

**ADVANCES IN LIQUID CRYSTALS**

**A SPECIAL VOLUME OF ADVANCES IN CHEMICAL PHYSICS**

**VOLUME 113**

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# ADVANCES IN LIQUID CRYSTALS

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ADVANCES IN CHEMICAL PHYSICS  
VOLUME 113

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## PREFACE

This special volume of *Advances in Chemical Physics* is devoted to recent developments that have helped our understanding of the properties of liquid crystals. As now recognized, research on liquid crystals is of interest to chemists, physicists, materials scientists, biologists, and electrical and electronic engineers. Various aspects of research in this area, especially ferroelectric and antiferroelectric liquid crystals (FLCs and AFLCs), have grown rapidly. In particular, many basic research issues associated with FLCs and AFLCs achieving the goal of video rate full color displays have been addressed. This volume describes a number of important contributions that enhance our understanding of the properties of such liquid crystals. It also incorporates contributions to our understanding of the alignment and the self-order of discotics, and the relaxation phenomena in nematics. It is hoped the topics presented will stimulate new research in these aspects of liquid crystals.

The first chapter, by D. Guillon, addresses the topic of molecular engineering—specifically how to structurally engineer a molecule with ferroelectric properties. Guillon also demonstrates that molecules exhibiting such properties need not be chiral molecules, and that the molecules only need to induce chirality in the macroscopic structure. The second chapter, by R. Shashidhar, J. Naciri, and B. R. Ratna, describes recent developments in ferroelectric liquid crystalline materials with large electroclinic coefficients. These materials are highly promising for applications owing to their analog gray-scale capability and short response times. In the third chapter, L. M. Blinov describes the usefulness of the pyroelectric technique in its static and dynamic forms for investigating the polar mesophases and in searching for new liquid crystal materials, i.e., structures with ferroelectric/antiferroelectric properties. In the chapter by R. Zentel, E. Gebhard, and M. Brehmer, the authors address the synthesis and molecular structure of ferroelectric LC-elastomers (FLCE). FLCEs combine the liquid crystalline order of the ferroelectric phase and the rubber-like elasticity of a polymer network. In FLCEs, switching the electrical polarization leads to a mechanical deformation which, in turn, produces an internal stress in the polymer network. This field-induced stress results in a piezoelectric response; thus, the sample may vibrate as a result of the application of an AC electric field. The cross-linking needed to produce elastomeric behavior is carried out either within the siloxane sublayers (producing fast-switching elastomers) or

between the separated siloxane sublayers (producing elastomers with favored ferroelectric switching).

In the chapter by F. Kremer, H. Skupin, W. Lehmann, L. Hartmann, P. Stein, and H. Finkelmann, the authors describe the experimental procedures and results of their measurements of the piezoelectric modulus of materials. The usefulness of time-resolved FTIR spectroscopy in providing a microscopic basis for understanding the macroscopic piezoelectricity is described. A. Kocot, J. K. Vij, and T. S. Perova describe the orientational effects in ferroelectric and antiferroelectric liquid crystals in the next chapter. They review the recent work on time-resolved FTIR spectroscopy of FLC polymers and show how polarized IR spectroscopy studies provide a microscopic basis for understanding of ferroelectricity and antiferroelectricity. The chapter by Yu. P. Panarin and J. K. Vij provides a review of the structure and properties, both static and dynamic, of antiferroelectric liquid crystals. The structure of ferroelectric phases is given in terms of existing models and a model being proposed, thereby suggesting that their experimental results should lead to new theories and/or models for the molecular structure of ferroelectric phases. In the contribution by S. J. Elston and N. J. Mottram, the authors discuss some of the fundamental issues associated with the order parameter variation in smectic liquid crystals caused by an externally applied mechanical stress. The chapter by T. S. Perova, J. K. Vij, and A. Kocot reviews issues concerning the alignment, order parameter, and structure of discotic liquid crystals studied by FTIR spectroscopy. Experiments on the switching mechanism in a ferroelectric liquid crystal dibenzopyrene using both polarized and time-resolved FTIR spectroscopy are reviewed. Finally, in the last chapter, W. T. Coffey and Y. P. Kalmykov discuss rotational diffusion and dielectric relaxation in nematics for a general case that the dipole moment is directed at an angle to the molecular axis of symmetry. Their approximate, but elegant formulas are presented in a form that can be compared with results from dielectric spectroscopy.

