ADVANCES IN LIQUID CRYSTALS

A SPECIAL VOLUME OF 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 ferrielectric 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 ferrielectric 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
# CONTENTS

**Molecular Engineering for Ferroelectricity in Liquid Crystals**
*By Daniel Guillon*

**Large Electroclinic Effect and Associated Properties of Chiral Smectic A Liquid Crystals**
*By R. Shashidhar, J. Naciri, and B. R. Ratna*

**Pyroelectric Studies of Polar and Ferroelectric Mesophases**
*By L. M. Blinov*

**Ferroelectric LC-Elastomers**
*By Rudolph Zentel, Elisabeth Gebhard, and Martin Brehmer*

**Structure, Mobility, and Piezoelectricity in Ferroelectric Liquid Crystaline Elastomers**
*By F. Kremer, H. Skupin, W. Lehmann, L. Hartmann, P. Stein, and H. Finkelmann*

**Orientational Effects in Ferroelectric and Antiferroelectric Liquid Crystals Using Infrared Spectroscopy**
*By A. Kocot, J. K. Vij, and T. S. Perova*

**The Structure and Properties of Antiferroelectric Liquid Crystals**
*By Yu. P. Panarin and J. K. Vij*

**Order Parameter Variation in Smectic Liquid Crystals**
*By Steve J. Elston and Nigel J. Mottram*
CONTENTS

STRUCTURE AND ORIENTATION OF MOLECULES IN DISCOTIC LIQUID CRYSTALS USING INFRARED SPECTROSCOPY

By T. S. Perova, J. K. Vij, and A. Kocot

ROTATIONAL DIFFUSION AND DIELECTRIC RELAXATION IN NEMATIC LIQUID CRYSTALS

By William T. Coffey and Yuri P. Kalmykov

AUTHOR INDEX

553

SUBJECT INDEX

571
MOLECULAR ENGINEERING FOR
FERROELECTRICITY IN LIQUID CRYSTALS

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CONTENTS

I. Introduction
II. Conceptual and Theoretical Aspects
   A. Ferroelectricity in Tilted Smectic Phases
   B. The Boulder Model
   C. Molecular Statistical Theory of Ferroelectric Ordering
   D. Indigenous Polarization Theory
   E. Ferroelectricity from Achiral Calamitic Molecules
   F. Induced Ferroelectricity from Achiral Banana-Shaped Molecules
III. Molecular Design for Smectic C* Phases
    A. Role of the Dipole Moment Strength
    B. Location of the Chiral Center
    C. Molecular Modeling
    D. Role of the Enantiomeric Excess
    E. Role of the Terminal Aliphatic Chains
    F. Fluorination of Smectogenic Molecules
    G. Influence of Siloxane Groups
    H. Other Forms of Chirality
IV. Molecular Designs for Other Polar Phases
    A. Polyphilic Derivatives
    B. Perfluorinated Swallow-Tailed Compounds
    C. Achiral Banana-Shaped Molecules
V. Ferroelectricity in Columnar Mesophases
   A. Chiral Columnar Mesophases
   B. Columnar Mesophases with Axial Polarity
VI. Antiferroelectricity in Liquid Crystals
VII. Conclusion
Acknowledgments
References

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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 materials.

![Chemical structure and mesomorphic behavior of the first smectic C* ferroelectric liquid crystal synthetized by P. Keller and co-workers](image)

**Figure 1.** Chemical structure and mesomorphic behavior of the first smectic C* ferroelectric liquid crystal synthetized 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

![Symmetry elements of the smectic C and smectic C* phases.](image)
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:

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

\[ E_c = \frac{\pi^4}{4} K_{33} \frac{\theta^2}{p^2P} \]  

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 \( \theta_{\text{str}} \) 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:

\[
P = \sum_{i} D_i P_i \tag{3}
\]

