

FERROELECTRIC LIQUID CRYSTALS

A UNIQUE STATE OF MATTER

David M. Walba

OUTLINE

1	Introduction	2
2	Ferroelectric Polarization in Liquid Crystals—a Novel Chirality Phenomenon	2
2.1	Polar order in condensed matter	2
2.2	Polar liquids—ferroelectric liquid crystals	4
2.3	The geometry of the C* phase and the convention for the sign of P	9
2.4	Optoelectronics using FLC thin films in the SSFLC geometry	10
2.5	Measurement of the sign and magnitude of P using SSFLC cells	14
3	Empirically Designed FLC Compounds	15
3.1	Empirical rules for FLC design and FLCs known prior to 1980	15
3.2	Empirically designed FLCs reported between 1980 and 1985	18
3.3	Breaking the 100 nC/cm ² barrier—some modern high polarization FLCs	22
3.4	Smectic C hosts and chiral guests—evaluation of C* materials by mixing	22
4	Early Models for the Molecular Origins of the Polarization in FLCs	25
5	The Boulder Model for the Molecular Origins of P	27
6	Tests of the Boulder Model	31
6.1	Nonylbenzoates substituted with dipoles on the alkyl tail.	31
6.2	An interpretation of the polarization of alkoxyphenylbenzoates	36
6.3	FLC Polymers	42
7	Conclusion	44
8	Acknowledgements	44
9	Reference	44

1 Introduction

The study of ferroelectric liquid crystals (FLCs), a class of materials first discovered just fifteen years ago, has developed into a rapidly growing multidisciplinary field involving physicists, electrical and computer engineers, and chemists. Problems of both fundamental scientific interest and a more practical nature are being addressed, as research teams work towards an improved understanding of the physics and chemistry of FLCs, as well as developing devices such as flat panel computer displays and components of sophisticated optical computing systems based upon the technology.

In this paper, the symmetry argument for the ferroelectricity of FLC phases, and a description of geometry of the supramolecular assembly is presented. In addition, a brief discussion of basic FLC devices is given to impart some understanding of how important FLC properties are measured, and how the compounds might be used. The focus of this paper, however, is upon the chemistry of FLCs, with emphasis on stereochemistry and the relationship between molecular structure and the macroscopic electric polarization which characterizes these materials and makes them unique among known liquids.

2 Ferroelectric Polarization in Liquid Crystals—a Novel Chirality Phenomenon

2.1 Polar order in condensed matter

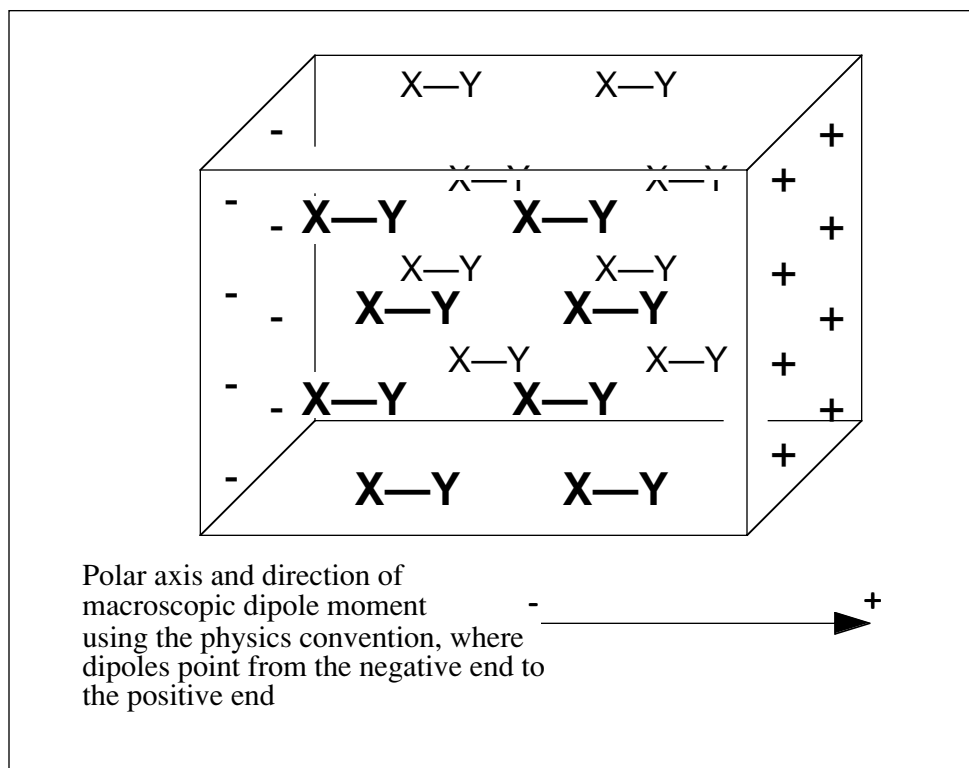
The existence and consequences of polar order in organic materials is scientifically fascinating and technologically important. In order to understand the order occurring in FLCs, it is useful to begin with a very brief description of polar order in macroscopic organic samples in its most common context—single crystals.¹

Thus, it is quite common for organic molecules to crystalize such that the resulting macroscopic self-assembly (a single crystal) possesses polar orientation of functional groups, as illustrated schematically in Figure 1 with a hypothetical crystal structure of the molecule X—Y. The drawing illustrates a cubic "slice" of the crystal, and in the crystal all the molecules are pointing in the same direction, along a polar axis.

As indicated, if the molecule X—Y possesses a dipole moment ($\delta^-X—Y\delta^+$), then the crystal would possess a macroscopic electric dipole, oriented along the polar axis. Indeed, the term "electrically polar" has been suggested as a general descriptor for crystals possessing such order,^{1a} though this seems non-ideal since polar order can occur without measurable electric polarization (e.g. if the dipole moment of X—Y were vanishingly small).

As indicated in the Figure, the physics convention is used to describe the direction of a dipole moment. This point about dipole direction is important, and some further discussion is warranted. Thus, in chemistry, dipoles are generally considered to be pointing from positive to negative. This is contrary to the physics convention, however, where an electric field, for example between parallel charged plates, always points from the positive plate to the negative plate (the direction a positive charge would move in the field). Because of the convention regarding the direction of electric fields, dipoles in physics point from negative to positive. This is how the dipole would prefer to orient in the field between the charged plates, such that the dipole is pointing in the same direction as the field.