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# INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

I. PRIGOGINE  
STUART A. RICE

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# MOLECULAR ENGINEERING FOR FERROELECTRICITY IN LIQUID CRYSTALS

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- VII. Conclusion
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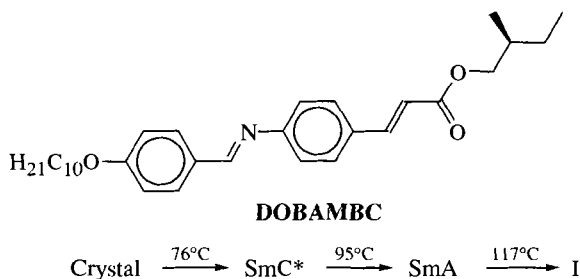
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## I. INTRODUCTION

Polar order in condensed matter represents an area of high fundamental and technological interest. Indeed, one of the most spectacular phenomena in crystals was revealed in 1921 in Rochelle salts (tartrate of potassium and sodium) [1]. In such materials a spontaneous polarization has been evidenced below a certain temperature called Curie temperature; the direction of this polarization could be changed by applying an external electric field. This property has been called ferroelectricity, from the analogy with ferromagnetism.

Many years later and with the development of optoelectronics, the transposition of such a ferroelectricity to anisotropic liquids is the subject matter of a large number of research studies. In particular, during the last two decades the possibility of taking advantage of the bistability of ferroelectric smectic C\* liquid crystals, in fast electro-optical devices, has driven much interest in these systems [2]. The molecular conception of these compounds was directly deduced from the original work of R. B. Meyer [3], who predicts, using a symmetry argument, that tilted smectic phases (smectic C, I, or F) obtained with chiral molecules having a transverse dipole moment, should exhibit a spontaneous polarization. Meyer's predictions have been rapidly confirmed with the synthesis of the first smectic C\* ferroelectric liquid crystal (DOBAMBC) [4], whose chemical structure and thermotropic behavior are shown in Fig. 1.

Then, the first generation of ferroelectric liquid crystals (FLC) materials was designed according to this concept in order to obtain a large spontaneous polarization, which generally leads to a short response time. In this context, a large number of smectic C\* compounds with various polar groups and diverse chiral centers [5–9] that we will discuss in more detail below have been synthesized. More recently, other forms of chirality, such as axial chirality or planar chirality, have been explored in the design of FLC



**Figure 1.** Chemical structure and mesomorphic behavior of the first smectic C\* ferroelectric liquid crystal synthesized by P. Keller and co-workers [4].

materials. A new family of achiral molecules (banana shaped-molecules) that exhibit an electric polarization [10] when submitted to an electric field under the same conditions as do the more classical ferroelectric calamitic liquid crystals in the so-called SSFLC cells has also appeared in the last several years. This quite fascinating behavior has impelled several teams around the world to investigate this new type of materials, mainly from the experimental point of view [11]. Finally, other types of ferroelectricity in liquid crystals have been explored, such as the longitudinal ferroelectricity in orthogonal smectics resulting from a specific molecular design and the ferroelectricity in columnar liquid crystals.

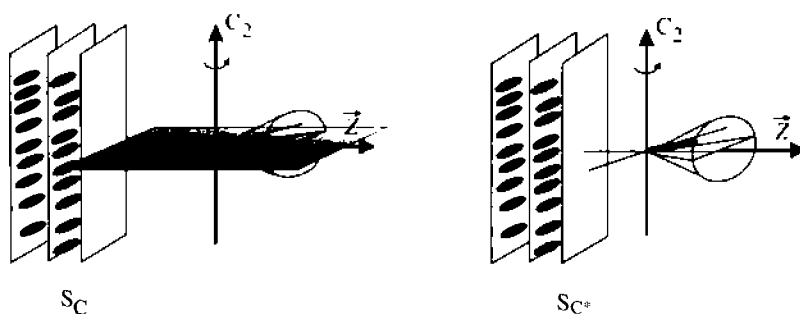
Before going into these different aspects of ferroelectricity in liquid crystals further, let us first consider the few theoretical concepts which are currently used to describe the physical properties of FLC and to predict the type of molecular architecture needed for efficient electro-optical properties.