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.
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]:

\[ \vec{P} = \mu (\vec{n} \cdot \vec{z}) (\vec{n} \wedge \vec{z}) \]  
\[ \mu = \frac{-15}{4} \left( \frac{\rho^2}{kT} \right) (\vec{s} \cdot \vec{d}) d^2 \Gamma (D/L)^6 (2\chi_\perp + 15\Delta \chi + \Delta \chi_\perp) \]  
\[ \Gamma = (\vec{d} \cdot \vec{a}) [(\vec{m} \wedge \vec{d}) \cdot \vec{a}] \]
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 \( \Delta \chi_\perp \approx (\chi_{xx} - \chi_{yy}) \) 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

\[\text{Figure 6. Schematic of a chiral molecule with a substitution group in the alkyl chain. The vectors are defined in the text (adapted with permission from Ref. [20]).}\]
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° 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 amphipathic 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 C2 axis. As a result, a transverse polar order occurs along the C2 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
spontaneous polarization using this theory indicate a reasonable agreement with experimental values [25].

E. Ferroelectricity from Achiral Calamitic Molecules

A distinct approach to producing new polar materials consists in using a polyphilic effect for the formation of polar self-assemblies [26,27] exhibiting longitudinal ferroelectricity along the long molecular axis, in contrast to the previous structures explored where ferroelectricity is present in a direction perpendicular to the molecular axis. Polyphilic molecules with A–B–C–A structure contain three (or eventually more) different moieties with a distinct chemical nature; due mainly to the amphipathic character, these subunits have a tendency to segregate in microdomains in space [28] (intralamellar polyphilic effect; see Fig. 9). If the molecule is noncentrosymmetric with both ends being of the same chemical nature, then centrosymmetric or noncentrosymmetric stacking of individual layers leads to antiferroelectric or ferroelectric materials, respectively. As a consequence, longitudinal electric polarization could be obtained in smectic phases of polyphilic molecules where the centrosymmetric arrangement of the layers is disfavored. In such a phase, called also smectic $A_p$ phase (p for polar) in the literature [29], the driving forces are chemical and steric, which lead to the appropriate sequence of layers. Moreover, if the molecules are tilted within each layer, the smectic $C_p$ phase thus obtained is different from the classical smectic $C^*$ widely discussed before. In this case, the polarization is
expected to lie along a well-defined axis, which can be the layer normal or any other direction. As a consequence, it is possible to imagine tailoring mesomorphic materials with specific polarizations. However, it should be emphasized here that this longitudinal polarization cannot be easily rotated by an electric field.

Systems with more than three different types of layers can also exhibit polarization. Let us consider, for example, molecules containing two different rigid parts and two flexible chains of quite different lengths; they could self-assemble into layers formed with distinct sublayers (Fig. 10). Finally this concept can be extended to a number of nonchiral oligomers of mesogens, and of main chain polymers formed of mesogens and several nonchiral block copolymers. All these systems may form layered structures in which the molecular dipoles are oriented side by side and parallel. In order for the system to be stabilized, the incompatibility between the different sublayers should dominate with respect to the unfavorable dipolar lateral interactions.

Figure 9. Schema of strategy to obtain polar mesophases using polyphilic effect. (a) Intralamellar polyphilic effect leading to the formation of polar smectic layers; (b) interlamellar polyphilic effect leading to the formation of polar condensed phase [with permission from Nature 359, 621 (1992), Macmillan Magazines Ltd.].
Figure 10. Self-assembly of molecules (containing four different molecular species) into a ferroelectric layered system. Each individual layer is formed with distinct sublayers.

More generally, from the point of view of the different forces acting in the case of molecules with A–B–C structure, the intralayer dipole–dipole interactions are expected to be much more important than the interlayer ones, since the interlayer spacing (about 30 to 50 Å, for example with calamitic mesogens) is much larger than the average lateral distance (about 5 Å between individual molecules within the smectic layers). The intralayer chemical interactions (amphiphilic interactions) have a tendency to promote polar order in a single layer. This kind of interaction should be more important than the intralayer dipole interactions which, in contrast, favor the antiferroelectric order inside one single layer. Finally, the interlayer dipole interactions (between fixed molecular dipoles) should be more important than the interlayer van der Waals interactions which promote antiferroelectric order between successive smectic layers, in order for the system to exhibit a global ferroelectric order. Theoretical calculations indicate that a ferroelectric arrangement of twin-molecules, formed by two rigid mesogenic moieties linked to a central flexible spacer and ended by two similar flexible aliphatic chains, is energetically allowed [30].

