11 Photomicrographs of compound AP-18-NN-18. Homeotropic texture of (a) the SmAPᵦ phase at 100°C and (b) the SmAPᵦ phase 80°C. Homogeneous texture (c) in the SmAPᵦ phase at 100°C; and (d) in the SmAPᵦ phase at 84 °C. The sample thickness was 5.2 µm.

When the compound was introduced into homogeneous cells, the sample gave the fan-shaped texture characteristic of the SmA in both phases (Fig 3.11 (c) and (d)). The extinction directions in both phases were parallel to the layer normal, certifying the orthogonal smectic phase. During cooling the texture was retained and phase transition only caused continuous birefringence change in the texture.

(3) Electro-optical Study

Perfect aligned planar cells can help to identify the molecular behavior under an electric field. Through applying an electric field (20 V/m/µm) (Fig. 3.12) the birefringence slightly increases from 0.094 to 0.101 in the SmAPᵦ and from 0.117 to 0.122 in the SmAPᵦ phase, respectively. The higher value of the SmAPᵦ compared to SmAPᵦ in the field-on state, where all molecules are oriented with their dipole
moments along the electric field, is caused by slightly higher orientational order of long molecular axes in the antiferroelectric phase (SmAP\textsubscript{A}). The reorientation of molecules under the field in both phases occurs without changing the optical extinction directions, which is also consistent with the orthogonal nature of the two phases.

![Figure 3.12 Homogeneous textures of AP-18NN-18 under electric field. (a) Field off state, $\Delta n = 0.094$, and (b) field-on state, $\Delta n = 0.101$ in the SmAP\textsubscript{R} phase at 103\degree C. (c) Field off state, $\Delta n = 0.117$, and (d) field-on state $\Delta n = 0.122$, in the SmAP\textsubscript{A} phase at 85 \degree C. Cell thickness was 4.6 \mu m.](image)

Switching current was recorded on applying a triangular wave electric field to a planar cell at various temperatures. In the SmAP\textsubscript{R} phase, one broad peak for each half cycle was obtained as shown in Fig. 3.13(a). Such a peak can be attributed to the field induced reorientation of local polar domains from random distribution to the field direction through a Langevin process, which is a typical behavior of the SmAP\textsubscript{R} phase [1-5]. In the lower temperature phase, SmAP\textsubscript{A}, two current peaks per half cycle were detected (Fig.3.13 (b)), indicating that the ground-state structure of the mesophase is antiferroelectric. The spontaneous polarization ($P_s$) values calculated from the switching current in SmAP\textsubscript{R} and SmAP\textsubscript{A} are $\sim 170$ nC/cm\textsuperscript{2} (97 \degree C) and $\sim 300$ nC/cm\textsuperscript{2} (87 \degree C), respectively.
3. SmAP<sub>R</sub> Phase

Figure 3.13 Switching current response recorded by applying a triangular wave voltage to a 5.2 µm-thick cell. (a) SmAP<sub>R</sub> at 97 °C (140 V<sub>pp</sub>, 6 Hz) and (b) SmAP<sub>A</sub> at 87 °C (140 V<sub>pp</sub>, 0.2 Hz). In order to resolve the double switching current peak in SmAP<sub>A</sub> phase the frequency of the applied voltage has to be below 1 Hz.

4) SHG Study

The polar order in both phases was monitored by the SHG method. The intensity of the SHG signal as a function of temperature with and without an applied electric field is given in Fig. 3.14.

Figure 3.14 Temperature dependence of the SHG intensity in a homogeneously aligned 4.8 µm-thick cell on cooling from the isotropic phase. Open triangles represent a zero field run and closed circles represent data obtained under applying 10 V DC field to the
When the materials were tested without an electric field, no signal could be obtained at any temperature, indicating that neither of the two polar phases has macroscopic spontaneous polarization. Upon field application, polar order is easily induced in the SmAP$_R$ phase; i.e., SHG signal gradually increased on cooling and reached a maximum value near the SmAP$_R$ to SmAP$_A$ phase transition. That is because molecular dipoles cooperatively orient in the layer by the application of an electric field and with reducing temperature the coherence length gradually increases. On the contrary, in the low temperature phase, SmAP$_A$, the induction of polar order is associated with a threshold for the structure change from SmAP$_A$ to SmAP$_F$. Since this threshold voltage increases with lowering temperature, the SHG signal under the same voltage decreases rapidly on cooling in SmAP$_A$ phase.

5) Dielectric measurements

The dielectric measurements were conducted in planar cells. The overall dielectric behavior as functions of temperature and frequency is shown as a 3-D plot of imaginary part of dielectric permittivity ($\varepsilon''$) recorded in a cooling process (Fig. 3.15(a)). In the whole temperature range, two relaxation modes are visible. The higher frequency mode can be attributed to the noncollective motion of polar molecules, its relaxation frequency follows the Arrhenius law: $f_{\text{Arrh}}=f_0 e^{-E_a/kT}$, with activation energy $E_a = 151$ kJ/mol, and the dielectric strength $\Delta \varepsilon$ slightly increases with reducing temperature. The lower frequency mode shows critical behavior near the phase transition, thus can be attributed to collective movement of dipole moments. The relaxation frequency $f_r$ reaches the minimum (~3 Hz) and mode strength maximum (~30), at the phase transition, that indicates long living polar fluctuation in the system on approaching
phase transition. Since $f_r$ is proportional to the strength of interlayer polar interactions in the system (the stronger interaction the higher relaxation frequency) [11] its low value at $T_c$ indicates that for this material interlayer polar coupling is weak. The low dielectric response in the SmAP$_A$ phase is consistent with the proposed antiferroelectric model of this phase.

Figure 3.15 (a) 3-dimensional plot of imaginary part of dielectric permittivity of AP-18NN-18 material. Two relaxation modes caused by cooperative motion and non-collective movement of dipole molecules can be seen at low and high frequencies,
respectively. (b) Relaxation frequency $f_r$ and (c) dielectric strength $\Delta \varepsilon$ of the both dielectric modes as a function of temperature. Homogeneous aligned cell with the thickness of 5.4 $\mu$m was used in the dielectric measurement.

The effect of DC bias on the relaxation mode was also examined in both polar phases. In the SmAP$_R$ phase the relaxation frequency increased, simultaneously with decreasing dielectric strength, under increasing bias voltage (Fig. 3.16(a)). This is because bias filed suppresses the collective motion of molecular dipoles. This behavior is consistent with the expected ferroelectric-like characteristic of the SmAP$_R$ phase. On contrast, in the SmAP$_A$ phase, DC bias field causes at first the increase of dielectric strength of the mode and its shift to the lower frequency, due to partial distortion of antiferroelectric order in adjacent layers leading to the induction of non compensated polarization. However the increase of the bias voltage above the threshold (the electric field required to impose ferroelectric state) results in nearly total suppression of the mode (Fig. 3.16(b)). The relaxation originating from non-collective movement of molecular dipoles is scarcely affected by a DC bias field.

![Figure 3.16](image)

**Figure 3.16** DC bias effect of the imaginary part of dielectric permittivity in (a) SmAP$_R$ phase and (b) in SmAP$_A$ phase. The cell used here was 6.5 $\mu$m with planar alignment.
3.3.3 Discussion

Through a sequence of characterization introduced above, the electro-optical behavior of the acetophenone core materials are exposed. Now the problem becomes how the polarization developed in these two polar orthogonal phases. The temperature dependence of x-ray study gives some hint.

As seen in Fig. 3.17(a), in all studied materials, the layer spacing, $d$, shows noticeable negative thermal expansion in all temperature range of LC phases. Negative thermal expansion is typical for orthogonal smectic phases, it was observed in SmAP$_R$ and even in smAP$_{AR}$ [12] of other compounds. For acetophenone core compounds reporting here, in the SmAP$_R$ phase $d$ increases on cooling more apparently than in the SmAP$_A$ phase; the slope of $d$ vs. $T$ is $\sim$0.2 A/K for SmAP$_R$, which is an order of magnitude larger than observed for calamitic orthogonal smectics, and 0.03 - 0.05 A/K for SmAP$_A$, with higher values for longer homologues. This implies that the mechanisms of layer spacing changes in each phase are different. The layer spacing in SmAP$_R$ phase is shorter than the molecular length $L$. The reason could be the partial interdigitation of alkyl chains between adjacent layers, as was also observed in the nonpolar SmA phase composed of bent-core molecules [13-14]. In such nonpolar phase individual molecules rotate freely particularly at higher temperatures and the overall shape of rotating bent-core molecules can be regarded as bulky middle part with much thinner flexible molecular ends (Fig. 3.17(b) right). Packing of such objects into layers requires pronounced interdigitation of molecular tails between the layers to fill the space effectively. Of course, full interdigitation is not possible because of gauche conformations of flexible chains [15] and their thermal dynamic motion. We expect that in the SmAP$_R$ phase with lowering temperature the rotation around long molecular axis is frozen gradually as the coherence length for polar order is growing (proved by SHG), resulting in lower degree of interdigitation thus increase of layer thickness.
The situation is illustrated in Fig. 3.17(b). At higher temperatures, the size of polar domains is very small, so that the molecules rotate almost freely, as mentioned above (right side of the figure). This is supported by SHG measurements (see Fig. 3.14); i.e., SmAP$_R$ is SHG inactive under certain field strength at higher temperatures. Since macroscopic polar order is induced via Langevin process, i.e., competition between polar interaction and thermal agitation, SHG does not emerge if the polar domain is too small to be oriented. The evolution of polar domains proceeds with decreasing temperature. Hence molecular packing becomes tight at lower temperatures. In the vicinity of the transition to the SmAP$_A$ phase, the adjacent layer correlation shown in left side of Fig. 3.17(b) is realized. For non-rotating molecules the efficient packing does not require strong inter-correlation, since the cross section of the middle part of molecule is not much different than its end parts. In the intermediate temperature range, a situation shown in the middle of Fig. 3.17(b) may occur, since the evolution of polar domain occurs dynamically. Thus the negative thermal expansion in SmAP$_R$ can be interpreted by the continuous variation of the ratio of the three typical situations.

In the SmAP$_A$ phase molecular rotation is frozen and layers spacing is larger than in the SmAP$_R$ phase, although it is still much smaller compared with the molecular
length with fully extended chains. Moreover, the $d$ value still increases with decreasing temperature. These facts suggest that the increase of layer spacing with decreasing temperature mainly originates from the increase of orientational order of long molecular axes and the change of the chain conformation (decreasing number of gauche conformations on cooling). These effects are also valid for the SmAP$_R$ phase.

3.3.4 Summary

This series of acetophenone core mesogens shows transition from the uniaxial orthogonal phase with local polar order (SmAP$_R$) to the antiferroelectric non-tilted smectic phase (SmAP$_A$). It gives much wider temperature range ($\Delta T \sim 40^\circ\text{C}$) of the target phase SmAP$_R$ which is considered to be a candidate for fast response display devise in the future.

Within the resolution of the used techniques (x-ray diffraction, dielectric and electro-optic), it seems that the transition is continuous or weakly first order, which is allowed for phases of different symmetry ($D_{\infty v}$ for SmAP$_R$ and $D_{2h}$ for SmAP$_A$, respectively). The correlation length of polar order in the SmAP$_R$ phase gradually increases as well as antiferroelectric interlayer correlations. The interlayer polar coupling is weak as indicated by a low value of relaxation frequency of a ferroelectric mode at the phase transition. It should be mentioned that recently Keith et al[16] reported another series of compounds showing the similar phase sequence.
3.3 Siloxane Sublayer Stabilized SmAP$_R$ Phase

3.3.1 Background and Materials

Various methods have been tried on designing bent-core mesogens to acquire macroscopic polarization or super structural chirality.[17] Several works have reported that carbosilane as well as siloxane groups have great influence on mesophase behavior, especially on spontaneous polarity.[18-20] This is mainly due to the nano-segregation of the siloxane units into sublayers located at the inter-layer interfaces. These sublayers influence the coupling between the layers which modifies the self-assembling of the bent-core molecules. For this reason a large variety of bent-core molecules based on oligosiloxane[21] and carbosilane [22] segments have been synthesized in recent years.

With the purpose of getting better performing polar SmA compounds, our colleague also brought siloxane units into the methylbenzene core SmAP$_R$ molecules. Although in the siloxane bulky modified series of materials, more than ten compounds were synthesized, only a few of them with tiny modification on one arm of original molecules could maintain the uniaxial SmAP$_R$ phase. Here the molecular construction and phase sequence of the SmAP$_R$ compounds with single siloxane terminal are given in Table 3.4.