## II. CONCEPTUAL AND THEORETICAL ASPECTS

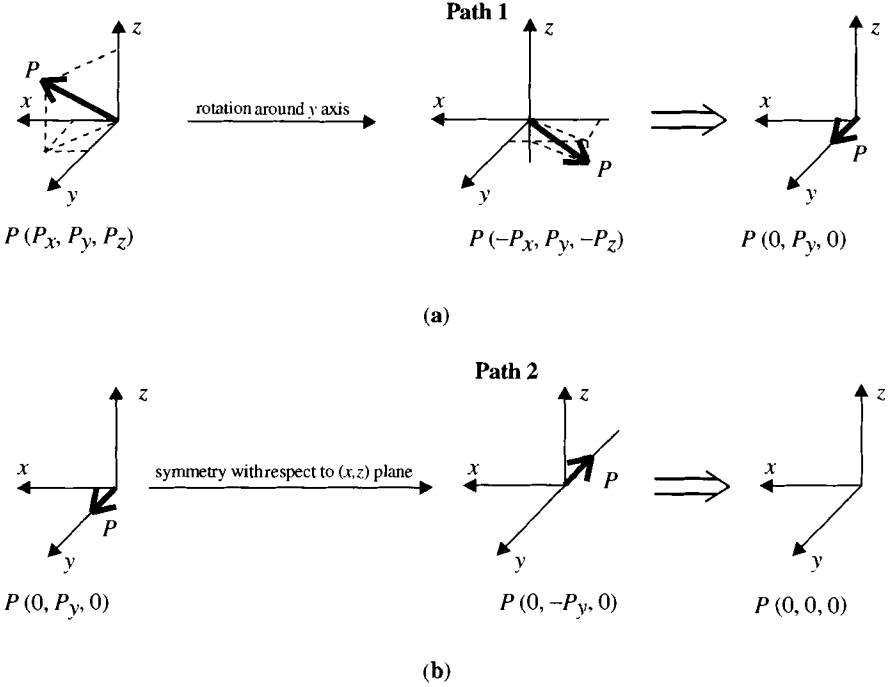
### A. Ferroelectricity in Tilted Smectic Phases

The introduction of chirality into calamitic molecules leads to a reduction in the symmetry of the classical smectic C phase and to the presence of a helical structure characteristic of the smectic C\* phase. While the smectic C phase belongs to the  $C_{2h}$  symmetry group, i.e., possesses three symmetry elements [one mirror plane ( $m$ ), one twofold axis ( $C_2$ ), and one inversion center ( $i$ )], the smectic C\* phase belongs to the symmetry group  $C_2$  with only one symmetry element, the twofold rotation axis (Fig. 2).

Based on the Neumann's principle, it is known that any macroscopic physical property should adhere to the symmetry properties of the phase. If we consider a vector  $P$ , which can symbolize any physical property, and if we



**Figure 2.** Symmetry elements of the smectic C and smectic C\* phases.



**Figure 3.** Two symmetry operations applied to the vector  $P$ . (a) Path 1: rotation around  $y$  axis; (b) path 2: reflection with respect to the  $(x,z)$  plane.