In a more recent paper [31], Prost and co-workers have shown that calamitic polyphilic molecules with A–B–C–A structure are better candidates for obtaining longitudinal ferroelectric smectic phases than
calamitic molecules with A–B or A–B–C structure. They considered A–B–C–A and A–B'–C–A molecules (F⁺ and F⁻ molecules) where the dipoles in the B moieties are respectively inverted and developed a Landau theory for a F⁺/F⁻ mixture, where the competition between ferroelectricity and other forms of ordering such as antiferroelectricity are discussed. Depending upon the concentration of F⁺ molecules in the mixture, a variety of different possible structures result, among them a “stripe” phase with an interlayer ferroelectric and an intralayer antiferroelectric arrangement, or a ferroelectric longitudinal phase (inter- and intralayer ferroelectric ordering).

F. Induced Ferroelectricity from Achiral Banana-Shaped Molecules

In a structural study of main-chain polymers with two different spacers, Watanabe et al. [32] reported that a bilayer smectic phase could be obtained. This phase with a C₂ᵥ symmetry could thus be ferroelectric even if the system is nonchiral. This can be achieved if two different aliphatic spacers with odd numbers of carbon atoms are introduced into the polymer backbone in a regular, alternate way, so that they can segregate into specific microdomains. In such a system, the ferroelectricity is parallel to the layers.

Following the same direction but with low molecular weight compounds, a ferroelectric smectic phase has been obtained from banana-shaped achiral molecules [10] under electric field. In this case, the origin of the electric field-induced ferroelectricity was ascribed to the very efficient packing of the banana-shaped molecules within the smectic layers, resulting in a polar phase with C₂ᵥ symmetry. Because of their specific shape, the molecules can be closely packed and also aligned in the direction of bending (Fig. 11). Each layer is biaxial and the refractive indices are different in the bent direction (y axis) and in the direction normal to the y axis (x axis). There is a twofold axis along the y axis and two mirror planes perpendicular to the x and z (normal to the layers) axis, respectively, but there is no mirror plane perpendicular to the twofold axis. As a result, it is expected that spontaneous electric polarization will be obtained along the y axis, i.e., in the bent direction. This close packing of the molecules leads to a packing of the dipoles, producing a polar order parallel to the plane of the smectic layers; the same effect had been proposed earlier to explain the molecular origin of the spontaneous polarization in the chiral smectic C* phase of banana-shaped molecules [33].

In a very recent paper [11], D. R. Link et al. reported the results of optical microscopy studies of such compounds in freely suspended films and in bookshelf electro-optical geometries. They demonstrated that the bulk states are either antiferroelectric–racemic with a layer polar direction and handedness changing sign regularly from layer to layer, or antiferroelectric–chiral
with a uniform layer handedness. They conclude that the chirality of the smectic phase observed depends essentially on two factors: on the one hand, the intralayer collective polar ordering of the banana-shaped molecules, and on the other, the intralayer collective tilt of the molecular planes. The corresponding stabilization of adjacent layers can be easily changed by applying a weak electric field, resulting in a transition from an antiferroelectric state to a ferroelectric one.

III. MOLECULAR DESIGN FOR SMECTIC C* PHASES

One of the main objectives which has driven the synthesis of many smectic C* materials was the goal of obtaining high-spontaneous-polarization materials which at the same time exhibit good thermal stability. The absolute value of the spontaneous polarization is a critical parameter because it determines the main parameters of the electro-optical properties. However, the synthesis of a large number of FLCs with different structures has shown that the values of the spontaneous polarization measured were fairly low with respect to the values which were expected from the magnitude of the molecular permanent dipole moment [34]. These low values were attributed to the free rotation of the molecules in the phase. It is clear that the degree of free rotation will depend upon the molecular
architecture, and particularly upon the steric constraints induced by the molecules within the smectic layer. Other molecular physical properties may also play a role in the establishment of the spontaneous electric polarization in the smectic C* phases. These are the magnitude of the dipole moment, the positions inside the molecule of the chiral center and the dipole, the coupling between the dipole and the chiral center, and the value of the tilt angle of the molecules within the smectic layers.