Table 3.4 Molecular structure and phase transition temperatures (°C) of the single siloxane terminal bent-core liquid crystals.

\[ \text{Table 3.4} \]
3. SmAP\textsubscript{R} Phase

<table>
<thead>
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<th>Name</th>
<th>m</th>
<th>n</th>
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<th>Col\textsubscript{1}</th>
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<th>Iso</th>
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<td>● 97</td>
<td>● 139</td>
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</table>

By comparing the temperature range between each compound and combing the reported materials[23], it is notices that introducing siloxane bulky group has expended temperature range of the SmAP\textsubscript{R} phase and also lead to emerge of two columnar phases. It also helped to stabilize the general mesogenic phase down to room temperature. Simultaneously the alkyl chain length is playing an essential role as well. The longer alkyl chain connected to siloxane terminal results in the higher clear point and wider SmAP\textsubscript{R} range (KGJ309 vs. KGJ350). While, if keep the siloxane arm for the same length, longer “free chain” gives lower isotropic temperature and slightly wider SmAP\textsubscript{R} range (KGJ350 vs. KGJ344).

3.3.2 Results

(1) Texture observation

From the fan shape texture in the planar cells, it is easy to identify the SmA type property below the isotropic phase. The extinct direction of focal conics is parallel to the polarizers. Vertical electric field can easily switch the polar phase, while only birefringence change could be recorded in the homogeneous texture (Fig.3.18(a) and (b)).
Figure 3.18 Homogeneous textures in a 5.2 µm cell (a) at field off state and (b) under 12 V_{pp}/µm vertical electric field at 120°C. Homeotropic textures in a 30-µm-thick Cr-electrode cell (c) at field off state and (d) under 10 V_{pp}/µm in-plane electric field. The width of electrodes and the gaps between electrodes is 10µm.

To observe the in-plane switching of the SmAP_{R} phase, homeotropic cell with comb-shape chromium electrode was used. In the absence of an electric field, a uniform dark image was seen from the isotropic to SmAP_{R} phase, indicating the uniaxiality. Some minute defects confirmed the Iso-Sm transition. While under 10 V_{pp}/µm in-plane electric field, brightness was observed between Cr electrodes. That’s because the molecules are reoriented by the external field and birefringence is induced through Langevin process, which is the same as in other SmAP_{R} compounds [3-10-12].

(2) Switching Current and SHG

The reverse response current recorded under triangular wave field is given Fig.3.19. The single wide peak which is characteristic of the random polarized orthogonal SmAP_{R} is recorded in this series of compounds without any doubt. The spontaneous polarization (P\_s) calculated from intergrading the switching current peak is
~380nC/cm² and this is near the typical value for other SmAPR mesogens.

Figure 3.19 Polarization reverse current of KGJ 344 at 118 °C in the SmAPR phase. The applied field is 100 Vpp, 6Hz triangular wave and the cell thickness is 5.5 µm.

The development of polarization as a function of temperature is examined by second-harmonic generation under an electric field. Since all three liquid crystal phases do not show macroscopic polarization, no SHG signal emerged under field-off state. By applying rectangular wave field to homogeneous cells, field induced polarization was recorded both in heating and cooling process. It is seen that with reducing temperature, SHG signal gradually raised and achieve a maximum value at the phase transition point. The behavior in the SmAPR phase is due to the gradually increase of coherent length of molecular cooperative orientation with reducing temperature. While, when temperature exceeded the phase transition, SHG signal suddenly dropped to zero indicating that the columnar phase under SmAPR phase is unable to response to field. As the matter of fact, in the aligned sample, this series of material showed B1-like phase which is confirmed by X-ray diffraction.
3. SmAP$_R$ Phase

![Figure 3.20](image)

**Figure 3.20** SHG result of KGJ344 under 80 $V_{pp}$ rectangular wave field. 5.0-$\mu$m-thick planer cell was used.

3) X-ray diffraction results

To understand the steric effect of siloxane bulky groups and to identify the orientation structure of each mesophases, x-ray is an indispensable method. The x-ray beam was irradiated parallel to the substrate surface and the sample was aligned in homeotropic geometry. The high number harmonics of the diffraction peaks along the meridian line implies the well defined layer structures of the SmAP$_R$ phase. The diffused signal of wide angle scattering appeared along the equatorial line indicated the non-tilted liquid like order within layers. (Slight up/down asymmetry of the 2D pattern is due to the shadow of the sample heating stage.)

It should also be mentioned that in the wide angle signal range, in fact there are two peaks partially overlapping each other. One wider peak corresponding to $d_2=4.6\text{Å}$ represents the mean distance between bent cores of LC molecules. While, the other smaller peak with relevant length $d_1=7.5\text{Å}$ signifies the distance between the siloxane bulky terminals. Another interesting phenomenon is that in the small angle region, the 2$^{\text{nd}}$ order reflection is weaker than the 3$^{\text{rd}}$ order harmonic which is opposite to all the reported SmAP$_R$ phase materials and also distinct from the siloxane/carbosaline modified bent-core liquid crystals.[21-24]
Figure 3.21 2D x-ray pattern of KGJ350 and the relevant intensity as a function of 2θ angle obtained from integration over azimuthal angle at 120°C.

4) Layer stabilization

It is mentioned in chapter 2 that the in-plane cells which have electrodes printed on one substrate would lead to bending of electric field (Fig. 2.3). In the investigation of siloxane compounds, by accident we found that compare to the original SmAP$_{R}$ materials with two flexible alkyl chain terminal, siloxane SmAP$_{R}$ compounds have much better stablized layers. Figure 3.22 gives the in-plane switching of original material K2315 and the siloxane compound KGJ350, respectively.
Figure 3.22 Homeotropic textures of in-plane switching: compound K2315 at 129 °C (a) under 180 V field and (b) at field-off stage; Compound KGJ350 at 110 °C (c) under 180 V and (d) at field off stage. Both cells are of the same condition: 10 µm thick, homeotropic alignment SE1211, rectangular wave field 10 Hz.

By comparing the Fig. 3.22 (a) and (c) under electric field, we noticed that in both of the two materials, field induced biaxiality occurred. It is also obviously seen that the layer deformed seriously by the bending electric field in the K2315 cell (significant bright lines at the boundary of electrodes), as shown in Fig. 3.22(a). The deformed layers could recovered slowly when the electric field is removed (Fig. 3.22(b)). By contrast, the cell of siloxane compound performs much better: no matter the external electric field is on or off, the boundary of electrodes is immaculate indicating that the layers in this material are stabilized even if under bent field.
Figure 3.23 In-plane switching of KGJ350 at 108 °C under 10 Hz rectangular wave field. (a) Before applying electric field; under (b) 20 V, (c) 60 V and (d) 100 V in-plane electric field. Electrode width is 4µm and gap between electrodes is 4 µm, too. Cell thickness is 10 µm.

In order to better illustrate the layer stabilization effect, we also used the narrow gap Cr cells which given severe bending of electric field (Fig. 2.3(c)) to confirm the behavior of compound KGJ350. By cooling down from isotropic phase slowly, uniform homoepotropic alignment was obtained in spite of several tiny defects. It should be explained that in Fig. 3.23(a) before turning on field the minor brightness along electrodes comes from the reflection and scattering light of Cr electrodes. By gradually increasing external field, the increasing of field induced biaxiality (brightness of the gaps between electrodes) is observed (Fig. 3.22 (b) to (d)). Even when the field reached 100V (~25 Vpp/µm), the boundaries of electrodes are still neat for both under and removal of electric field.

3.3.3 Discussion

Through a sequence of experimental examine, we are aware of the performance of this interesting series of siloxane compounds. Now we can consider the molecular organization of such system.

(1) Existence of Siloxane Sublayers
From the X-ray diffraction pattern it was found that in contrast to the original SmAP<sub>R</sub> compound K2315, in the siloxane materials diffuse signal of wide angle region contents two maxima corresponding to the mean distance between siloxane bulky (d<sub>1</sub>) and bent central units (d<sub>2</sub>), respectively (Fig. 3.24). This is the clear evidence that the spherical terminal bulks are self-assembled into sublayers and give a periodicity of d<sub>1</sub>=7.5 Å.

Considering the calculated length of KGJ350 molecule of all-tran conformation L=53.7Å which is much shorter than the measured layer spacing d=59.0–61.1Å, it is reasonable to believe that the bent part of molecules are intercalated in the center of each layer and the rigid siloxane tail are segregated at the cross section of adjacent layers into sublayer structure, as shown in Fig. 3.24(c).

(2) Layer Stabilizing Effect
The in-plane switching of homeotropic cells already revealed that the introducing of single siloxane terminal can help to protect the layered structure of smectic phase (Figs. 3.22 and 3.23).

**Figure 3.25** High resolution x-ray diffraction results of 1st order reflection (a) K2315 and (b) KGJ 350 under in-plane electric field. Free surface cell with 10-µm-electrode and 10-µm-gap coated with polyimide SE1211 was used in this experiment. Molecular model of (c), (d) K2315 at field off/on state; (e), (f) KGJ350 at field off/on state, respectively.

How the molecules response to field and what kind role the bulky parts have played in such procedure have to be clarified. With the supporting of high resolution X-ray diffraction results, we are able to monitor the field induced reorientation in both
the original compound K2315 and the siloxane SmAP\textsubscript{R} material KGJ350. For compound K2315 which exhibits the traditional SmAP\textsubscript{R} phase, by gradually increasing field from 0 V to 80 V, the signal intensity reduced to half of the field off state and the layer thickness also decreased from 49.36 Å (at 0 V) to 49.14 Å (at 80 V), as shown in Fig. 3.25(a). Such tendency is just a reverse of the phenomena reported by Ortega et al in the dark conglomerate phase [25]. As a result it is reasonable to assume that in the SmAP\textsubscript{R} phase, before applying an electric field, the polar domains are randomly distributed in the system showing uniform homeotropic alignment (Fig. 3.25(c)). When in-plane electric field is applied to the sample, the field direction is bent because of the geometry of the cell (as explained in chapter 2). Therefore, two effects occurred simultaneously: (i) the polar molecules rotate to the field direction and (ii) the layers bent with the curved electric field, as demonstrated in Fig. 3.25(d).

On the other hand, the siloxane materials have rather rigid layers (Fig. 3.25(e)). Before applying electric field, the local dipole moments can point to any direction and a uniaxial phase appeared. However, when the electric field is turned on, the banana shaped polar center switched with an electric field, but the siloxane sublayers act as backbone and holding the layers to maintain straight even though the external field is crooked (Fig. 3.25(f)). This model is supported both by the X-ray 2\textdegree scan of KGJ350 under electric field (layer spacing sustains exactly the same at field on/off state) and the electro-optical study (neat boundary of in-plane switching) as shown in Fig. 3.25(b) and Fig. 3.23, respectively.

3.3.4 Summary

In this part of work, we characterized a new series of bent-shaped liquid crystals which were derived from the methylbenzene core SmAP\textsubscript{R} compounds by introducing a sphere siloxane bulky group into one flexible terminal. The temperature range of the SmAP\textsubscript{R} phase is considerably expended to as wide as \(\sim 40 \, ^\circ\text{C}\) and two columnar phases were observed below the smectic phase.
Through X-ray diffraction, the sublayers structure generated by self-segregation of siloxane bulks is identified. By POM observation, EO study and SHG measurement, the ferroelectric-like behavior of the SmAP$_R$ phase is confirmed. Moreover, the stiff siloxane sublayers can perform as backbone to stabilize the smectic structure and prevent layer deformation even under bending/strong external electric field. Possible molecular models are given for both conventional methylbenzene SmAP$_R$ compound and the siloxane materials. The models are supported both by high resolution x-ray diffraction and EO study.

3.4 Conclusions

In this chapter, I reported a numerous SmAP$_R$ compounds belonging to distinct series which were obtained by various modification of the original molecule.

In the methylbenzene core compounds, it is found that too short alkyl terminal tails can lead to missing of smectic phase and only the B$_1$-type phase which is composed of 2D fragments were observed. Introducing the unsaturated chain into both bent arms can also result in the disappearance of the SmAP$_R$ phase. Minor decrease of isotopic temperature was recorded in materials with only one unsaturated arm (for example, KGJ29). But the wider range of the SmAP$_R$ phase was not observed as expected. By mixing two methylbenzene core compounds, the temperature range of the SmAP$_R$ phase could be expanded.

If the central core is replaced by acetophenone which gives larger steric effect than methylbenzene core, the mesogens will show the transition from the uniaxial orthogonal phase with local polar order (SmAP$_R$) to the antiferroelectric non-tilted smectic phase (SmAP$_A$). Much wider temperature range ($\Delta T \sim 40^\circ C$) of the target phase SmAP$_R$ is also realized by replacing the central unit. Through x-ray diffraction, dielectric and electro-optic, it is regarded that the transition is continuous or weakly
first order, which is allowed for phases of different symmetry (D_{∞v} for SmAP_{R} and D_{2h} for SmAP_{A}, respectively). The correlation length of polar order in the SmAP_{R} phase gradually increases as well as antiferroelectric interlayer correlations. The interlayer polar coupling is weak as indicated by a low value of relaxation frequency of a ferroelectric mode at the phase transition.