apply to it the symmetry operations (Paths 1 and 2 in Fig. 3) corresponding to the smectic A phase, it is clear that the resulting vector is cancelled. In the case of chiral smectic  $C^*$  phases, the mirror plane does not exist any more, and the only symmetry element is the twofold axis,  $C_2$ , along  $y$ . After applying the corresponding single symmetry operation (path 1 in Fig. 3), one component of  $\vec{P}$ , along  $y$ , cannot be cancelled. In this case, if the vector  $\vec{P}$  symbolizes a transverse dipole moment, there is a resulting spontaneous polarization in each smectic layer which acts along the  $C_2$  axis, i.e., in a direction perpendicular to the tilt plane defined by the director  $\vec{n}$  and the normal to the smectic layers  $\vec{z}$ .  $\vec{P}$  verifies the relation:

$$\vec{P} = P_0(\vec{z} \wedge \vec{n}) \quad (1)$$

The spontaneous polarization can only take two opposite directions. However, as the chirality of the molecules induces a helical variation of the director  $\vec{n}$  from layer to layer, the direction of the spontaneous polarization  $\vec{P}$  turns from one layer to the next one. As a consequence, the

spontaneous polarization is cancelled as soon as the total thickness of the sample is larger than the helical pitch. This is the reason why some authors prefer to call this phase an “helielectric” phase [12] rather than a ferroelectric one. However, the spontaneous polarization can be observed when the helical structure of the smectic C\* phase is broken. This can be achieved according to several different processes:

- When a shearing in the plane of the smectic layers is applied to the smectic C\* phase, the helical structure is distorted, and a polarization appears perpendicularly to the shearing direction.
- The distortion, and even the cancellation of the helical structure, can be obtained by applying an electric field perpendicularly to the helical axis. The smectic C\* phase then transforms into an unwound smectic phase corresponding to the classical biaxial smectic C phase. The threshold of the electric field needed to unwind the helical structure in the smectic C\* phase is given by

$$E_c = \frac{\pi^4}{4} K_{33} \frac{\theta^2}{p^2 P} \quad (2)$$

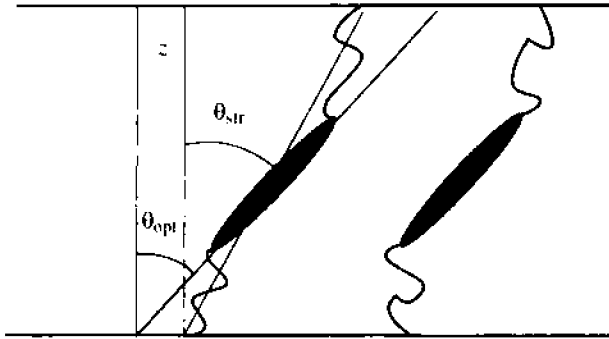
where  $K_{33}$  is the elastic constant,  $p$  the helical pitch traced by  $\vec{n}$ ,  $\theta$  the tilt angle of the molecules in the smectic layers, and  $P$  the spontaneous polarization.

- The removal of the helical structure by the elastic interactions between the smectic C\* phase and treated surfaces can be obtained when the sample is confined in a thin cell, for which the thickness is either less than or of the order of the helical pitch. This type of cell is called SSFLC (Surface Stabilized Ferroelectric Liquid Crystal) [13].
- In the case of mixtures of ferroelectric liquid crystals, the removal of the helical structure can be achieved by mixing at least two compounds having the opposite sense of helix, with the helical pitches being in the same order. The compensation of the right and left helices of these materials leads to an unwound smectic C\* phase exhibiting a nonzero spontaneous polarization.

## B. The Boulder Model

To analyze the smectic C phase from a molecular point of view, it is necessary to consider the molecules as objects that are more complex than a simple rigid rod. Indeed, through a comparison of the values of the tilt angle obtained by different techniques (X-ray diffraction, optical microscopy), it has been shown [14] that the molecules can be better described as objects having a zigzag shape in the smectic C phase. Thus the molecule within





**Figure 4.** Schematic representation of a calamitic molecule in the smectic C phase [13].  $\theta_{\text{opt}}$  is the tilt angle which can be measured by optical means, and  $\theta_{\text{stir}}$  corresponds to the tilt angle (steric angle) which can be deduced from X-ray investigations.