Figure 1. Cubic "slice" of a hypothetical polar crystal composed of molecules $\delta^-X-Y\delta^+$. The crystal possesses one polar axis, and the magnitude of the electric polarization can be expressed as charge/unit area at a surface normal to the polar axis, or as dipole moment/unit volume.



The magnitude of the macroscopic dipole moment of a polar crystal could be expressed in Debye/crystal. In these units, large single crystals could possess impressive sounding dipole moments. For example, if the X—Y dipole were 1 Debye, and the volume occupied by each molecule were 50\AA^3 , then the dipole moment of a 1 mm^3 crystal would be $\cong 2 \times 10^{19}$ Debye!

A more meaningful way to express the magnitude of the electric dipole is in terms of a polarization density, i.e. dipole moment/unit volume, or more commonly charge/unit area (e.g. in units of Coulombs/cm²). Given the density of the medium and the molecular weight of the molecules (molecules/unit volume), the former units can be converted to the chemically convenient form of Debye/molecule (giving the net component of the molecular dipole oriented along the polar axis). Herein, the net macroscopic polarization density, which is a vector quantity, is denoted as **P**, and is referred to as simply the polarization.

For all known examples, electrical polarity only occurs in liquids when the material is chiral. Indeed, there is a relationship between chirality and polarity, but due to unfortunate usage of terms, this relationship is a source of some confusion. It therefore seems useful to discuss the relationship between polar order, acentricity (non-centrosymmetry) and chirality explicitly.

First, as suggested in Figure 1, an achiral self-assembly can possess polar order. Indeed, achiral polar crystals composed of achiral or racemic compounds are common (an interesting example is given in this paper). Thus, chirality is certainly not necessary for macroscopic polarity. Also, a

non-racemic mixture of organic molecules does possess restrictions upon the possible symmetries of the medium. Specifically, there can be no improper axes of symmetry in the point group describing the chiral material. This implies that there can be no inversion center in such a material, which is therefore denoted as non-centrosymmetric, or acentric.

The crucial point is this. While all polar media are acentric, an acentric medium is not necessarily polar. That is, a chiral material need not possess polar order. A very easy example to visualize is a chiral melt, or solution of chiral, non-racemic molecules. Such a medium is isotropic, and clearly cannot possess a polar axis, any macroscopic polarization, or indeed any property described by a vector. The medium is, however, acentric, and exhibits the property of optical activity (an axial second rank tensor). This point is not limited to isotropic media. There are many non-centrosymmetric crystal classes, wherein the crystals are composed of chiral molecules of a single antipode, but which are not polar. Common examples are crystals in class 222, e.g. crystals in space groups P222 or P2₁2₁2₁.²

The confusion arises from the fact that in crystallography, the term "polar crystal class" is used synonymously with "non-centrosymmetric crystal class", even when no net macroscopic polar order occurs in the non-centrosymmetric crystal.² In this paper, the term polar order (or just polar) is used to describe media with symmetry allowing the existence of a macroscopic dipole moment. Such a medium could be composed of chiral or achiral molecules. All polar media are non-centrosymmetric, but not all non-centrosymmetric media are polar. Finally, all chiral media are non-centrosymmetric, but not all chiral media are polar.

In general, the magnitude of **P** of a polar crystal is dependent upon temperature, and crystals exhibiting a change in polarization with temperature are termed pyroelectric. Pyroelectricity is a very valuable effect, and is confined only to materials possessing polar order. In some cases, relatively rare in organics, the direction of **P** can actually be switched by application of an external electric field. A polar crystal capable of such switching is termed ferroelectric, by analogy with ferromagnetism.

In addition, the magnitude of **P** changes with pressure applied to the crystal, leading to the phenomenon of piezoelectricity. Piezoelectricity is also very valuable (e.g. modern microphones are based upon the phenomenon), and can occur in most (but not all) non-centrosymmetric crystals—even those which are non-polar.² Finally, macroscopic polar order in a crystal leads to certain potentially useful nonlinear optical (NLO) properties. Thus, for example, polar crystals in general possess "symmetry-allowed" non-zero second order hyperpolarizability $\chi^{(2)}$. The second order hyperpolarizability, like piezoelectricity, is not limited to polar crystals.

The technological importance of these "effect" solids (piezoelectric, pyroelectric, ferroelectric and nonlinear optical) has driven considerable research directed towards achieving controlled, polar orientation of organic functional groups in macroscopic materials. For example, in addition to crystals, macroscopic polar order has been achieved in electrically polled polymer glasses,^{3,4} by polar deposition of Langmuir-Blodgett multilayers,⁵ and by controlled growth of self-assembling multilayers.⁶ Many novel materials potentially useful for their NLO properties, piezo- and pyroelectricity have been obtained by these techniques.

2.2 Polar liquids—ferroelectric liquid crystals

For practical and scientific reasons, the possibility of spontaneous polar order in liquid phases is a fascinating prospect. Naturally, as discussed above, no isotropic medium can be polar. However,

Ferroelectric Liquid Crystals

the existence of anisotropic liquids has been known now for over 100 years. All anisotropic liquids are termed liquid crystals (LCs), and a great wealth of "crystal structure" classes and molecular structures have been explored in the context of liquid crystal chemistry and physics.⁷

Liquid crystals may be divided into two broad classes; lyotropic LCs and thermotropic LCs. Lyotropic LCs occur only when two immiscible phases are present—often water and an amphiphilic organic compound or mixture. Phases occurring in synthetic lipid vesicles and biological membranes are considered as liquid crystalline. While lyotropic LCs are extremely important—aside from biological materials, some high strength polymers, such as Kevlar, are created by exploiting lyotropic liquid crystallinity—they lie outside the scope of this discussion. Recent research from the laboratories of Blinov, however, has successfully demonstrated ferroelectricity in a lyotropic system (dipalmitoyl phosphatidyl choline with 30% wt ethylene glycol and 15% cholesterol),⁸ and the obvious potential biological relevance of this work suggests that the study of ferroelectric lyotropics will become increasingly important in the future.

Thermotropic liquid crystals, the class upon which this discussion will focus, are pure compounds or homogeneous mixtures possessing one or more anisotropic liquid phases at temperatures between the melting point, below which the material exists as a crystalline solid, and "clearing point", above which the material exists as an isotropic liquid. Of course, the melting point and clearing point are temperatures, with the liquid crystal phases occurring in certain temperature ranges between the melting point and clearing point—thus the term thermotropic LCs.