Another interesting modification is to introduce spherical siloxane bulky groups into one bent terminal or the original SmAP_{R} compound with methylbenzene center. The SmAP_{R} phase range is expanded as it was anticipated. X-ray diffraction proved the existence of sublayers structure generated by self-segregation of siloxane bulks. By POM observation, EO study and SHG measurement, the ferroelectric-like behavior of the SmAP_{R} phase is confirmed. Moreover, the stiff siloxane sublayers can perform as backbone to stabilize the smectic structure and prevent layer deformation even under bending/strong external electric field. Possible molecular models are given for both for free tail methylbenzene compound and the siloxane materials.
References of chapter 3


"Paraelectric-Antiferroelectric Phase Transition in Achiral Liquid Crystals"

"An Optically Uniaxial Antiferroelectric Smectic Phase in Asymmetrical Bent-Core Compounds Containing a 3-Aminophenol Central Unit"

"Dimorphism Sma-B2 in Bent-Core Mesogens with Perfluorinated Terminal Chains"

"Paraelectric-Antiferroelectric Transitions in the Bent-Core Liquid-Crystalline Materials"

"Development of Polar Order in Liquid Crystalline Phases of a Banana Compound with a Unique Sequence of Three Orthogonal Phases"

"Bent-Core Liquid Crystals: Polar Order, Superstructural Chirality and Spontaneous Desymmetrisation in Soft Matter Systems"

"Bent-Core Mesogens with Branched Carbosilane Termini: Flipping Suprastructural Chirality without Reversing Polarity"

"Banana-Shaped Liquid Crystals with Two Oligosiloxane End-Groups: Field-Induced Switching of Supramolecular Chirality"

"First Example of a Third-Generation Liquid-Crystalline Carbosilane Dendrimer with Peripheral Bent-Core Mesogenic Units: Understanding of “Dark Conglomerate Phases”"

"The Influence of Shape and Size of Silyl Units on the Properties of Bent-Core Liquid Crystals—from Dimers Via Oligomers and Dendrimers to Polymers"

"Structural Investigation of Carbosilane Liquid Crystalline Dendrimers"
[23] Christina Keith, R. Amaranatha Reddy, Anton Hauser, Ute Baumeister and Carsten

"Silicon-Containing Polyphilic Bent-Core Molecules: The Importance of Nanosegregation for the Development of Chirality and Polar Order in Liquid Crystalline Phases Formed by Achiral Molecules"


"The Carbosilane Unit as a Stable Building Block for Liquid Crystal Design: A New Class of Ferroelectric Switching Banana-Shaped Mesogens"


"Electric-Field-Induced Phase Transitions in Bent-Core Mesogens Determined by X-Ray Diffraction"
Chapter 4

Polar Switching in SmA\textsubscript{d}P\textsubscript{A} phase

In chapter 3, several series of LC compounds showing uniaxial SmA phase with randomly distributed local polar domains are described. In contrast to those materials, a new compound which has only one flexible terminal chain connected to the bent central and performs a biaxial orthogonal phase is investigated in this chapter. The interesting behavior as well as possible molecular organization is presented in the following part.

4.1 Background and Studied Compound

Wirth et al first predicted the existence of the biaxial and orthogonal smectic theoretically [1]. The first biaxial smectic A phase with experimental proofs was observed in a mixture of liquid crystalline side chain polymer and a monomeric compound [2]. Adequate evidence for the existence of a biaxial smectic A phase in a binary mixture of low molecular mass compounds has been published by Pratibha et al [3]. Sufficient experimental proof for a biaxial SmA phase showing antiferroelectric characteristics has been provided by Eremin et al [4].

In this chapter, an unsymmetric bent-core compound which has a strong dipole CN group instead of alkyl chain connected to one arm of the central unit. The molecular structure and phase sequence is given as follow.

\[
\begin{align*}
\text{Heating:} & \quad \text{Cr-134.8°C-SmA\textsubscript{d}P\textsubscript{A}-149.0°C-SmA\textsubscript{d}-150.2°C-Iso} \\
\text{Cooling:} & \quad \text{Iso-149.5°C-SmA\textsubscript{d}-148.3°C-SmA\textsubscript{d}P\textsubscript{A}-112.6°C-Cr}
\end{align*}
\]
4.2 Electro-optical Study

4.2.1 Texture Observation

The fundamental identification based on texture observation is done with both homeotropic and planar samples. First, I would like to show the homeotropic texture changes upon in-plane electric field applied in the SmA$_d$P$_A$ phase under crossed polarizers. In homeotropically aligned cells, a schlieren texture with both 4- and 2-brush defects were observed (Fig. 4.2(a)). An in-plane electric field was applied across a gap of 50 µm, where the electric field was 45° to crossed polarizers, and the temperature was fixed at 138 °C. By applying a rectangular electric field, the texture changed (Fig. 4.2(b) and (c)), and became uniformly bright (Fig. 4.2(d)) even under very low voltage below 1 V/µm. During the whole process, no threshold could be observed.

![Homeotropic texture of NCB-C18 observed in a 5.6-µm-thick cell at 138 °C under various in-plane DC fields.](image)

When we decrossed the polarizers and checked the homeotropic texture carefully, the brightness of some area interchanged under uncrossing polarizers which indicates the existence of chiral domains. The interesting point is that in this material under crossed polarizers, both dark and bright areas present in the texture (Fig. 4.3(b)). Domains of opposite
optical rotation existed only in the dark parts and they can be clearly observed in Fig.4.3 (a) and (c) by decrossing polarizer and analyzer by +10 deg. and -10 deg., respectively. Beside the dark parts (chiral domains), the bright areas show no significant change under uncrossed polarizers and such domains are regarded as racemic domains.

**Figure 4.3** Chiral domains recorded in the homeotropic cell of NCB-C18 under decrossed polarizers. (a) Decrossed by +10 deg.; (b) Crossed polarizers; (c) decrossed by -10 deg.

Homogeneously aligned sample shows a fan-shaped texture. A few stripes existed in the absence of a field (Fig. 4.4(a)), and could be gradually suppressed by applying a weak field (Fig. 4.4(b) and (c)). Obvious birefringence change was followed under higher field like 4.5 V/µm as shown in Fig. 4.4(d). We found that birefringence color change was continuous, and the overall textural change was reversible. We also conducted X-ray diffraction experiments under an electric field and no noticeable change in the layer spacing was observed, indicating that the antiferroelectric to ferroelectric transition occurs keeping the layer spacing unchanged.
4.2.2 Switching Current and Spontaneous Polarization

The polarization reversal current was measured at various temperatures to clarify the switching behavior. The applied field was a triangular wave voltage of 120 V$_{pp}$ with frequency of 9 Hz. At 138.9 °C, multiple switching current peaks was detected, as exposed in Fig. 4.5 (a). Similar phenomena have been observed in SmCP phase by other authors.[5-6] Since a small switching current peak was observable even in the isotropic phase near the position of the shoulder to the sharp peak, we suspect that there is also a contribution of ionic current. The remaining two peaks indicate that the ground state structure of the mesophase is antiferroelectric.

**Figure 4.4** Homogeneous texture of NCB-C18 in a 12.8-µm-thick cell at 145 °C under various vertical DC fields.

**Figure 4.5** (a) Switching current in the SmA$_d$P$_A$ phase by applying a triangular wave voltage of 120 V$_{pp}$ and with the frequency of 9 Hz at 138 °C. (b) Spontaneous polarization ($P_s$) as a function of temperature. Cell thickness is 4.8 µm.
The variation of spontaneous polarization ($P_s$) as a function of temperature is shown in Fig. 4.5(b). The $P_s$ value increases rapidly from around 30 nC/cm$^2$ to around 260 nC/cm$^2$ after the transition to the polar phase and drops sharply to zero at crystallization. The temperature dependence of $P_s$ is similar to the typical SmC$^*$ liquid crystals except near the crystallization temperature.

### 4.3 Nonlinear Optics

We measured SHG to track the polarization development of this liquid crystal compound. Here SHG results as a function of temperature and electric field are given. In the absence of an electric field, no SHG signal was observed in the whole temperature range, implying that this phase has no macroscopic polar domains. On the other hand, by applying a rectangular wave field to planar cells, comparatively strong SH signal was detected in the SmA$_d$P$_A$ phase both in heating and cooling runs. This phenomenon is evidence that the polarization in the SmA$_d$P$_A$ phase is induced by an external field. Fig 4.6(a) shows the temperature dependence of the SHG signal under a rectangular wave voltage of 80 V$_{pp}$. In the cooling process, the SHG signal emerged quickly from zero and showed a maximum value when the transition to SmA$_d$P$_A$ occurred. Then the signal gradually decreased with reducing temperature. The insignificant decrease could be explained by the increase of scattering caused by rigid boundaries of local domains on cooling. At 113 °C, the SHG intensity drops to zero upon crystallization. Similar tendency was also observed in the heating procedure.
Figure 4.6 (a) SHG intensity as a function of temperature in both cooling (squares) and heating (open circles) runs in a homogeneous sample under an applied rectangular voltage of 80 V$_{pp}$ and at a frequency of 10 Hz. (b) SHG intensity as a function of applied voltage at 140 °C. Cell thickness is 8.9 µm.

The electric field dependent SHG signal is shown in Fig. 4.6 (b). The measurement was carried out at 140 °C in a cooling process in an 8.9µm homogeneous cell. SHG signal gradually increased with increasing field, and saturated above 120 V$_{pp}$. It is noticed that no distinct threshold voltage was observed in the SHG intensity change, which is in consist with the low energy barrier between the grand state and the field induced FE state.

4.4 Dielectric Permittivity

We also measured the dielectric permittivity as a function of frequency from 1 Hz to 1 MHz at various temperatures to investigate the cooperative movement of LC molecules. It is noticed that in the isotropic phase (T-T$_{t_{SmAdP\alpha}}$= +1) only one low frequency ionic relaxation is observed near 20 Hz. In the SmAdP$\alpha$ phase another relaxation near 100 kHz emerges and it is temperature dependent. In order to confirm that the low frequency relaxation is due to the ionic relaxation, we increased the DC bias voltage up to 40 V and found that the low frequency dielectric constant reduced and the ionic relaxation could be suppressed almost completely as the ions were swept away from the bulk under DC bias field as seen in Fig. 4.7(c). On the contrary, another relaxation at about 100 kHz rather increased with increasing bias voltage.
4. SmA$_d$P$_A$ phase

Figure 4.8. Dielectric permittivity in the SmA$_d$P$_A$ phase. (a) Real part $\varepsilon'$ and (b) imaginary part $\varepsilon''$ as functions of frequency at various relative temperatures ($T - T_{SmA}$). (c) Effect of DC bias field on the dielectric constant in isotropic phase. Cell thickness is 12.8 $\mu$m.

The Cole-Cole plot of real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the dielectric constants at a temperature of 138 °C is shown in Fig. 4.9. As it is mentioned that the low frequency dielectric relaxation is due to the ion, we used data from 100 Hz to 1MHz to describe the dielectric relaxation. Single semicircular arc clearly suggests that there is only one relaxation and further it is Debye type as the data is well fitted with the Debye equation. Thus we use Debye equation to analyze the frequency dependent dielectric data at various temperatures and DC bias fields.
The dielectric strength and the dielectric relaxation time were obtained as fit parameters. The variation of the dielectric strength ($\Delta \varepsilon$) as a function of temperature is shown in Fig. 4.10 (a). It is seen that the dielectric strength increases rapidly from 4 in the isotropic phase and attain a maximum at the Sm$A_d$P$_A$ to Sm$A_d$ transition. The value of $\Delta \varepsilon$ decreases slightly as the temperature is lightly lowered due to the gradually increase of viscosity in cooling process. From Fig. 4.10(b) we can see that the relaxation time ($\tau$) also rapidly increases from ~0.6 $\mu$s to 1.3 $\mu$s at the Sm$A_d$-Sm$A_d$P$_A$ phase transition. Such rapid increase of $\tau$ in Sm$A_d$P$_A$ is due to the rapid growth of polar order. The average polarization direction is along the bending direction and is parallel to the layer. In the Sm$A_d$P$_A$ phase, relaxation time is almost independent of temperature.

**Figure 4.9** A single semicircular arc shape Cole-Cole plot of the dielectric permittivity of NCB-C18 at 138 °C in the Sm$A_d$P$_A$ phase.

**Figure 4.10** Variation of (a) dielectric strength $\Delta \varepsilon$; (b) relaxation time $\tau$ as a function of
The relaxation at about 100 kHz is attributed to that of the molecular motion associated with this polarization response. Figure 7 shows the effect of DC bias field on this relaxation mode. It is discerned that relaxation strength and relaxation time are almost constant up to 1.2 V/µm. When the voltage continues to raise, both of them increase continuously with the increasing electric field.