A. Role of the Dipole Moment Strength

Figure 12 illustrates, through the investigation of three compounds with similar molecular structures, the effect of the lateral dipole moment on the value of the spontaneous polarization, $P_s$. In the case of DOBAMBC, the value of $P_s$ at 76°C is $3 \text{nC/cm}^2$. This value is very small when compared to those measured in ferroelectric crystals, in the order of the $\mu$C/cm$^2$. Indeed,

![DOBAMBC](image1)

$|P_s| = 3 \text{nC/cm}^2$

![HOBACPC](image2)

$|P_s| = 15 \text{nC/cm}^2$

![HOBACNPC](image3)

$|P_s| = 176 \text{nC/cm}^2$

Figure 12. Example of variation of the spontaneous polarization as a function of the magnitude of the dipole moment.
to estimate the effective dipole moment per molecule, one has to use the expression \( \mu_{\text{eff}} = P_s / \rho_0 \), where \( \rho_0 \) is the number density of the molecules. Assuming that the volumic density of DOBAMBC is about 1 g/cm\(^3\) (which is a classical value for calamitic liquid crystals [35]), the effective molecular dipole is quite low, close to \( 10^{-2} \) Debyes. Knowing the actual value of the transverse dipole of DOBAMBC, \( \mu_\perp \approx 1.5 \) D, the yield factor which measures the strength of the polar order leads to \( f = \mu_{\text{eff}} / \mu_\perp \approx 10^{-2} \). This low value of the polar order parameter indicates clearly that the value of the spontaneous polarization in DOBAMBC is far from what would be expected were all dipoles oriented in the same direction. When the methyl group of the chiral center is replaced by a chlorine atom, the value of \( P_S \) at saturation, 15 nC/cm\(^2\), is five times higher than that obtained for DOBAMBC. Moreover, with the substitution of the chlorine atom for a cyano group, well known to exhibit a strong dipole moment (about 4 Debyes), \( P_S \) reaches a saturated value of 176 nC/cm\(^2\).

### B. Location of the Chiral Center

The magnitude of the dipole moment is not the single parameter for the variation of the spontaneous polarization. Until now, it had been shown and accepted that the positions of both the chiral center and of the transverse dipole moment inside the molecular architecture must be taken into account [36,37]. We have considered above (Sect. III.A) the case of molecules in which the transverse dipole moment is localized at the same position with respect to the rigid core (Fig. 12). Let us examine now the effect of the chiral center at different positions (Fig. 13). For example, in the case of DOBAMBC, the spontaneous polarization becomes 15 times higher when the chiral center is moved closer to the rigid core of the molecule (DOBA-1-MBC compound [38], \( P_S = 42 \) nC/cm\(^2\)). Another example is illustrated by the comparison of the MBRA8 and MORA8 compounds, which were the first ferroelectric liquid crystals exhibiting a stable smectic C* at room temperature [39]. In this case also, and despite the fact that the rigid cores are not exactly the same, the \( P_S \) values obtained are higher when the chiral center and the dipole moment are close to the rigid core [40].

These effects have to be analyzed in the framework of the general description of the smectic phases: the lateral arrangement of the molecules is mainly determined by the interactions between the rigid and polarizable parts, whereas the aliphatic chains are in a disorganized state. Thus, if the chiral center and the transverse dipole moment are localized in the aliphatic chains far from the rigid core, the conformational freedom of the chains would induce a minimum coupling between these two fundamental molecular characteristics. Finally, the introduction of chirality very close to the rigid core will deeply break the symmetry of the smectic C phase.