In general, the phase behavior of liquid crystalline compounds, often termed mesogens, is observed both upon heating from the crystalline solid, and upon cooling from the isotropic liquid. Not surprisingly, supercooling also often occurs, and in many instances LC phases are only observed upon cooling, at temperatures below the melting point. Such phases are termed monotropic, and are not thermodynamically stable, but are kinetically stable and in general observable reproducibly. When LC phases are observed upon heating the sample, then they are thermodynamically stable phases of the material, and are termed (somewhat unfortunately) enantiotropic.

While many liquid crystal phases ("crystal classes") have been characterized, we focus on the typical phases illustrated in Figure 2. As indicated in the Figure, we assume that the phases and transition temperatures are the same upon heating and cooling of this particular hypothetical mesogen. Thus, given "rod-shaped" molecules, in the isotropic liquid the molecules are randomly oriented, and the centers of mass of the molecules are moving as in any isotropic liquid. Upon cooling, the compound could simply freeze into a crystalline solid.

Often, however, upon cooling the isotropic melt, at some well defined phase transition temperature a new liquid phase occurs wherein the molecular rods are oriented parallel to each other. If no other order is present, such a phase is called nematic. In the nematic phase, the centers of the rods still possess isotropic liquid order, but with the rods aligned as they are, the phase is strongly anisotropic (e.g. with respect to dielectric constant and index of refraction), as is easily observed under the polarizing microscope. The long axis of an individual molecule, as well as the axis along which the molecules are oriented in the phase, is termed the director, which is often denoted by a unit vector \hat{n} .

Upon cooling the nematic phase, often a new liquid phase in which the molecules self-assemble into layers, occurs. Such layered phases are termed smectic liquid crystals, and if the director is parallel to the layer normal (i.e. the molecules are standing straight up relative to the plane of the

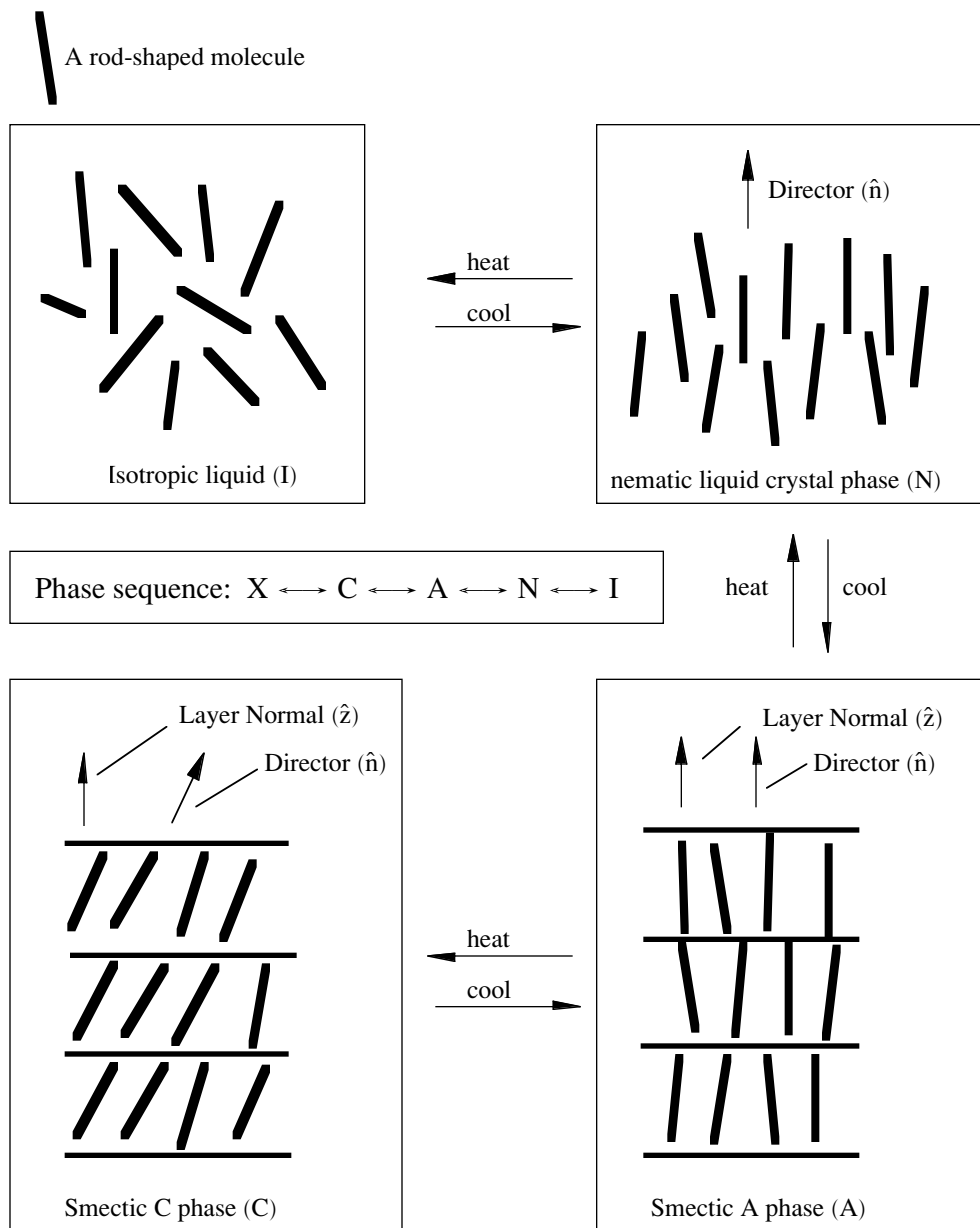


Figure 2. Some thermotropic liquid crystal phases.

layers), then the phase is termed smectic A. As indicated in the Figure, the layer normal is generally denoted by the unit vector \hat{z} .

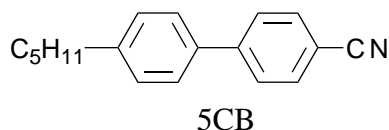
Finally, a more ordered phase often occurs below the smectic A, in which the molecules are tilted with respect to the layers. The angle made between the layer normal and the director is termed the **tilt angle**, denoted by θ , and is generally temperature dependent. The tilt defines a plane—containing \hat{n} and \hat{z} —called the **tilt plane**. This phase, called the smectic C simply because it was the third smectic phase discovered chronologically, is the most important from the point of view of ferroelectricity in liquid crystals.