![Graph showing relaxation time and dielectric strength as a function of DC bias field.](image)

**Figure 4.11** Variation of relaxation time $\tau$ (squares) and the dielectric strength $\Delta \varepsilon$ (open circles) as a function of DC bias field.

The DC bias effect can be explained as follow: by applying a DC field, macroscopic polarization emerges by distorting the antiferroelectric structure to the ferroelectric one, so that the dielectric strength increases. Similar phenomenon has been observed in the antiferroelectric smectic C* (SmC$_A^*$).

### 4.5 Discussion

Based on X-ray, EO, SHG and dielectric studies, we can consider a possible model of this antiferroelectric SmA phase. From X-ray analysis data; i.e., the calculated individual molecular length $L$ is 46.4 Å, while the layer thickness experimentally obtained is $d=54.5$ Å,
suggesting an interdigitated structure. This suggests a partially interdigitated structure which was proposed by Sadashiva et al [7-8]. Although there might be two type of molecular packing: (a) only one arm of bent-centrals are intercalated and (b) the whole bent-core are interdigited (as shown in Fig 4.12(a) and (b), respectively). In this material only case (b) is reasonable.

![Molecule coupling model](image)

**Figure 4.12** Molecule coupling model of (a) one arm of bent-centrals intercalated and (b) whole bent-core are interdigited. (c) Simple model of the field-induced antiferroelectric-ferroelectric transition.

The electronic response model is shown in Fig. 4.12(c). In the absence of a field, the bent core of molecules is parallel to substrate surfaces because of an electrostatic interaction between molecules and surfaces and packing entropy effect (middle of Fig. 4.12(c)). In this arrangement, the polarization component along the layer normal is totally cancelled [9], whereas macroscopic layer polarization emerges parallel to the layer. Because of the antiferroelectric orientation, this layer polarization is also cancelled between adjacent layers, so that no macroscopic polarization can be detected without applying an electric field, being consistent to SHG non-activity. However, when an external field is applied on the sample, the
layer polarization reorients toward the field direction, as shown in the Fig. 4.12(c), i.e., the paired molecules rotate about their molecular long axis or the layer normal. It is clear that the birefringence increases by applying an external field, being consistent to the texture change shown in Fig. 4.2 and Fig. 4.4.

Usually field-induced antiferroelectric-ferroelectric transition is associated with threshold behavior both in classical SmC\textsubscript{A}* [10] and bent-core B\textsubscript{2} [11] phases. In the present case, however, all the measurements indicate thresholdless behavior. One of the possible ideas is the existence of helical structure. Fig. 4.3 shows textures of homeotropically aligned cells under decrossed polarizers. The brightness of some areas interchanged by slightly rotating an analyzer clockwise or counterclockwise, indicating the existence of chiral domains. The phenomenon is similar to the spontaneous chiral domain formation observed in the B\textsubscript{4} [12] and dark conglomerate [13] phases. However, this sample is quite different from those showing such phases. Moreover, the observed phenomenon is slightly different: Besides the chiral domains, which show brightness change in oppositely decrossed polarizers, there exist bright areas, which show no significant change under uncrossed polarizers.

In this nontilted (orthogonal) SmA\textsubscript{d}P\textsubscript{A} phase, the molecular long axis is parallel to the layer normal and the polar direction lies in the layer planes. Hence, there are two two-fold rotation axes along the polar (bending) direction and perpendicular to it at the layer boundaries. In addition bending plane is a mirror plane, so that the local symmetry of the SmA\textsubscript{d}P\textsubscript{A} phase is D\textsubscript{2h}. For the SmA\textsubscript{d}P\textsubscript{A} phase to be chiral, a helical structure is quite possible to be formed. Therefore, three domains, two chiral and one nonchiral, are attributed to right- and left-handed helix and nonhelical domains, respectively. By applying an electric field, helix unwinding and antiferroelectric to ferroelectric deformation take place at the same time. This may be the reason why the threshold of the field-induced antiferroelectric-ferroelectric is not so distinct. Further studies would be necessary to clarify the helical structure.

4.6 Conclusion

In this chapter, an asymmetric bent-core liquid crystal exhibiting SmA\textsubscript{d}P\textsubscript{A} phase is characterized by means of polarizing optical microscopy, SHG, EO, X-ray, and dielectric
measurements. The SmA$_d$P$_A$ phase is SHG active only under electric field and a characteristic dielectric relaxation appears at about 100 kHz attributed to the rotation of the molecules about the long axis. The DC field enhances this dielectric relaxation, suggesting the polar order nucleated by the DC bias effect. The field-induced antiferroelectric to ferroelectric (SmA$_d$P$_A$–SmA$_d$P$_F$) transition occurs continuously without a distinct threshold. Two possible models are suggested to interpret this continuous transition, i.e., very low barrier between the two phases and the existence of helical structure. Both ideas are supported by the present experiments.
References of Chapter 4


"New Variants of Polymorphism in Banana-Shaped Mesogens with Cyano-Substituted Central Core"


"Optical Investigations on a Liquid-Crystalline Side-Chain Polymer with Biaxial Nematic and Biaxial Smectic-a Phase"


"An Orientational Transition of Bent-Core Molecules in an Anisotropic Matrix"


"Experimental Evidence for an Achiral Orthogonal Biaxial Smectic Phase without in-Plane Order Exhibiting Antiferroelectric Switching Behavior"


"Continuous Transition from Antiferroelectric to Ferroelectric Switching Liquid Crystalline Phases in Two Homologous Series of Bent-Core Mesogenic Dimers Based on Carbosilane Spacer Units"


"Switching of Banana Liquid Crystal Mesophases under Field"


"Biaxial Smectic a Phase in Homologous Series of Compounds Composed of Highly Polar Unsymmetrically Substituted Bent-Core Molecules"
4. SmA$_d$P$_A$ phase


"A Polar Biaxial Smectic a Phase in New Unsymmetrical Compounds Composed of Bent-Core Molecules"


"Tristable Switching in Surface Stabilized Ferroelectric Liquid Crystals with a Large Spontaneous Polarization"


"Important Role Played by Interlayer Steric Interactions for the Emergence of the Ferroelectric Phase in Bent-Core Mesogens"


"Study on Helical Structure of the B4 Phase Formed from Achiral Banana-Shaped Molecule"


"Low-Birefringent, Chiral Banana Phase Below Calamitic Nematic and/or Smectic C Phases in Oxadiazole Derivatives"
In chapter 3 and 4, the uniaxial SmAP phase and the antiferroelectric SmA,P_A have been presented. It should be mentioned that sometimes only slight variation of molecular construction will lead to significant change of phase behavior. In this chapter, I would like to present a new series of material which have hydrogen bonding (H-bonding) in the system and gives antiferroelectric behavior. What’s more, it is also a uniaxial phase in the absence of electric field and shows AF property, which is for the first time observed.

5.1 Background

It is known that molecular interaction has essential effects on not only in appearance of mesophases but also in their thermal stability. Hydrogen bonding is one of the typical molecular interactions responsible for the organization of molecules. Hydrogen bonding, intermolecular as well as intramolecular, plays an important role in design and engineering of architecture of many rod-like, disc-like and polymeric materials [1-2]. However in the bent-shaped liquid crystals most of the mesogenic molecules possess only covalent bonds. The first bent core liquid crystals, containing non-covalent bonds, were described by T. Kato in 1992 [3]. Hydrogen bonding interactions in liquid crystals could be introduced in two general ways: by the introduction of appropriate functional groups, e.g. amide groups or a hydroxy group in ortho position to an azomethine group or through the complexation of two different components, in which one of them plays a role of H-donor (e.g., carboxylic acid) and the second one plays a role of H-acceptor (e.g., pyridine derivatives). Recently, a few reports were published, which described banana shape compounds possessing intra-
intermolecular hydrogen bonding. In these examples, intermolecular H-bonding is formed between H-atom of the hydroxyl group and the N-atom of the imine linkage [4]. Intermolecular H-bonding appeared in different combinations of stilbazole derivatives with carboxylic acids, which acted as H-acceptors and H-donors respectively [58].

Since the discovery of the SmAPR phase, several series of compounds with diverse structure have been synthesized. The molecule has two ester groups attached to the central unit 1,3-substituted phenyl ring with a methyl substitution as a central unit and a stilbene bridge as a main element in the structure. The molecules have an asymmetry, which arises in different lateral substituents and/or terminal alkoxy chain lengths. Some of them have one or both unsaturated chain(s). Recently we showed that even symmetric molecules, which have 1,3-dihydroxyacetophenone as a central unit and stilbene arms, can exhibit the SmAPR phase. However, no compounds, which are expected to have H-bonding, have been examined for stabilizing the SmAPR phase.

5.2 Hydrogen Bonding and Mesomorphic Properties

Two series of asymmetric bent-core compounds possessing 3-aminophenol and its N-methyl derivative as a central unit were synthesized, as shown in Table I. The synthesis procedure is reported in K.Gomola’s paper [9]. The liquid crystalline behavior of both series was investigated by polarizing optical microscopy (POM), differential scanning calorimetric (DSC), electro-optical studies, X-ray diffraction and SHG measurements. Transition temperatures and associated enthalpies obtained from DSC thermograms are shown in Table I, where SmAPAR stands for a new phase which has polar (P) antiferroelectric (sub A) SmA random (sub R) characteristics (see other experimental results later). Here random means that the paired bent directions (polar plane of antiferroelectric domain) have only a short-range order, but random in long range. For references Table I also includes previously obtained compounds possessing two ester groups attached to the central unit, 1,3-substituted phenyl ring.[10-11] The DSC thermograms of \textbf{N-H NO}_2\textbf{NO}_2 show three mesophases. Based on the microscope observation and X-ray measurement the high temperature phase was identified to
be a non-tilted smectic phase with polar order (SmAP\textsubscript{AR}), while both low-temperature phases were assigned to have columnar structure. The low temperature columnar phase remains even at room temperature. For asymmetric analogue N-H NO\textsubscript{2}Cl, when one nitro group was replaced by chlorine atom, the sequence of mesophases was retained. The compound N-H Cl\textsubscript{2}Cl, in which both nitro groups were replaced with chlorine atoms, gave unknown enantiotropically smectic phase. The reference compounds, COO NO\textsubscript{2}NO\textsubscript{2}, COO NO\textsubscript{2}Cl, and COO NO\textsubscript{2}Cl\textsubscript{2}, showed the conventional so-called banana phases but not SmAP\textsubscript{AR}, as shown in Table 5.1.

### Table 5.1. Transition temperatures (°C) and associated enthalphy values (in parentheses, kcal/mol) as determined by DSC at a scanning rate of 10 °C/min.

<table>
<thead>
<tr>
<th>Code</th>
<th>X</th>
<th>Y</th>
<th>L</th>
<th>Mesomorphic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-H NO\textsubscript{2}NO\textsubscript{2}</td>
<td>NO\textsubscript{2}</td>
<td>NO\textsubscript{2}</td>
<td>Col\textsubscript{2} 92.9[1.4]</td>
<td>Col\textsubscript{1} 185.8[1.5]</td>
</tr>
<tr>
<td>N-H NO\textsubscript{2}Cl</td>
<td>NO\textsubscript{2}</td>
<td>Cl</td>
<td>Col\textsubscript{2} 119.0[4.9]</td>
<td>Col\textsubscript{1} 185.9[1.2]</td>
</tr>
<tr>
<td>N-H Cl\textsubscript{2}Cl</td>
<td>Cl</td>
<td>Cl</td>
<td>Cry 152.9[27.4]</td>
<td>SmX 197.3[19.5]</td>
</tr>
<tr>
<td>N-CH\textsubscript{3} NO\textsubscript{2}NO\textsubscript{2}</td>
<td>NO\textsubscript{2}</td>
<td>NO\textsubscript{2}</td>
<td>Cry 74.9 [10.6]</td>
<td>Iso</td>
</tr>
<tr>
<td>N-CH\textsubscript{3} NO\textsubscript{2}Cl</td>
<td>NO\textsubscript{2}</td>
<td>Cl</td>
<td>Cry 70.8 [9.1]</td>
<td>Iso</td>
</tr>
<tr>
<td>COO NO\textsubscript{2}NO\textsubscript{2}\textsuperscript{a}</td>
<td>NO\textsubscript{2}</td>
<td>NO\textsubscript{2}</td>
<td>Cry 141.8[28.0]</td>
<td>B\textsubscript{1} 149.8[1.3]</td>
</tr>
<tr>
<td>COO NO\textsubscript{2}Cl\textsuperscript{a}</td>
<td>NO\textsubscript{2}</td>
<td>Cl</td>
<td>Cry 113.1[13.2]</td>
<td>B\textsubscript{1RT} 146.9[17.5]</td>
</tr>
<tr>
<td>COO Cl\textsubscript{2}Cl\textsuperscript{a}</td>
<td>Cl</td>
<td>Cl</td>
<td>Cry 116.4[18.9]</td>
<td>B\textsubscript{7} 144.4[18.2]</td>
</tr>
</tbody>
</table>