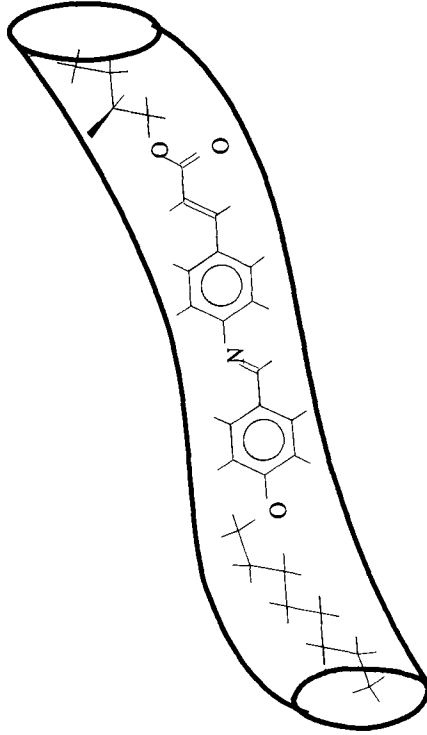
a smectic C layer is symbolized by a central part (corresponding to the polarized part) with a tilt angle  $\theta_{\text{opt}}$  (as measured by optical method) and two terminal parts corresponding to the disorganized aliphatic chains, which are less tilted on average than the central one (Fig. 4).

According to the model developed by Walba and his collaborators [15], one molecule can be simulated by a surface with a constant molecular field. The interactions with the neighboring molecules are then averaged as a function of time. This surface, called “binding site,” should hold the intrinsic characteristics to the symmetry of the phase. It would be a sphere in the case of the isotropic phase, a cylinder in the case of the nematic and smectic A phases. For the smectic C mesophase, the authors propose a bent cylinder. This model is in agreement with the “zigzag” model described. As shown in Figure 5, the optimal energetic conformation of the zigzag model fits quite well inside the bent cylinder. For such a molecular system, the polarization is then given by the following expression:

$$P = \sum_n D_i P_i \quad (3)$$

where  $D_i$  is the density of conformation  $i$ , and  $P_i$  is the total contribution of the conformation  $i$  to the polarization.

In this model, the authors consider the polarization as a manifestation of a form of molecular recognition [16–18]. The rotations of the chiral molecules are biased, resulting in nonzero dipole moment perpendicular to the tilt plane. Of course, the degree of rotation will depend upon the molecular architecture, and in particular upon the steric constraints induced by the chiral molecules.



**Figure 5.** One “zigzag” shaped molecule inserted in a bent cylinder (adapted with permission from Ref. [15]).

### C. Molecular–Statistical Theory of Ferroelectric Ordering

In a molecular–statistical theory of ferroelectric ordering in the smectic C\* phases, it is claimed that the spontaneous polarization is caused by specific chiral and polar interactions between the chiral center of the molecule and the polarizable core of the nearest neighboring molecule [19]. When the molecules have large dipoles in the chiral center, the predominant interaction of this nature is the induction interaction between the dipole and the polarizability of the neighboring molecule, modulated by the asymmetric shape of the molecule. The spontaneous polarization is thus given by the following expressions [20]:

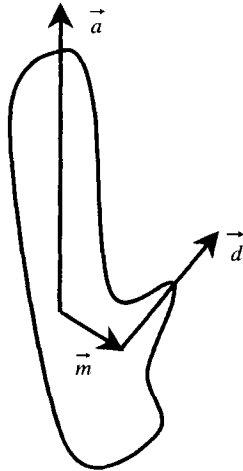
$$\vec{P} = \mu(\vec{n} \cdot \vec{z})(\vec{n} \wedge \vec{z}) \quad (4)$$

$$\mu = -15/4(\rho^2/kT)(\vec{s} \cdot \vec{d})d^2\Gamma(D/L)^6(2\chi_{\perp} + 15\Delta\chi + \Delta\chi_{\perp}) \quad (5)$$