The smectic C (or just C) phase is the most ordered of all liquid crystal phases wherein no nearest neighbors are invariant in time (i.e. true "monomeric" liquids). Thus, the C phase consists of a

Ferroelectric Liquid Crystals

stack of true two dimensional liquids—within the layers the centers of the rods move as an isotropic two dimensional liquid, but motion across layers is much less free.

A priori there is no reason why any of these phases cannot possess polar order and exhibit a macroscopic polarization. For example, consider a nematic phase of 5'-n-pentylcyanobiphenyl molecules (5CB, a famous nematic LC used in watch displays). If the cyano groupings of 5CB would all point in the same direction (or even if any excess of dipoles pointed in the same direction) in the nematic phase, then a macroscopic electric polarization would clearly result. There is no fundamental physical law preventing such spontaneous order—similar events occur in crystals routinely. Indeed, discussion of the possible existence of ferroelectric smectic A phases appeared in the literature many years before ferroelectricity in any liquid was demonstrated.⁹



However, no evidence for the existence of ferroelectricity in a nematic or smectic A phase has ever actually been obtained. Empirically, all evidence to date shows that, while the molecules self-assemble with their directors parallel, no polar order along the director has ever been observed in any liquid crystal phase. This empirical fact is sometimes stated as follows: The properties of all known LC phases are invariant with sign of the director; [$\hat{n} \longrightarrow -\hat{n}$].

In addition, polar order has never been observed normal to the director in any untilted LC phase, even when the phase is chiral (i.e. composed of chiral, non-racemic molecules). Thus, chiral nematic and chiral smectic A phases belong to the family of materials which are chiral, acentric and anisotropic, but not polar.

If a ferroelectric liquid is the goal, liquid crystals seemed decidedly uncooperative. Though polar order often occurs spontaneously in crystals, LC phases seem to spontaneously orient only just up to the point of polar order, but never cross the line. And this is where things stood until 1973, when physicist Robert Meyer saw a way of forcing polar order upon a liquid crystal system based upon a simple but profound symmetry argument, as follows.^{10,11}

It is useful here to consider the point group symmetry of LC phases. This is somewhat different than point group symmetry of crystals, where the average nuclear positions are invariant. However, it is natural to consider the symmetry of a liquid as the group of symmetry operations which leave the phase unchanged on the time average. Thus, a restatement of the empirical rule [$\hat{n} \longrightarrow -\hat{n}$] is that all known LC phases possess at least one C_2 axis normal to the director.

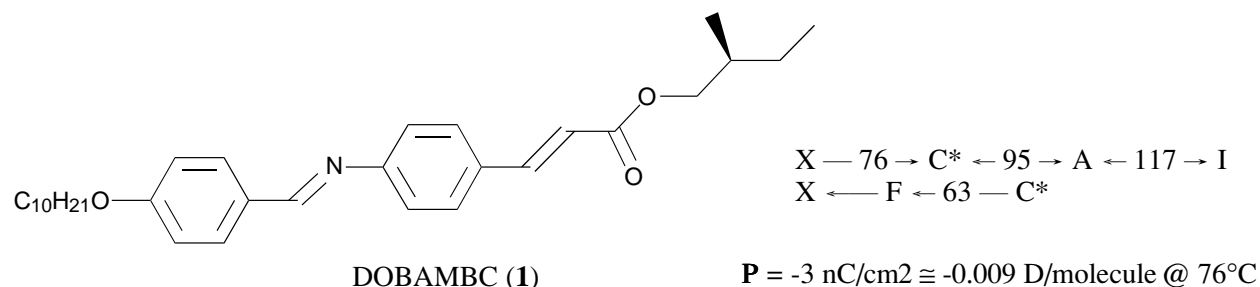
Now consider the symmetry of the C phase. First, the occurrence of the layers and tilt in the C phase is an experimental fact unequivocally established by high resolution X-ray scattering experiments. Such experiments cannot, of course, give the location of the atoms as in a single crystal, but the layer structure and average director orientation can be observed.

Given the layers and tilt, the maximum symmetry an achiral C phase can possess includes one C_2 axis normal to the tilt plane, and a σ plane congruent with the tilt plane. There can be no other symmetry elements consistent with the layers and director tilt. Also, breaking either of these symmetry elements would afford polar order. However, since no C phase has ever been shown to

possess polar order, apparently all C phases do possess the maximum possible symmetry consistent with the layers and tilt.

While single component chiral C phases had been known since 1971,¹² Meyer was the first person to realize the simple fact that a chiral phase can possess no reflection symmetry, and therefore the maximum possible symmetry for a chiral C phase is C_2 ! Any medium with C_2 symmetry must possess polar order, and therefore Meyer was able to make his famous prediction that a chiral C phase (denoted C^*) would be ferroelectric (making the reasonable assumption that the direction of the polarization in the polar LC phase would be switchable).¹⁰

While symmetry requires that a C^* phase be ferroelectric, there is no requirement that the magnitude of the polarization be measurable in such a material. It was therefore a real landmark event when in 1975 Meyer, along with Liébert, Strzelecki, and Keller, published the first experimental results demonstrating observable polarization in a ferroelectric liquid crystal (FLC).¹¹ The chemical subject of this early work was (S)-2-methylbutyl 4-(4-decyloxybenzylideneamino)-cinnamate (DOBAMBC, **1**), which served as a standard FLC material for many years, and whose properties have been measured by a variety of methods. The structure, phase sequence, and measured polarization of DOBAMBC are given below.



The structure is typical of C phase mesogens, possessing a rigid core and two "floppy" tails. In the phase sequence, X indicates crystalline solid, F indicates the highly ordered smectic F phase, C^* indicates the smectic C^* phase, A indicates the smectic A phase, and I represents isotropic liquid. The numbers are transition temperatures in degrees centigrade. Thus, DOBAMBC possesses an enantiotropic C^* phase between 76° and 95°C , with a maximum measured polarization of -3 nC/cm^2 , or about $-0.009 \text{ Debye/molecule}$, at 76°C . As suggested by the diagram, the C^* phase supercools considerably, and the smectic F phase is monotropic.

With the synthesis and evaluation of DOBAMBC, the experimental study of the phenomenon of ferroelectricity in liquids began. Since then, an explosion of research and invention aimed at using and improving these novel materials has occurred. For example, we estimate that FLC-related patents, including inventions relating to both devices and chemistry, currently appear at the rather startling rate of 10/week! In addition, research in academic and industrial chemistry, physics and engineering groups is proceeding apace. In the following sections, a brief discussion of the most important basic FLC device geometry is given, along with a short description of how this device is used to measure FLC properties of new materials.