The introduction of an amide linkage led to the formation of a hydrogen bonding between molecules, which would stabilize columnar liquid-crystalline mesophases. In case of compounds in the second series N-CH\textsubscript{3} X,Y, where a hydrogen of amide was replaced by a methyl group, both materials lost liquid crystalline properties. These facts suggest the
importance of intermolecular hydrogen bonding. Hence we measured FT-IR spectra of $N-H \text{NO}_2\text{Cl}$ as a function of temperature. All materials of series $N-H X,Y$ showed a broad band in a range 3350-3331 cm$^{-1}$ at room temperature, which is characteristic of the hydrogen bond of the amide group (Fig. 1 (a)) [12]. The absorption of the amide I band (C=O) emerges in the region of 1654 cm$^{-1}$. The lower frequency (larger wavenumber) of a C=O stretching in IR spectra is explained by the existence of H-bonding [13]. The FT-IR absorption spectra for $N-H \text{NO}_2\text{Cl}$ at 100 (Col$_2$), 150 (Col$_1$), 200 (SmAP$_{AR}$) and 225 °C (Isotropic phase) around 3400 cm$^{-1}$ are shown in an inset of Fig. 1. In the Col$_2$ phase (100 °C) N-H peak was sharp and its intensity was also higher, suggesting stronger H-bonding comparing to that in other phases. The absorption peak wavelength of the N-H vibration shifted stepwise to higher wavenumbers at the phase transition temperature (Fig. 5.1(b)), indicating considerable decrease of H-bond interactions with increasing temperature. Decreased absorbance was also associated with this change. At 225 °C, in isotropic phase, the N-H vibration shows very low intensity and high wavenumber frequency. Moreover the wavenumber of the C=O vibration increased up to 1680 cm$^{-1}$. These facts suggest that the N-H groups are free from hydrogen bonding in the isotropic phase. We also excluded the formation of H-bonding between amide-ester groups, as the C=O vibration peak position of the ester group did not depend on temperature.

![Figure 5.1](image)

**Figure 5.1** (a) FT-IR spectroscopy of $N-H \text{NO}_2\text{Cl}$ in different phases. (b) N-H stretching
vibration in temperature-variable. Stepwise changes in the peak wavenumbers are clearly displayed between these phases.

We also carried out X-ray diffraction measurements in both unoriented and oriented samples, where the X-ray beam was incident almost parallel to a homeotropically aligned surface. In the SmAP\textsubscript{AR} phase, diffraction peaks due to smectic layer parallel to the substrate surface were observed along meridian line (not shown). Diffuse scattering appeared along the equatorial line, signifying the liquid-like non-tilted arrangement of molecules within each layer. The layer spacing continuously increased from 43.9Å to 45.4Å in the SmAP\textsubscript{AR} phase (Fig. 3(a)), which is characteristic of SmAP\textsubscript{R} [14].

![Figure 5.2](image)

**Figure 5.2** (a) Variation of layer spacing as a function of temperature. 2D X-ray diffraction pattern of (b) Col\textsubscript{1} (160 °C) and (c) Col\textsubscript{2} (80 °C) phases.

The significant drop of the layer spacing $d$ at 185 °C shows the first order transition from smectic to columnar phase. Figure 5.2 (b) and (c) shows wide angle two-dimensional X-ray diffraction patterns in the two distinct columnar phases. In a small angle region several sharp peaks were observed in the powder X-ray diffraction. Because the smallest and next smallest angle peaks do not correspond to the first and second order diffractions of the smectic layers, a two dimensional columnar frustrated layer structure could be identified. At 150 °C, the
5. SmAP\textsubscript{AR} phase

Lattice parameters of the Col\textsubscript{1} phase is as follows: \(a = 118.1\) Å, \(c = 49.96\) Å, and the angle between \(a\) and \(c\) is \(\beta = 113.4^\circ\). The Col\textsubscript{2} phase exhibited more highly defined diffractions along small angle region and less diffuse outer scattering with its maxima around the equator (Fig. 3c). The lattice parameters \(a = 112.8\) Å, \(c = 57.96\) Å, \(\beta = 124.2^\circ\) were obtained at 80 °C in the Col\textsubscript{2} phase. The x-ray pattern did not change even cooled down to room temperature.

5.3 Antiferroelectric behavior

In order to evidence the emergence of the SmAP\textsubscript{AR} phase, compound N-H NO\textsubscript{2}Cl was selected for various experiments.

5.3.1 Electro-optical Study

The textures at various temperatures in cells with distinct surface treatments are shown in Fig. 5.3. On cooling from the isotropic phase, typical fan-shaped textures in planar cells appeared (Fig. 5.3 (a)). By applying an electric field, only slight birefringence change could be seen with an extinction direction remains the same, indicating the non-tilted (SmA) character of this phase. When the phase transition occurred to Col\textsubscript{1}, the focal conic texture was broken by small fragments, indicating the breaking of layer structure (Fig. 5.3 (b)). When temperature was reduced further, the transition to another columnar phase can be observed under a microscope (Fig. 5.3 (c)). In a homeotropically aligned sample, a uniform dark image (Fig. 5.3 (d)) was observed in the highest mesophase, indicating unaxial phase, being consistent to the SmAP\textsubscript{AR} phase. By contrast, typical mosaic textures with lower and higher birefringence were observed in the Col\textsubscript{1} and Col\textsubscript{2} phases (Fig. 5.3 (e) and (f)).
Polarization reversal current was measured in a 5.2-µm-thick homogeneous cell to identify the polar structure of the SmAP\textsubscript{AR} phase. Interestingly, two split switching current peaks were recorded in compound N-H NO\textsubscript{2},Cl at 189 °C, as shown in Fig. 5.4(a), indicating an antiferroelectric behavior. With gradually decreasing temperature, the first peak moved forward to the second peak, and the two peaks became an overlapped single wide peak at 187 °C (Fig. 5.4 (b)).
Figure 5.4 Switching current in the SmAP$_{AR}$ phase recorded at relative temperatures (a) 4 °C and (b) 2 °C above the Sm-Col phase transition. The applied electric field was 95 V$_{pp}$ triangular wave and the cell was 5.2-µm thick.

5.3.2 SHG Results

To examine the field-induced polarization, the field dependence of SH signal in the SmAP$_{AR}$ phase was also measured. The measurement was carried out at 4 °C above the Sm-Col transition in a cooling process by applying a rectangular wave voltage to a 4.7-µm-thick cell. The result shown in Fig. 5.5 (b) is quite different from that in SmAP$_R$; i.e., the SH signal started to increase with a threshold around 40 V$_{pp}$ and saturated above 70 V$_{pp}$, whereas thresholdless increase describable by Langevin process was observed in SmAP$_R[15]$. This is the prime difference between the SmAP$_R$ and SmAP$_{AR}$ phases. In addition, the temporal change of the SH signal intensity under a triangular wave field (90V$_{pp}$) shows a hysteresis behavior; i.e., the onset and termination of the SH signal occurred at different voltages (or phases), as shown in Fig. 5.5 (c). The hysteresis and associated tristable switching behavior obtained are consistent to the two switching current peaks and also strongly indicate the antiferroelectric behavior.
5.4 Discussion

The tristable switching has ever been reported even in the ferroelectric liquid crystals by Itoh. et al [16] in addition to a conventional antiferroelectric liquid crystals. In this case, the helical state was strongly stabilized because of its ultrashort pitch, so that the tristable switching was observed. To consider the molecular orientational structure in the SmAP\textsubscript{AR} phase, we should take into account five experimental facts: (1) Orthogonal smectic phase, (2)
antiferroelectric (tristable) switching behavior, (3) existence of threshold for the field-induced transition, (4) optical uniaxiality, and (5) no helical structure. The most plausible model satisfying these conditions is the SmAP$_{AR}$ phase; i.e., local SmAP$_A$ structure for (1)-(3) and randomized polar plane for (4) and (5). We are continuing further experiments to definitely confirm the molecule level arrangement and the dynamic switching process.

![Molecular model of (a)SmAP$_R$ phase and (b)SmAP$_{AR}$ phase.](image)

**Figure 5.6** Molecular model of (a)SmAP$_R$ phase and (b)SmAP$_{AR}$ phase.

Finally we have to note the novelty of the SmAP$_{AR}$ phase. It is physically natural that a short-range order develops to a larger scale without a threshold, as in the case of the SmAP$_R$ phase, where a polar order develops without a threshold due to Langevin process (Fig.5.6 (a)). By contrast, in SmAP$_{AR}$, randomly ordered short-range antiferroelectric domains first gradually change their polar planes to the electric field without a threshold, establishing macroscopic antiferroelectric order without showing macroscopic polarization, as shown in Fig. 5.6(b).

However, the detection is not easy because of the following reasons: (1) This development appears as only a slight birefringence change; (2) At a certain electric field, field-induced antiferroelectric-ferroelectric phase transition occurs. This type of field-induced transition usually occurs with a distinct threshold. This is true in chiral smectic [17] and bent-core liquid crystals [18], and also in the present case. The SmAP$_{AR}$ phase is unique since this is not only
the new phase with a short-range order but also the phase showing a field-induced transition with a distinct threshold, as mentioned above.

5.5 Conclusions

The mesomorphic properties of asymmetric bent-core compounds possessing 3-aminophenol and N-methyl-3-aminophenol as a central unit are reported in this chapter. FT-IR spectroscopy confirmed the existence of hydrogen bonds between amide-amide groups of neighboring molecules. The extensive H-bonding induced liquid crystalline and enhanced the phase stability and also induced a novel smectic phase SmAP_{AR}. Based on various experiments such as SHG and switching current measurements, it is confirmed that the SmAP_{AR} phase has a polar-plane-randomized antiferroelectric structure. Proper molecular model and the difference between SmAP_{R} and SmAP_{AR} are given according to a variety of experimental results.
References of Chapter 5

"Thermotropic Liquid Crystals Formed by Intermolecular Hydrogen Bonding Interactions"

"Self-Assembly of Liquid Crystalline Complexes Having Angular Structures through Intermolecular Hydrogen Bonding"

"Nonsymmetrical Five-Ring Achiral Banana-Shaped Liquid Crystals Comprising Salicylaldimine Mesogenic Segment "

"Self-Assembled Bent-Core Side-Chain Liquid Crystalline Polymers"

"New H-Bonded Complexes and Their Supramolecular Liquid-Crystalline Organizations"

"Noncovalent Interactions as a Tool to Design New Bent-Core Liquid-Crystal Materials"

"Hydrogen-Bonded Banana Liquid Crystals"

[9] Kinga Gomola, Lingfeng Guo, Damian Pociecha, Fumito Araoka, Ken Ishikawa and

~ 100 ~
5. SmAP_{AR} phase


"An Optically Uniaxial Antiferroelectric Smectic Phase in Asymmetrical Bent-Core Compounds Containing a 3-Aminophenol Central Unit"


"Liquid Crystal Phases Formed by Asymmetric Bent-Shaped Molecules"


"Bent-Shaped Mesogens without an Azomethine Joint"


"Symmetric Liquid Crystal Dimers Containing Hydrazide Groups: Parity - Dependent Smectic Structure, Hydrogen Bonding and Substitution Effect"


"Syntheses and Characterization of Novel Asymmetric Bent-Core Mesogens Exhibiting Polar Smectic Phases"


"Electric-Field-Induced Polar Biaxial Order in a Nontilted Smectic Phase of an Asymmetric Bent-Core Liquid Crystal"

"Helicoid-Stabilized Tristable Switching in Ferroelectric Liquid Crystal Mixtures with Ultrashort Pitch"


"Antiferroelectric Liquid Crystals: Interplay of Simplicity and Complexity"


"Longer-Terminal-Chain-Sensitive Phase Structures in Mixtures and Nonsymmetric Molecules of Bent-Core Mesogens"
Chapter 6

Spontaneous Macroscopic Ferroelectric SmA Phase

The first liquid crystal with ferroelectric behavior was reported by Meyer et al [1], who showed that molecular chirality reduces symmetry of the tilted smectic C phase sufficiently to allow for the long range polar order. The discovery of bent-core mesogens gave a new route to achieve the macroscopic polar order [2]. In this chapter, one interesting bent-shaped material which generates orthogonal phase (SmA) but performs macroscopic polarization [3] even in the absence of an electric field is investigated in details.