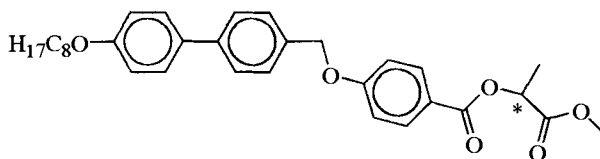
$$\Gamma = (\vec{d} \cdot \vec{a})[(\vec{m} \wedge \vec{d}) \cdot \vec{a}] \quad (6)$$

where  $\vec{n}$  is the director and  $\vec{z}$  is the smectic plane normal. The quantity  $\mu$  is expressed in terms of molecular model parameters. The term  $\vec{d}$  is the dipole moment of the chiral centre,  $\vec{s}$  is the transverse dipole which reflects the polar asymmetry of the molecular shape in the transverse direction,  $\chi_{\perp} = (\chi_{xx} + \chi_{yy})/2$  is the transverse molecular polarizability,  $\Delta\chi = \chi_{zz} - \chi_{\perp}$  is the anisotropy of the molecular polarizability, and  $\Delta\chi_{\perp} \cong (\chi_{xx} - \chi_{yy})$  is the anisotropy of the transverse polarizability. Finally,  $\rho$  is the number density of molecules,  $L$  is the molecular length and  $D$  is the average molecular diameter. The predominant contribution comes from the anisotropy of the polarizability,  $\Delta\chi$ , and as a consequence, the spontaneous polarization is approximately proportional to  $\Delta\chi$ .  $\Gamma$  is a parameter which measures the molecular chirality. It depends upon the orientation of the dipole in the chiral centre with respect to the long molecular axis  $\vec{a}$  and the vector  $\vec{m}$  pointing from the center of mass of the molecule to the chiral center. The vectors  $\vec{a}$ ,  $\vec{m}$ , and,  $\vec{d}$  are shown in Figure 6.

The most important factor in this theory is the value and the orientation of the dipole,  $\vec{d}$ , in the chiral center of the molecule. This polar bond directly attached to the chiral center takes part in the chiral and polar intermolecular interactions, and increases the spontaneous polarization substantially. In such a description, the spontaneous polarization is proportional to the cube of this dipole,  $P_s \propto d^3$ . According to the authors, this result can be used to explain the strong dependence of the spontaneous polarization as a function of the value of the dipole in the chiral center and of the location of other



**Figure 6.** Schematic of a chiral molecule with a substitution group in the alkyl chain. The vectors are defined in the text (adapted with permission from Ref. [20]).



**Figure 7.** Molecular structure of 1MC1EOPBB.

dipole bonds around it [21]. In particular, when two polar bonds are attached on both sides of the chiral carbon, it has been shown that the spontaneous polarization can be considerably increased, as in the case of 1MC1EOPBB (Fig. 7).

#### D. Indigenous Polarization Theory

Starting from the symmetry arguments suggesting that chirality and transverse dipoles are sufficient to give rise to ferroelectricity but cannot predict the value of the polarization, Photinos and Samulski [22] have recently developed a model showing that polarity can be obtained even for the most symmetric flexible molecules that can form a nonchiral smectic C phase. According to this theory, which they called the Indigenous Polarity Theory (IPT), the intermolecular interactions giving rise to ferroelectricity are primarily excluded volume interactions which turn out to be the same as those producing the smectic phase itself.

In their model, the authors consider the mesogen molecule, as sketched in Figure 8. The molecule is constituted of three linear segments representing the mesogenic core (in the middle) and two terminal chains linked to the core. The latter are allowed to perform simultaneous  $180^\circ$  flips about the core. For clarity in Figure 8, one side of the planar molecule is black and the other white [23]. In order to respect the core-chain segregation constraints due to the amphiphathic character of the constituent parts of the molecule [24], the cores would expose both of their sides with equal probability (no polarity) whereas the chain segments would expose their black side more than the white one, along the given direction of the  $C_2$  axis. As a result, a transverse polar order occurs along the  $C_2$  axis (indigenous polarity). If a dipole moment were attached perpendicular to the black side of the chain segments, then a spontaneous polarization would be obtained. The polarity does not result from the favoring of one conformation over the other one, but rather from the coupling of the conformations with orientations.

In summary, the IP theory states that the spontaneous polarization originates from a statistical biasing of mesogen conformations that derives from steric interactions in tilted smectic layers stacked one over the other. The temperature dependence of the polarization would simply be a direct consequence of molecular packing considerations. Recent computations of