Y

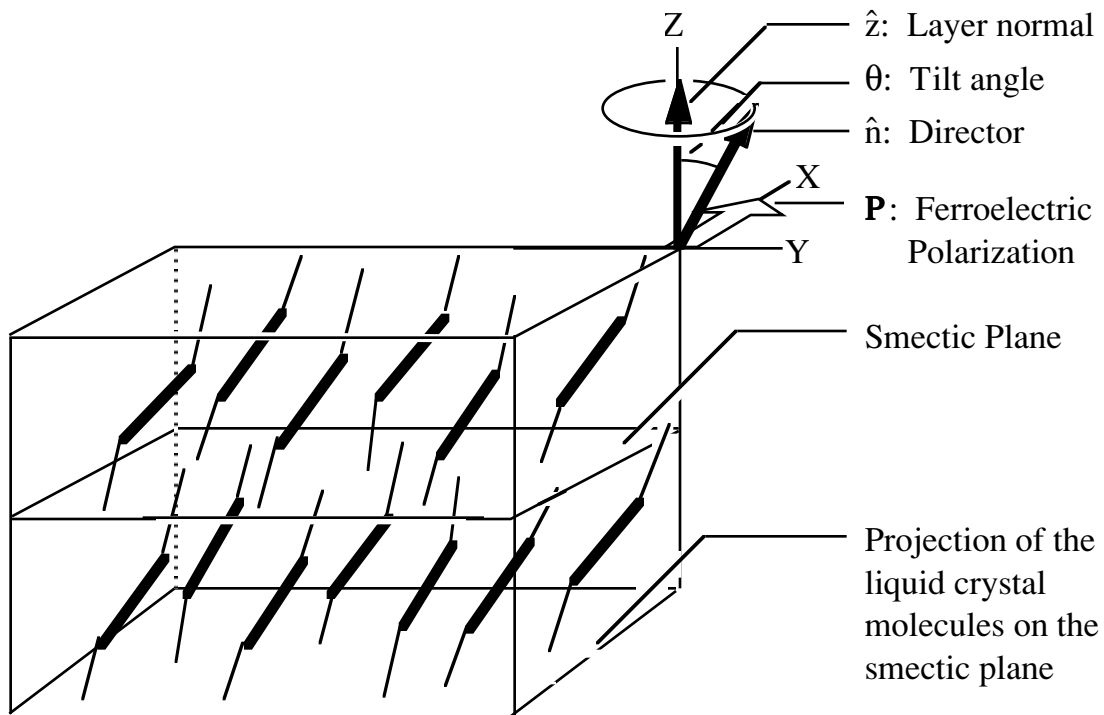


Figure 3. A 3D "slice" of C* phase viewed normal to the tilt plane.

2.3 The geometry of the C* phase and the convention for the sign of **P**

In order to discuss important properties such as the sign of **P** in FLCs, it is necessary to gain some feeling for the geometry of the system. The illustration of C phase order in Figure 2 represents an orthographic projection about one molecule deep, with the layer normal vertical, and the tilt plane congruent with the plane of the page. In Figure 3, a 3-D perspective of a symbolic C* phase from almost the same vantage point, just off the axis normal to the tilt plane, is given. The phase possesses C_2 symmetry, with the C_2 axis oriented normal to the page. The only non-zero component of the ferroelectric polarization **P** is oriented along this axis, normal to the tilt plane, as shown.

The ferroelectric polarization, being a "chirality phenomenon", has a sign for a given material. Enantiomeric materials possess equal magnitude and opposite sign of **P**. By convention, if the polarization vector **P** points in the direction of the cross product of the layer normal and the director ($\hat{z} \times \hat{n}$, a unit vector normal to the tilt plane), then the material is said to possess positive polarization (remember that **P** points from the negative end to the positive end of a dipole). If **P** is opposed to $\hat{z} \times \hat{n}$, then the material has negative polarization. Thus, the material schematically represented in Figure 3 has positive polarization.

In an achiral C phase, while locally the molecules all tilt in the same direction, macroscopically all director tilts lying on the tilt cone indicated in the Figure are degenerate, and indeed the director can "wander" on the tilt cone in passing through the phase for large distances (\cong microns).

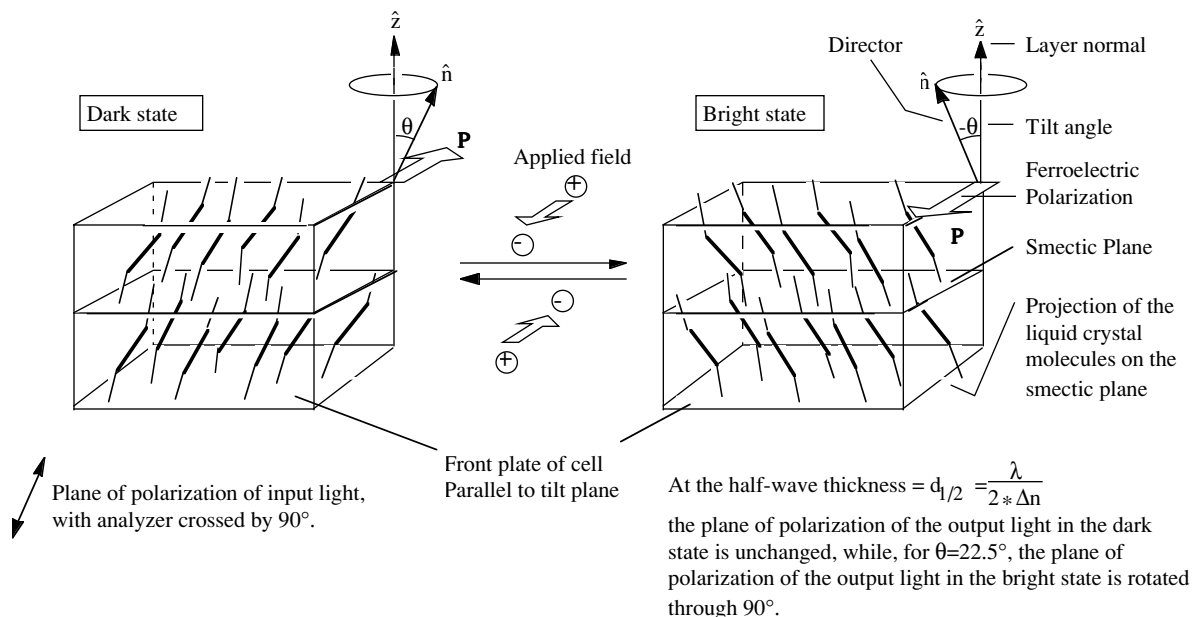


Figure 4. The SSFLC light valve.