6.1. Background and Studied Compounds

As mentioned in the previous chapters, the shape of bent molecules restricts rotation of molecules around their long axis and leads to spontaneous correlation of molecular transverse dipole moments so the polar smectic layers can be obtained. While, most of the phases formed by banana mesogens have an antiferroelectric (AF) interlayer structure since the AF ground state is stabilized by the energetic (system favors apolar structure) and entropic effect (interlayer fluctuations) [4-5]. Walba et. al. attempt to suppress the antiferroelectric interlayer order by introducing branched terminal chains into bent core molecule [6]. Several bent-shaped materials with FE switching were reported, having chiral alkyl chains [7], oligosiloxane [8] or oligocarbosilane [9] terminal bulky groups. However, so far ferroelectric properties were encountered only in tilted smectic phases.

In this chapter, we present unambiguous evidence for ferroelectric behavior observed in a non-tilted smectic phase composed of asymmetric bent-core molecules with carbosilane group at terminal chain. Molecular structure and phase sequence of the studied bent-shaped mesogen W586 are given in Fig. 6.1. The asymmetric molecule has a flexible alkoxy chain
terminated with a carbosilane bulky group at one arm of the bent core and highly polar cyano group connected to the other arm.

![Molecular structure and phase sequence for compound W586. The transition temperature are taken from DSC in cooling run.](image)

**Figure 1** (a) Molecular structure and phase sequence for compound W586. The transition temperature are taken from DSC in cooling run.

### 6.2 Structure Identification

#### 6.2.1 X-ray Diffraction

The X-ray diffraction study was done for homeotropically aligned samples. As shown in 2D pattern in Fig. 6.2(a) and (b), both phases have layered structure with temperature independent and nearly identical periodicity, which confirms orthogonal nature of both phases, and liquid-like order inside the layers (diffused signal in wide angle region). The lower temperature SmA phase has much better defined layers, as evidenced by larger number of harmonics of the main signal. The layer spacing in both phases has much weaker temperature dependence than in the SmAPR phase [10]. The measured layer thickness \( d = 60.5 \) Å is considerably larger than calculated length of the most extended, all \( \text{trans} \) conformer, \( L = 55.1 \) Å (Fig. 6.2(c) inset). Two diffused maxima in the wide-angle region of X-ray diffraction patterns, at 6.5 Å and 4.5 Å, reflect the mean distances of the carbosilane end groups and the alkyl chains of bent-core molecules, respectively. Apparently carbosilane and alkyl chains are self-segregated in space, into distinct sublayers. Similar asymmetric profile of the wide angle scattering has been also reported for other bent-core mesophases with either siloxane or carbosilane bulky groups.
6. SmA<sub>d</sub>P<sub>f</sub> Phase

**Figure 6.2** 2D X-ray diffraction patterns obtained for an aligned sample (a) in the SmA<sub>d</sub> phase at 150 °C and (b) in the SmA<sub>d</sub>P<sub>f</sub> phase at 120 °C. (c) X-ray intensity in the SmA<sub>d</sub> and SmA<sub>d</sub>P<sub>f</sub> phases as a function of 2θ obtained by integration of above patterns over azimuthal angle. The wide angle signal is composed of two peaks (arrows) with maxima corresponding to 6.5 Å and 4.5 Å.

### 6.2.2 Texture Observation

The mesogenic textures were observed under a polarizing microscope both in homeotropic and planar cells. Directly below the isotropic phase, a uniaxial orthogonal phase, SmA, (Fig. 6.3(a)) without spontaneous polarization is observed that undergoes transition to a polar smectic A (SmAP) phase on further cooling. The transition from apolar to polar orthogonal phase is accompanied by appearance of pale schlieren texture in homeotropic cells. Four-brush defects with strength of ±1 that are related to continuous reorientation of director by 2π around point defect as well as two-brush ‘chess-board’ defects [11] that are related to discontinuous reorientation of director by 2π about around point defect are visible in the sample placed between crossed polarizers (Fig. 6.3(b)).
6. SmA$_d$P$_f$ Phase

**Figure 6.3** Microscope textures (a) in the SmA$_d$ phase at 145 °C and (b) in the SmA$_d$P$_f$ (phase at 125 °C) in a homeotropic cell; planar texture in (c) the SmA$_d$ and (d) SmA$_d$P$_f$ phases, respectively, in a 10.2-µm-thick homogeneous cell. Planar texture in (e) thin (3.3-µm-thick) and (f) thick (25-µm-thick) cells in the SmA$_d$P$_f$ phases, respectively. Stripes across focal conic domains are visible for thicker cells.

In planar cells both smectic phases showed focal-conic texture. In the upper phase the fans were smooth and typical for SmA phase (Fig. 6.2 (c)). In the lower temperature smectic phase the stripes across the focal-conic domains were observed (Fig. 6.2 (d)), and the density of stripes increased with cell thickness. Apparently stripes can be nearly suppressed by strong surface anchoring in thin cells (Fig. 6.2 (e)). This phenomenon may originate from the interaction between the polarization splay and the surface anchoring which would be...
discussed later.

6.3 Ferroelectric Behavior

6.3.1 Electro-optical Study

Polar properties of the SmA₉PF phase were confirmed by the observation of switching under an external electric field.

![Fan texture observed in a 10.2-µm-thick planar cell. (a) Before applying an electric field stripes across fan-shape domains can be seen. (b) Under 0.1 V/µm DC field and (c) under 0.2 V/µm DC field, the birefringence of the whole texture increases, and the stripes disappears in (c). (d) Switching current recorded under a triangular wave field of various amplitudes for a 25-µm-thick planar cell.](image)

A single broad current peak at each half cycle was observed by applying a triangular wave field (Fig. 6.4(d)), which is typical for the ferroelectric response. Upon reducing the
amplitude of the applied field, the current peak became broader but the corresponding $P_s$ value did not change. The peak becomes only visually sharper when plotted against time; it has the same broadness against the field. In other words, the switching starts at the same field. The switching is accompanied by the increase of birefringence and disappearance of stripes crossing the focal conic domains, but no changes in the extinction directions in the microscopic texture (Fig. 6.4(a-c)).

**Figure 6.5** (a) The hysteresis loop recorded at 125 °C, indicating the bistable ferroelectric switching. (b) Spontaneous polarization $P_s$ calculated from hysteresis loop as a function of temperature.

The switching was bistable with a single hysteresis loop (Fig. 6.5(a)). The temperature dependence of the spontaneous polarization ($P_s$) is also shown in Fig. 6.5(b). $P_s$ appears at the SmA$_d$ - SmA$_d$P$_f$ phase transition and gradually increases with decreasing temperature.

### 6.3.2 SHG Results

In order to investigate the polar order of smectic phases, second harmonic generation (SHG) measurements were carried out both with and without applying electric field, on cooling down from the isotropic phase. In contrast to previously reported SmAP phases,
which were all SHG inactive in the absence of an external electric field, [1214] the material studied here shows small zero-field SHG signal in the low temperature phase (Fig. 6.6). This confirms non-compensated spontaneous electric polarization, thus ferroelectric properties of the phase (SmA_dP_F) in the ground state.

![Figure 6.6](image.png)

**Figure 6.6** SHG intensity as a function of temperature, measured in ground state (red) and under rectangular wave field, 10 Hz, 60 V_{pp} (black). A 5.3-µm-thick rubbed planar cell is used in this measurement.

Applying an external electric field causes pronounced increase of SH signal magnitude, since most probably in planar cells the polarization is partially compensated in ground state, e.g. due to surface interactions (see discussion part later). Under an electric field SHG signal becomes non-zero at temperature slightly higher than T_c, since external field induces electric polarization in paraelectric SmA_d phase close to the phase transition. Shift of the phase transition temperature under an electric field is also visible by texture observation; in the homeotropic cells weak birefringence can be induced above SmA_dP_F - SmA_d transition temperature, as shown by Fig. 6.6. This is similar to the phenomena found in the SmAP_{R} phase. [12-15]

### 6.3.2 Dielectric Permittivity

With the purpose to explore both the individual and collective motions of molecules for
the studied system, the dielectric dispersion measurements were performed in a broad temperature range. The real and imaginary parts of the dielectric constant against temperature and frequency are plotted in 3-dimensional form in Fig. 6.7 (a) and (b), respectively.

![Figure 6.7](image)

**Figure 6.7** Frequency and temperature dependence of the (a) real and (b) imaginary parts of the complex dielectric permittivity measured on cooling for a 10.2-µm-thick homogeneous cell.

In the paraelectric SmA<sub>d</sub> phase, close to the transition to the ferroelectric phase, the dielectric relaxation mode originating from the cooperative motion of dipole moments emerges gradually. As the temperature is lowered in the SmA<sub>d</sub> phase the mode relaxation frequency \( f_r \) decreases and its strength \( \Delta \varepsilon \) increases (Fig. 6.8 (a)); typical behavior for the soft mode near Curie temperature. In the SmA<sub>d</sub>P<sub>f</sub> phase the dielectric strength and the relaxation frequency of the mode are nearly temperature independent. Slight decrease of \( f_r \) on cooling is due to the gradual increase of viscosity. However, the observed relaxation mode in the SmA<sub>d</sub>P<sub>f</sub> strongly depends on the cell thickness, with increasing the thickness the strength of the mode grows and the relaxation frequency reduces. In a 1.6-µm-thick cell \( \Delta \varepsilon \) is around 200 and in the 10.2- and 25-µm-thick cells it exceeds 1000 and 2000, respectively, which is much higher compared to almost all the reported bent-core mesogens. Similar thickness dependent \( \Delta \varepsilon \) was observed in the ferroelectric chiral SmC* phase.
Figure 6.8 (a) Relaxation frequency ($f_r$) and dielectric strength ($\Delta \varepsilon$) vs. temperature obtained by fitting dielectric data to Cole-Cole formula. (b) Cell thickness dependence of relaxation frequency and dielectric strength of the Goldstone mode in SmA$_d$P$_F$ phase. The curves are guides for the eyes.

The effect of the dc bias field on the relaxation mode was also studied (Fig. 6.9). As the field reached a critical value, the mode was quickly damped since the bias field suppressed the polarization fluctuations. The critical field was strongly thickness dependent, being \( \sim 1.2 \) V/\( \mu \)m for a 3.3-\( \mu \)m cell and \( \sim 0.05 \) V/\( \mu \)m for a 25-\( \mu \)m cell, which implied that threshold voltage also decreased with increasing cell thickness. Interestingly, the relaxation frequency also decreased with bias field, which is opposite to the typical behavior of the ferroelectric phase.[16]

By applying the bias field it was possible to see that actually two modes contribute to dielectric response in the Sm-A$_d$P$_F$ phase: strong Goldstone-like (phason mode) and much weaker soft (amplitude) mode. Under the bias field the Goldstone-like mode is quickly quenched, and thus the soft mode becomes clearly visible (Fig. 6.9). The critical voltage that suppresses the Goldstone-like mode was strongly thickness dependent: It decreased with increasing cell thickness, being \( \sim 1.2 \) V/\( \mu \)m for a 3.3 \( \mu \)m cell and \( \sim 0.05 \) V/\( \mu \)m for a 25 \( \mu \)m cell. Interestingly, while the relaxation frequency of the soft mode increases with increasing bias
field, the relaxation frequency of the Goldstone-like mode decreased, which is opposite to the typical behavior observed in the FE phase.

Figure 6.9 Imaginary part of dielectric permittivity in the SmA_dP_\text{F} phase at 125°C measured under bias electric fields. External field suppresses easily the Goldstone mode, making higher frequency soft (amplitudon) mode visible. Note that with applying bias field Goldstone mode moves to lower frequencies.

6.4 Discussion

(1) Sublayer Structure

SHG, dielectric and electric switching experiments consistently show that a phase transition from the paraelectric to the ferroelectric phase takes place in this compound. Besides, the microscope observations and the X-ray diffraction confirmed the orthogonal nature of both phases. From the previous experimental results we also know that the layer thickness $d$ (61.3 Å) measured from X-ray is considerably larger than the calculated length of the most extended conformer, $L$ (55.1Å). This implies a partially intercalated structure of both
smectic A phases (SmAd type) [17]. The relatively small difference between $d$ and $L$ suggests structure of the smectic layer in which the neighboring molecules overlap mesogenic cores but alternate, up and down, the position of their terminal carbosilane groups, as illustrated in Fig. 6.10. Similar packing scheme of asymmetric banana molecules was also proposed by Sadashiva et al. in the antiferroelectric SmAdP$_A$ phase.[18-19]

![Figure 6.10](image)

**Figure 6.10** Model of the layer structure in the SmA$_d$P$_F$ phase. Layer spacing $d$ and molecular length $L$ are also shown.