In a chiral C^* phase, a helical periodicity in the director orientation with a pitch of about 1-10 μm forms spontaneously. In moving through the phase along the layer normal, the director precesses about the tilt cone with a pitch of about 500 - 5,000 layers. The polarization is constrained to rotate in the phase following this helix, and the macroscopic polarization averages to zero in a typical bulk sample of chiral C^* material. It should be mentioned, however, that the helix is not an invariant property of the C^* phase, and C^* materials with essentially infinite helix pitch have been obtained. While both the polarization and the helix are manifestations of molecular chirality in the phase, they are not intimately related on the molecular level, and there is no fundamental correlation between, for example, the sign of the C^* helix, and the sign of \mathbf{P} .

2.4 Optoelectronics using FLC thin films in the SSFLC geometry

A priori, the ferroelectric nature of a C^* phase should afford a strong coupling between the orientation of the molecules and external fields, thereby leading to an electro-optic device with fast response. Upon the publication of Meyer's work, several research groups began work directed towards development of such a device. The presence of the C^* helix, and other complicating factors, foiled these attempts, however, until Clark and Lagerwall invented the surface stabilized ferroelectric liquid crystal (SSFLC) light valve.¹³

In the SSFLC geometry, the helix is spontaneously unwound due to surface interactions with bounding glass plates. In this case, when the director prefers a parallel orientation with respect to the surface of the plates, and the thickness of the "sandwich" is small relative to the helix pitch, only two "states", or director orientations relative to the surfaces, are allowed, as indicated in Figure 4. In one state, the molecules tilt right by the tilt angle θ , while in the other state they tilt left. In both cases, the ferroelectric polarization vector is pointing normal to the tilt plane (normal to the surface of the glass plates)—either "back" or "forward".

Due to the refractive index anisotropy of typical FLC molecules ($\Delta n \cong 0.1$) these two states have different optical characteristics. When the tilt angle $\theta = 22.5^\circ$, and the thickness of the cell is tuned

Ferroelectric Liquid Crystals

correctly relative to the refractive index anisotropy ($\cong 1.7 \mu\text{m}$ when $\Delta n=0.1$), then the cell behaves as a half wave plate, and can be aligned between crossed polarizers such that one state gives good transmission, while the other state shows good extinction. In the extinguishing state (dark state), the director is aligned parallel to the plane of polarization of the input light. The light passes through the phase unchanged, and is "caught" by the analyzer (a polarizer turned at 90° relative to the input plane).

In the transmitting state (bright state), the director is rotated by 45° (2θ) relative to the plane of polarization of the input light. At the half-wave thickness $= \lambda/(2*\Delta n)$, the output light is rotated through 90° , and passes through the analyzer. Thus, a full 90° "rotation" of plane polarized light is achieved in a layer typically only $1.7 \mu\text{m}$ thick! It is important to note that this rotation has nothing to do with the chirality of the molecules, but is rather a birefringence effect. Half way through the layer, the light is not plane polarized at 45° from the incident angle, but rather is circularly polarized (half the layer being $1/4$ wave thick).

In the absence of external fields, the two surface stabilized states are degenerate, and an SSFLC cell between crossed polarizers shows a mosaic of dark and bright domains under the microscope. However, when an electric field E above a threshold value (usually about $5 \text{ V}/\mu\text{m}$) is applied across the film by connecting electrically conducting glass bounding plates (usually simply glass plates coated with a thin film of the clear conductor indium tin oxide (ITO) commonly used in watch and computer displays) to a battery (for a $1.7 \mu\text{m}$ thick film, a 9 volt battery is sufficient to achieve the threshold field strength), the state with its polarization oriented with the field becomes more stable, and the molecules will "flip" about the tilt cone to align \mathbf{P} in the direction of E if it is not aligned.

The characteristic time required for this flip—the electro-optic rise time τ_r —is given by the equation 1, where τ_r is the time required to go from 10% \rightarrow 90% optical response to an applied voltage step of magnitude E , η is the orientational viscosity, and P is the ferroelectric polarization density, or magnitude of \mathbf{P} .¹⁴ Of course, reversal of the sign of the applied field causes the molecules to flip into the other surface stabilized state with rise time τ_r .

$$\tau_r \cong \frac{1.8\eta}{P * E} \quad \text{equ 1}$$

Given reasonable estimates of attainable values for these material parameters, we estimate that the theoretical limit on $\tau_r \cong 20 \text{ nsec}$,¹⁵ or 50,000 times faster than the optical response time in a fast twisted nematic LC cell (the type used for watch displays and active-matrix TV screens), and about 500,000 times faster than that for the supertwisted nematic cell used in the current generation of high contrast computer displays.

In addition, the SSFLC cell shows very high contrast (1,500:1 demonstrated), high spatial resolution, low power requirements, bistability, and other performance characteristics which make it particularly attractive for many optoelectronics applications.¹⁵ These specifications cannot be duplicated with any other existing technology.

While detailed discussion of FLC devices is beyond the scope of this paper, some mention of this aspect of the field serves to put the more chemically oriented work into broader perspective. And, while there are a great many potentially useful FLC-based devices, including the holy Grail of consumer electronics—flat panel high definition video screens—it seems appropriate to describe an