Therefore, this novel phase sequence, SmA$_d$ – SmA$_d$P$_F$, is probably a consequence of partial decoupling of the smectic layers due to the segregation of carbosilane molecular parts at the layer interface (Fig. 2d), as suggested in Ref. [16]. Formation of carbosilane sublayers leads to ferroelectric structure by weakening the tendency to parallel alignment of banana arms of molecules from the neighboring layers (entropic effect). Tendency for parallel packing of molecular arms is usually considered as a driving force for the antiferroelectric arrangement of transverse dipole moments in the consecutive layers. The sublayer formation, visible in both smectic phases by the appearance of additional X-ray signal at high angle region, is apparently more pronounced in the SmA$_d$P$_F$ phase, as evidenced by high number of harmonics of the main signal related to the layer periodicity.

(2) **Ferroelectric Model: Polarization Splay**

Studies performed in the ferroelectric phase in planar cells show that in the ground state the
polarization is not uniform across the cell thickness, as suggested by SHG measurements with and without applying an electric field. Instead, the polarization splay is enforced by surface conditions. Considering the anchoring energy and the polar effect at the material/glass boundary, one can expect that dipole moments of molecules close to the surface point either toward or out of the glass (Fig. 6.11 (a)). Since the two cell substrates are the same, the polarization splays between the cell edges to meet the boundary conditions, being parallel to the glass planes in the central part of the cell.

Figure 6.11 (a) Molecular model of polarization splay structure of SmA$_d$P$_F$ in a planar geometry in the ground state. (b) Polarization switches under application of an electric field. (c) Spatial variation of the $x$-component of the polar order parameter ($p_x$) across the cell ($x$) in units of the characteristic length ($\xi$) in the case of strong surface anchoring at $L/\xi = 1$ (solid line), $L/\xi = 5$ (dotted line) and $L/\xi = 15$ (dashed line). (d) Spatial variation of the order parameter component $p_x$ at different strengths of the bias field ($E_B$) at strong surface anchoring.
Degeneracy of the splay sign leads to the formation of domains divided by defects, visible as stripes in the fan shaped texture. The zero-field SH signal is observed due to both positive and negative splay domains, if the domain size is larger than the wavelength of light used for the measurements. This is actually the case, if we consider the fringes as boundaries of two splayed domains. In this case SHG is observable even if the two splay domains are equal in their areas within the laser beam spot. By applying a sufficiently high electric field, bent molecules are reoriented to the field direction (Fig. 6.11 (b)), which results in a significant increase in the SH signal magnitude. The critical field for polarization switching is cell thickness dependent, as the regions in which polarization is anchored by surfaces are relatively small compared to the bulk in thick cells. Moreover, the splay elastic energy density is larger in thinner cells, which makes the splayed polarization stable, whereas the splayed polarization can be easily deformed by applying an electric field in thick cells, resulting in lower critical field.

To study theoretically the spatial variation of the spontaneous polarization across the cell, we minimize the free energy. The free energy density is written in terms of the polar order parameter $\mathbf{\rho}$ which is a unit vector in the direction of the local spontaneous polarization, i.e. in the direction in which the molecular tips are oriented. Since polarization is a real vector in bent-core LCs, terms $(\mathbf{\nabla} \cdot \mathbf{\rho})^i$, with $i = 1, 2, 3…$ are allowed in the free energy density. In addition we have to consider the spontaneous polarization self interaction and the effect of the bias external electric field $E_B$. So the free energy density ($f$) is expressed as:

$$f = K_p(\mathbf{\nabla} \cdot \mathbf{\rho}) + \frac{1}{2} K_{p\perp}(\mathbf{\nabla} \cdot \mathbf{\rho})^2 + \frac{P^2}{2\varepsilon \varepsilon_0} - E_B P_0 P_x,$$

(1)

where $\mathbf{\rho} = (p_x(x), p_y(x))$ is the polar order parameter ($|\mathbf{\rho}| = 1$), $P_0$ is the magnitude of
polarization, ε is the static dielectric constant and \( K_{p1} \) and \( K_{p2} \) are elastic constants related to the splay of polarization. The linear term with \( K_{p1} \) is actually a surface term which favors splay of polarization. The second term stabilizes a finite polarization splay. The electrostatic term describes the polarization self interaction and the last term in Eq. (1) presents the coupling of polarization with the static external bias electric field. The condition for the equilibrium is given by the Euler - Lagrange equation:

\[
\frac{\partial f}{\partial p_x} - \frac{d}{dx} \left( \frac{\partial f}{\partial (dp_x / dx)} \right) = 0
\]

(2)

and by the boundary conditions

\[
\left[ \pm \frac{\partial f}{\partial (dp_x / dx)} + \frac{\partial f_S}{\partial p_x} \right]_{x=\pm L/2} = 0 ,
\]

(3)

As the surfaces are the same, polarization at the bottom and upper surfaces tends to point in the opposite direction and the surface energy \( f_S \) is expressed as:

\[
f_S = W_S (p_x \pm 1)^2 \bigg|_{x=\pm L/2}
\]

(4)

where \( W_S \) is the surface anchoring strength.

Inserting the free energy density (Eq. (1)) into the equilibrium condition (Eq. (2)) and introducing the dimensionless coordinate \( \tilde{x} = x / L \) leads to:

\[
\frac{d^2 p_x}{d\tilde{x}^2} - \frac{L^2}{\xi^2} p_x + \frac{E_g P_0 L^2}{K_{p2}} = 0 ,
\]

(5)

where

\[
\xi = \sqrt{\frac{K_{p2} \varepsilon_0}{P_0^2}} ,
\]

(6)

is a characteristic length over which the distortion in the orientation of the molecular tips is relaxed. The solution of Eq. (5) at boundary conditions given by Eq. (3) is obtained numerically (Fig. 6.11(c)). For cells with low thicknesses \( L \sim \xi \) the polar order profile across the cell is almost linear, for thick cells \( L >> \xi \) the profile is a soliton-like. In the bias field the equilibrium polar order profile is distorted, as dipoles, i.e. the tips of the molecules, rotate
towards the external electric field direction (Fig. 6.11(d)), so the average value of the x-component of the polar director, defined as 

\[
< p_x > = \frac{1}{L} \int_{-L/2}^{L/2} p_x \, dx
\]

increases with increasing bias field. The dependence on the bias field is linear (see the inset to Fig. 6.11 (d)).

**Figure 6.12** The voltage \( U_{1/2} = E_{1/2} L \) vs. \( L/\xi \) at weak surface anchoring \( W_s = 0.1 K_p^2/L \) (solid line) and at infinitely strong anchoring (dashed line); the dotted line presents the dependence at \( W_s = 6 K_p^2/L \) which is just above the critical value of surface anchoring; below this value the dependence of \( U_{1/2} \) shows a uniform increase with increasing cell thickness. In all cases: \( K_p L/K_{p2} = 1 \). The inset: Experimental results for \( U_{1/2} \) vs. \( L \), with \( U_{1/2} \) defined as the voltage at which the dielectric response falls to half its value in zero field.

We define the voltage across the cell at which the average value of polar order reaches \( \frac{1}{2} \) as \( U_{1/2} \). The plot of \( U_{1/2} \) as a function of cell thickness \( L \) for three different strengths of surface anchoring \( W_s \) is shown in Fig. 6.12. We see that there exists some critical value of the surface anchoring \( (W_s - 6K_p^2/L) \), below which \( U_{1/2} \) increases uniformly with the cell thickness. Above this value there is anomalous behavior: \( U_{1/2} \) decreases with increasing cell thickness at low cell thicknesses and turns to increase. If an experimental critical voltage is defined as a value at which the dielectric response under bias falls to one half of its initial value, we can compare qualitatively the experimental results (Fig. 6.12, inset) and theoretical predictions.
Since experimentally we observe monotonic decrease of $U_{1/2}$ with increasing cell thickness, we conclude that 1) we are in the regime of strong anchoring and 2) the correlation length is of the order of $\sim 10$ µm.

![Figure 6.13](image_url)

**Figure 6.13** (a) Relaxation frequency ($f_r$) of the dielectric response as a function of cell thickness at different ratios between the surface extrapolation length $\xi_S$ and the bulk correlation length $\xi$. The inset: experimental results. (b) The dielectric strength $\Delta \varepsilon$ as a function of $L/\xi_S$ at different ratios $\xi/\xi_S$. The inset: experimental results. Both graphs: solid line: $\xi/\xi_S = 10$; dashed line: $\xi/\xi_S = 3$; dotted line: $\xi/\xi_S = 1$. The theoretical values of frequency and the dielectric response are scaled so that the dependencies at different ratios $\xi/\xi_S$ can be shown on the same graph.

To account for the dielectric response (Goldstone mode) of the splayed structure, fluctuations $\delta p(x,t)$ from the equilibrium value of the polar order parameter $p_0(x)$ are introduced:

$$p_s(x,t) = p_0(x) + \delta p(x,t).$$  \hspace{1cm} (7)

The fluctuation part of order parameter can be expressed as

$$\delta p(x,t) = \delta p_0 \cos(q_w x) e^{-t/\tau}$$  \hspace{1cm} (8)

with $\tau$ being the characteristic time in which the system relaxes to the equilibrium state and $q_w$ the wave number which depends on the strength of surface anchoring. The system dynamics
is described by the Landau - Khalatnik equation:

\[
\frac{\partial \delta \rho(x,t)}{\partial t} = \frac{\partial f}{\partial \epsilon} \frac{d}{dx} \frac{\partial f}{\partial (dp_x / dx)}
\tag{9}
\]

where \( \gamma \) is the rotational viscosity. Introducing Eq. (8) into Eq. (9) gives

\[
\frac{1}{\tau} = \frac{P_0^2}{\gamma \epsilon E_0} + \frac{K_{p_2}}{\gamma} q_w^2
\tag{10}
\]

Inserting Eq. (8) into the boundary condition (Eq. 3) leads to the transcendental equation for \( q_w \):

\[
q_w L \tan(q_w L / 2) = L / \xi_S,
\tag{11}
\]

where \( \xi_S = K_{p_2} / W_S \) is the surface extrapolation length. At very strong anchoring \( \xi_S \to 0 \) and \( q_w L / 2 \to \pi / 2 \). If \( L / \xi_S << 1 \) then \( q_w^2 \approx 2 / (L \xi_S) \). However, if the surface extrapolation length is comparable to the cell thickness, then \( q_w \) has to be calculated numerically from Eq. (11) and we do not have a simple dependence of the relaxation time on the cell thickness. The Eq. (10) also gives the relaxation frequency of the dielectric response.

The dielectric response in the external sinusoidal field with frequency \( \omega \) and amplitude \( E_0 \) is given by

\[
\Delta \varepsilon = \lim_{\epsilon_0 \to 0} \frac{P_0(\delta p)_{\omega}}{E_0} \text{ and can be expressed as:}
\]

\[
\Delta \varepsilon = \frac{P_0^2}{\epsilon E_0} + K_{p_2} q_w^2 - i \omega \gamma
\tag{12}
\]

Fig. 6.13(a) gives the theoretical prediction for the relaxation frequency of the Goldstone mode as a function of cell thickness in the units of surface extrapolation length. The shape of the curve depends on the ratio between the surface extrapolation length (\( \xi_S \)) and the correlation length \( \xi \). The dielectric strength is proportional to \( 1 / \xi \) and is shown in Fig. 6.13 (b) for three values of \( \xi / \xi_S \). Comparing the theoretical prediction and the experimental results (inset in Fig. 6.13), we conclude that \( \xi_S \approx 0.1 \xi \) showing that surface extrapolation length is small compared to the bulk correlation length.
6.5 Conclusion

In this chapter, novel phase sequence with ferroelectric SmA\textsubscript{d}P\textsubscript{F} phase below paraelectric SmA\textsubscript{d} phase is found for asymmetric bent-core molecules with carbosilane terminal group. Both phases are non-tilted smectics with partially bilayer structure. The ferroelectricity of the SmA\textsubscript{d}P\textsubscript{F} phase was unambiguously confirmed by optical second-harmonic generation activity in the absence of an electric field, ferroelectric response, and high dielectric strength.

The long-range polar order is a consequence of weakened interlayer coupling due to the formation of carbosilane sublayers, which allows for the parallel order of dipole moments of bent-core molecules in the neighboring layers. It develops in the system gradually through the second-order phase transition. In the SmA\textsubscript{d}P\textsubscript{F} phase the strong surface anchoring results in the splay of polarization across the sample thickness and in the strongly thickness dependent polar fluctuations, as proved by the dielectric measurements (Goldstone-like mode). From the thickness dependence of the dielectric response and the threshold electric field the elastic constant related to the polarization splay and the rotational viscosity were estimated.
References of chapter 6


"Distinct Ferroelectric Smectic Liquid Crystals Consisting of Banana Shaped Achiral Molecules"

"Spontaneous Ferroelectric Order in a Bent-Core Smectic Liquid Crystal of Fluid Orthorhombic Layers"

"Bent-Core Liquid Crystals: Their Mysterious and Attractive World"

"Bent-Core Liquid Crystals: Polar Order, Superstructural Chirality and Spontaneous Desymmetrisation in Soft Matter Systems"

"A Ferroelectric Liquid Crystal Conglomerate Composed of Racemic Molecules"

"A Racemic Layer Structure in a Chiral Bent-Core Ferroelectric Liquid Crystal"

"Chirality and Macroscopic Polar Order in a Ferroelectric Smectic Liquid-Crystalline Phase"
6. SmA\textsubscript{d}P\textsubscript{F} Phase

Formed by Achiral Polyphilic Bent-Core Molecules


"The Carboisilane Unit as a Stable Building Block for Liquid Crystal Design: A New Class of Ferroelectric Switching Banana-Shaped Mesogens"


"Syntheses and Characterization of Novel Asymmetric Bent-Core Mesogens Exhibiting Polar Smectic Phases"


"Symmetry and Defects in the Cm Phase of Polymeric Liquid Crystals"


"Electric-Field-Induced Polar Biaxial Order in a Nontilted Smectic Phase of an Asymmetric Bent-CoreLiquid Crystal"


"Polar Switching in the Smectic-A\textsubscript{d}P\textsubscript{F} Phase Composed of Asymmetric Bent-Core Molecules"


"An Optically Uniaxial Antiferroelectric Smectic Phase in Asymmetrical Bent-Core Compounds Containing a 3-Aminophenol Central Unit"

"Ideal Liquid Crystal Display Mode Using Achiral Banana-Shaped Liquid Crystals"


"Ferroelectric Phases in a Chiral Bent-Core Smectic Liquid Crystal: Dielectric and Optical Second-Harmonic Generation Measurements"


"A Simple Molecular Theory of the SmA₁± SmA₃ Critical Point and Nematic Lake in Highly Polar Compounds"


"Biaxial Smectic a Liquid Crystal in a Pure Compound"


"Biaxial Smectic a Phase in Homologous Series of Compounds Composed of Highly Polar Unsymmetrically Substituted Bent-Core Molecules"
Bent-core liquid crystals have been an essential topic of research in the field of mesogens and soft mater physics for years. It is astound that the bending shape of molecules gave rise to such broad variety and amazing phenomena. Within recent decades, a large number of banana liquid crystal compounds are synthesized.

In addition to conventional banana phases (B₁–B₈ phases) which are characteristic to bent-core mesogens and intensively investigated, this dissertation is concentrated on another vital type of banana phases: the polar orthogonal smectic (SmAP) phases. In such phases, molecules align perpendicular to the smectic layer and the bending shape hinders rotation about their long molecular axes. The resultant closed packing of molecules brings about polarized layers or local polar domains. We would like to introduce several novel SmAP phases and their unique performances to the field of bent-core liquid crystals.

7.1. Distinct Bent-shaped Compound Showing SmAP₉ Phase

The SmAP₉ phase appears like a uniaxial phase and exhibits ferroelectric switching. This is because the phase consists of microscopic ferroelectric domains distributed randomly in the system, so that the phase is macroscopically nonpolar. But by applying an electric field, polarization is easily induced under the external field. The potential application of the SmAP₉ phase for a fast switching display device has been proposed and demonstrated by Shimbo et al. In this work, we tried to obtain a numerous SmAP₉ compounds through various modification of the original molecule.

By changing alkyl terminal length of methylbenzene core compounds, it is found that too short tails can lead to missing of smectic phase. Introducing the unsaturated chain into both
bent arms can also destroy the emergence of the SmAP$_R$ phase. Minor decrease of isotopic temperature was recorded in materials with only one unsaturated arm. But widening of the temperature range of the SmAP$_R$ phase was not observed. The phase behavior and the phase sequence beneath the smectic phase (B$_{1\text{RevTilted}}$ and crystal phase) remained the same as the saturated bent-core LCs. By mixing two methylbenzene core compounds, the temperature range of the SmAP$_R$ phase could be expanded.

If the central core is replaced to acetophenone, the mesogens will show transition from the uniaxial orthogonal phase with local polar order (SmAP$_R$) to the biaxial antiferroelectric non-tilted smectic phase (SmAP$_\Lambda$). Much wider temperature range ($\Delta T \sim 40^\circ C$) of the target phase SmAP$_R$ is also realized in this series of compound. Through x-ray diffraction, dielectric and electro-optic measurements, it is regarded that the transition is continuous or weakly first order, which is allowed for phases of different symmetry (D$_{\infty v}$ for SmAP$_R$ and D$_{2h}$ for SmAP$_\Lambda$, respectively). The correlation length of polar order in the SmAP$_R$ phase gradually increases as well as antiferroelectric interlayer correlations. The interlayer polar coupling is weak as indicated by a low value of relaxation frequency of a ferroelectric mode at the phase transition.

Another interesting modification is to introduce siloxane bulky groups into the terminal chain of bent molecules. The SmAP$_R$ phase range is expanded as we hoped. X-ray diffraction proved the existence of sublayers structure generated by self-segregation of siloxane bulks. By POM observation, EO study and SHG measurement, the ferroelectric-like behavior of the SmAP$_R$ phase is confirmed. Moreover, the stiff siloxane sublayers can perform as backbone to stabilize the smectic structure and prevent layer deformation even under bending/strong external electric field. Possible molecular models are given for both conventional methylbenzene compound and the siloxane materials.

### 7.2 Antiferroelectric Behavior of SmA$_d$P$_\Lambda$ Phase

In chapter 4, an asymmetric bent-core liquid crystal performing biaxial SmA$_d$P$_\Lambda$ phase is characterized. This partially intercalated smectic A phase performs tristable switching
indicating antiferroelectric behavior therefore named as SmA_dP_A phase. This phase is SHG active only under an electric field and a characteristic dielectric relaxation appears at about 100 kHz attributed to the rotation of the molecules about the long axis. The DC bias field enhances such dielectric relaxation, suggesting the polar order nucleated by the DC bias effect.

The field-induced antiferroelectric to ferroelectric (SmA_dP_A–SmA_dP_F) transition occurs continuously without a clear threshold. Two possible models are suggested to interpret this continuous transition, i.e., super low energy barrier between the two states and the existence of helical structure. Both of the two models are consistent with the present experiment results.

### 7.3 H-bonded SmAP_{AR} Phase

When H-bonding is launched into bent central part (possessing 3-aminophenol as a central unit) of the banana shaped liquid crystals, a novel optically uniaxial but clearly performing antiferroelectric switching behavior was discovered. In this sense, this phase is definitely different from the SmAP_R phase, so we call this phase SmAP_{AR} phase, where the subscript A stands for antiferroelectric and R represents the randomized microscopic polar domain.

The mesomorphic properties of the asymmetric bent-core compounds with H-bonding showing SmAP_{AR} phase are reported in chapter 5. The existence of hydrogen bonds between amide-amide groups of neighboring molecules was proved by FT-IR spectroscopy. Electro-optical study and SHG results confirm the uniaxiality and antiferroelectric behavior. Detailed comparison between SmAP_R and SmAP_{AR} phases and proper molecular models are given according to a variety of experimental results.

### 7.4 Spontaneous SmA_dP_F Phase

People have been attempting to achieve the macroscopic polar order in soft matters by searching for proper bent core molecules for years. It is amazing that finally Reddy et al. have
succeeded in suppressing the antiferroelectric order in the orthogonal smectic phase. In chapter 6, the unambiguous evidence of ferroelectric behavior observed in a non-tilted smectic phase is expressed.

The asymmetric bent-core molecules with carbosilane terminal group exhibit SmA phase with spontaneous ferroelectric order. X-ray diffraction identified this compound has non-tilted smectics with partially bilayer structure and this ferroelectric phase is named SmA<sub>d</sub>P<sub>F</sub>. The ferroelectricity was confirmed by SHG activity in the absence of an electric field, ferroelectric response, and high dielectric strength. The long-range polar order is a consequence of weakened interlayer coupling due to the formation of carbosilane sublayers, which allows for the parallel order of dipole moments of bent-core molecules in the neighboring layers.

In the SmA<sub>d</sub>P<sub>F</sub> phase the strong surface anchoring results in the splay of polarization across the sample thickness and in the strongly thickness dependent polar fluctuations, as proved by the dielectric measurements (Goldstone-like mode). From the thickness dependence of the dielectric response and the threshold electric field the elastic constant related to the polarization splay and the rotational viscosity were estimated.

![Figure 7.1 Structure of major works described in this dissertation and corresponding index ellipsoids for uniaxial and biaxial SmAP phases, respectively.](image)
7. Conclusions and Open Questions

If we look at the above four parts of work from a big picture, they can be summarized into two types (as shown in Fig. 7.1):

1. **The uniaxial SmAP phases**: SmAP$_R$ and SmAP$_{AR}$. In these phases, the uniaxiality was indicated by the uniform dark image in homeotropically aligned sample under polarizing microscope and was also confirmed through conoscope. It is believed that the size of the polar domain is uniaxial SmAP phase is small and only local short range FE/AF correlation order existed in the absence of an electric field.

2. **The biaxial SmAP phases**: SmAdP$_A$ and SmAdP$_F$. In biaxial SmAP phases, spontaneous macroscopic polar domains (FE/AF) existed and schlieren textures were observed in homoetropic cells under polarizing microscope implying the biaxiality of such phases.

7.5 Open Questions

Based on concentrated investigation of the interesting polar orthogonal (SmAP) phases in this dissertation, the structure, behavior and other features are better understood. Nevertheless, a number of details are still open questions worthy of further studying. For instance, for the chirality of the SmAP phases, which was observed in the SmAdP$_A$ (chapter 4) phase: How the molecules are organized and what is the key aspect for the appearance of such chiral domains?

Another significant and interesting problem is the anchoring principle and the anchoring energy of the SmAP phases, especially for SmAP$_R$ and SmAP$_F$, which may be used for industry in the future.
Publications and Awards

Papers

1. "Ferroelectric behavior of orthogonal smectic phase made of bent-core molecules"
   *Physical Review E*, 84, 031706, 2011

2. "Transition between two orthogonal polar phases in symmetric bent-core liquid crystals"
   *Soft Matter*, 7, 2895, 2011

3. "Polar switching in the smectic-$A_dP_A$ phase composed of asymmetric bent-core molecules"
   *Physical Review E*, 81, 011703, 2010

4. "Optically uniaxial antiferroelectric smectic phase in asymmetrical bent-core compounds containing a 3-aminophenol central unit"
   K. Gomola, Lingfeng Guo, D. Pociecha, F. Araoka, K. Ishikawa and H. Takezoe
   *Journal of Materials Chemistry*, 20, 7944, 2010

5. "First symmetrical banana compounds exhibiting SmAP$_R$ mesophase and unique transition between two orthogonal polar phases"
   *Chemical Communication*, 6592, 2009

6. "Syntheses and characterization of novel asymmetric bent-core mesogens exhibiting polar smectic phases"

~ 129 ~

*Journal of Materials Chemistry*, 19, 4240, 2009

7. "Kerr constant and third-order nonlinear optic susceptibility measurements in a liquid crystal composed of bent-shaped molecules"


*Physical Review E*, 78, 050701, 2008

**Patent (Japanese)**

Kinga Gomola, Lingfeng Guo. 竹添秀男, 特許出願番号: 2009-281532; 発明の名称: 液晶材料、液晶表示素子および液晶光空間変調素子; 提出日（出願日）: 2009/12/11

**Presentations**

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<tr>
<td>Nov. 2011</td>
<td>2011 TIT-Tsinghua Joint Workshop (poster)</td>
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<tr>
<td>Sep. 2011</td>
<td>Japanese Liquid Crystal Conference 2011 (poster)</td>
<td>Tokyo, Japan</td>
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<td>Aug. 2011</td>
<td>13th International Conference on Ferroelectric Liquid Crystals (oral)</td>
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<td>Jul. 2010</td>
<td>23rd International Liquid Crystal Conference Poland (oral)</td>
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<td>Mar. 2010</td>
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<td>2010 Tokyo Tech- EPFL Joint Workshop, Japan(oral and poster)</td>
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<tr>
<td>Sep. 2009</td>
<td>Japanese Liquid Crystal Conference 2009 (oral)</td>
<td>Tokyo, Japan</td>
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Awards

(1) Best presentation award for the paper entitled “Transition Between Two Orthogonal Polar Phases in Symmetric Bent-core Liquid Crystals” at Tokyo Tech-EPFL Joint Symposium, Hakone, Japan, Jan. 2010

(2) Best Poster Award for the paper entitled “Optically Uniaxial Smectic A Phase with Antiferroelectric Behavior” at Tokyo Tech-Tsinghua Joint Asia Materials Week International Symposium, Fuji-Yoshida, Japan, Nov. 2010

(3) Kosaisho Award (Rainbow Award) for the paper entitled “Orthogonal Smectic Phase with Spontaneous Macroscopic Ferroelectric Order” at 2011 Japanese Liquid Crystal Conference, Tokyo, Japan, Sep. 2011.