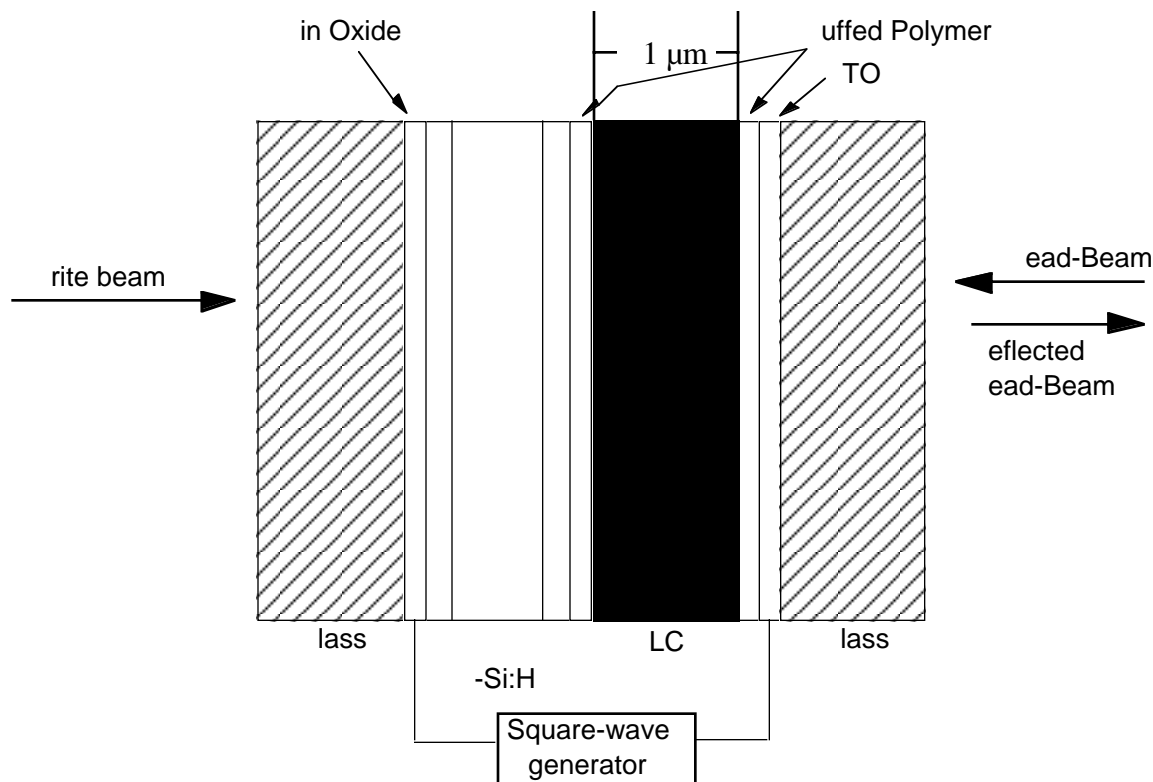


Figure 5. An optically addressed spatial light modulator.

exciting device invention recently disclosed by the Boulder FLC group aimed at applications in the emerging field of optical computing.

In the following paragraphs is briefly described an optically addressed spatial light modulator; a hybrid semiconductor/FLC thin film device which may be considered as a 2-D array of optical transistors.^{15,16} Discussion of this particular device seems appropriate since many of the advantages of FLC materials, and organics in general, in optical computing applications are illustrated.

Thus, a transistor may be considered as a switch, with electrical flow from an input (the source) to an output (the drain) controlled by a second input (the gate). Of course, an SSFLC cell is an electrically addressed optical switch, or shutter. Using an electrical input which can put either $+15\text{V}/\mu\text{m}$ or $-15\text{V}/\mu\text{m}$ across the SSFLC cell, the cell switches between transmitting and extinguishing. If one considers the input light as the source, the output light as the drain, and the electrical signal as the gate, then an SSFLC shutter behaves as an electrically addressed optical transistor.

Naturally, for many optical computing applications, both inputs (the source and the gate) as well as the output must be optical. Shown in Figure 5 is a device developed in Boulder which allows switching of a high resolution array of FLC shutters in parallel using optical input. This device is composed primarily of two thin films—the FLC layer and a three-layer film (p type, intrinsic, and n type, or p-i-n) of amorphous hydrogenated silicon (a-Si:H). The latter material is very commonly used for conversion of solar energy to electricity.

Ferroelectric Liquid Crystals

The FLC and silicon films are sandwiched between clear electrodes, such that an electrical field may be established across the entire device. The FLC film behaves similarly to the SSFLC device described above, except that the thickness is now tuned for "reflection mode". That is, light passes through a single plane polarizer, enters the FLC film, is reflected from the FLC/a-Si:H interface, passes through the FLC film again, and then is either transmitted or extinguished upon interaction with the polarizer, depending upon the state of the FLC molecules in the cell. Reflection mode devices of this type are very common in nematic LC technology (e.g. typical watch displays), and of course, since the light passes through the film twice, optimum FLC thickness is 1/2 that of a transmission mode device ($\cong 0.8 \mu\text{m}$).

The a-Si:H layer is a photodiode. It conducts electricity in only one direction ("forward bias") in the dark. Irradiation with light of energy above the band gap of the a-Si:H causes the layer to conduct also in the "reverse bias" direction. To operate the device, a forward bias field is applied to the cell to switch the FLC film into the dark state. Light falling on the device from the right (the read beam input), passes through the polarizer, then through the FLC film (with the director at 45° to the plane of polarization of the input light), and is reflected from the FLC/a-Si:H interface, but its plane of polarization will be rotated through 90° upon leaving the film, and very little light will get past the polarizer on the way out (the read beam output).

The applied field is now switched to the reverse bias direction. Since the a-Si:H layer is now insulating, the FLC does not feel enough field to switch, and nothing happens. That is until light hits the device from the a-Si:H side (the "write beam"). Where write beam light hits the device, the a-Si:H becomes conducting, charges appear on the FLC side of the a-Si:H film, and the FLC now feels a field strong enough to cause it to switch. When the FLC switches to the "bright" state (the director aligned with the plane of polarization of the input read beam), the read beam output is turned on.

This cycle—erase, reverse bias/write, erase—is continued as fast as the FLC switching speed will allow (with currently available materials, the a-Si:H is faster than the FLC). Clearly, this device can be considered an optical transistor, where the write beam is the gate, the input read beam is the source, and the output read beam is the drain. The device shows a very strong nonlinearity, since the FLC layer will only switch in reverse bias when enough charge is separated in the a-Si:H film (related to the number of photons absorbed by the film) to achieve the threshold switching voltage across the FLC.

While interesting, a single optically addressed switch running at 100 KHz (the currently achievable FLC bandwidth is $\cong 30\text{KHz}$, and the theoretical limit is about 1 MHz) is not particularly useful. Typical electronic devices can run much faster than this (a Mac II CPU runs at about 16 MHz). The advantage of the device described above is that the write beam can switch a small domain of ferroelectric liquid crystal, with the smallest "pixel" size approximately equal to the thickness of the FLC film ($< 1\mu\text{m}$). Thus, the FLC film can modulate light in two dimensions—such devices are termed spatial light modulators (SLMs). A view graph is a spatial light modulator which cannot be "programmed" or changed. An overhead projection display is a large electrically addressed SLM, but is slow.

The a-Si:H/FLC device is an optically addressed SLM capable of being erased and re-written from an optical input in $10\mu\text{sec}$. The spatial resolution of the device is limited by lateral diffusion of charge carriers in the silicon film, and by the thickness of the FLC film, but it is possible that the FLC film thickness will prove the ultimate limit. Given the demonstrated fact that it is possible to switch FLC pixels on the order of $1 \mu\text{m}^3$, one may calculate that the limit on resolution of the

optically addressed SLM is about 10^8 pixels/cm² (currently demonstrated resolution is $3 \times 3 \mu\text{m}$ pixels, or about 10^7 pixels/cm²).^{16b} With a band width (number of write/erase cycles/second) of 100 KHz, the pixel throughput rate of such a device would be 10^{13} pixels/second! That is, we have an array of 10^8 transistors with gates (write beam), sources (input read beam) and drains (output read beam), gain (the read beam can be brighter than the write beam), and automatic nonlinearity (sharp threshold) for switching between bistable states. The "wires" leading into and out of the devices are simply photons propagating through space (or some optically linear medium).

How can one write information to the device at 10^{13} bits/second? Simply by focusing the image from a lens onto the a-Si:H side of the device, and running real-world images past the device in real time (e.g. terrain passing by, or parts running down an assembly line). Once the image is transferred to the read beam output (which, of course, could be coherent light), many possible modes of optical processing could be implemented.

Thus, the advantage of this type of optoelectronic device is that the entire 2-D array of pixels may be written in parallel. The ease of achieving parallel "processing", and ease of interconnects, are two of the most important advantages of optical computing in general. The advantage of the FLC film as the optical modulator in the a-Si:H/FLC SLM is a combination of speed (not too impressive) and interaction strength (contrast and spatial resolution—highly impressive). Thus, even though the "clock" is very slow (100 KHz), the ability to write 10^8 pixels in parallel makes the "bit speed" much more respectable (100 fsec/bit in a 1 cm² device). Finally, it is very easy to create a thin FLC film on semiconductor. Achieving this with other faster (but lower interaction strength) photo-modulation layers (e.g. single organic or inorganic crystals) would be difficult.

2.5 Measurement of the sign and magnitude of \mathbf{P} using SSFLC cells

In addition to their great potential utility in optoelectronic devices, SSFLC cells provide simple methods for measuring the sign and magnitude of \mathbf{P} for FLC materials. Thus, starting with a C* material of unknown sign of \mathbf{P} , it is possible using this simple cell geometry to measure the sign of \mathbf{P} as follows.

Assuming the material possesses a smectic A phase above the C* phase, one may easily find the director in the smectic A phase by simply rotating the cell into extinction. At extinction, the layer normal and director are parallel to the plane of polarization of the input light (actually, at extinction the input plane of polarization is either parallel or perpendicular to the director, but the argument for determining the sign of \mathbf{P} is the same in either case). Application of an electric field and cooling of the sample into the C* phase will cause the director to tilt away from the plane of input polarization by either + or $-\theta$ ($\theta \cong 22.5^\circ$ for many typical FLC materials). Rotation of the cell by either $+22.5^\circ$ or -22.5° will re-establish the extinguishing condition. From this simple experiment it is possible to determine which way the director tilts for a given sign of the applied field—giving the sign of \mathbf{P} directly.¹⁷

The magnitude of \mathbf{P} is also often measured using the SSFLC cell.¹⁸ Thus, the standard cell, using glass plates with ITO coatings, is a parallel plate capacitor with the FLC as dielectric. The current passed by the cell in response to applied electric fields can easily be measured. Upon reversing the sign of the applied field on the cell, a very fast capacitive current peak is observed (resulting from polarization of electron clouds, and other "fast" events), followed by a slower current peak corresponding to the polarization reversal of the ferroelectric layer—when the molecules precess around the tilt cone to align the macroscopic polarization with the applied field.

The temporal response of the polarization reversal current peak corresponds to the electrooptic rise time of the cell (no measurable optical response is induced by the charge motions giving rise to the capacitive current). If the electrode area of the cell is known, then integration of the polarization reversal current peak (total charge passed during polarization reversal) and division by the electrode area affords a measure of the magnitude of \mathbf{P} . Of course, the rise time of the cell can be measured in the same type of experiment by simply recording the intensity of output light from a cell placed between crossed polarizers as a function of time from reversal of the applied field.

Early experiments characterizing FLC films were accomplished using DOBAMBC and similar materials possessing C^* phases only at elevated temperatures, and with low polarizations. In addition, these early FLC materials are Schiff bases, and are inconveniently unstable chemically. The invention of the SSFLC device by Clark and Lagerwall, however, launched an intensive search for new FLC materials with properties optimized for use in devices.

Of course chemical stability is important, as well as switching speed, polarization, birefringence and tilt angle. Also, different device geometries and applications require individually optimized materials. For example, arrays of pixels driven in parallel in devices such as the optically addressed SLM can use FLCs with high polarization, while multiplexed arrays (such as most computer displays), apparently require moderate polarization and the lowest possible viscosity to achieve adequate switching speeds and good multiplexability. The remainder of this paper describes work aimed at the design of FLC materials, treating the early work from a somewhat historical perspective, and finishing with an overview of work from the Boulder FLC chemistry laboratories.

3 Empirically Designed FLC Compounds

Important FLC properties, including polarization, orientational viscosity, birefringence, and tilt angle, derive directly from the structure of the FLC compounds. It is often stated that organic materials have great potential in optoelectronics simply because so many different structures are possible. In FLC chemistry, this statement seems to carry some weight. Thus, based upon some simple empirical rules, intuition, and an intensive screening effort, many useful FLC materials have been obtained. While our intent is not to provide an exhaustive list of the hundreds of FLC structural types which have been reported since 1975, a very brief description of the empirical considerations used to design early FLC materials, and discussion of some historically important early compound types, is given.

3.1 Empirical rules for FLC design and FLCs known prior to 1980

From August of 1973 to July of 1974, Meyer was spending a sabbatical at the Laboratoire de Physique des Solides in Orsay. At the time, this laboratory was well known as one of the outstanding contributors to liquid crystal physics, and also was home to a small group of synthetic chemists focussing on liquid crystals. Meyer, of course, was creating excitement at the prospect of ferroelectricity in C^* liquid crystals, and the challenge of actually obtaining a sample of a C^* material fell upon three chemists at the Lab—Keller, Liebert, and Strzelecki.

To this day, it is not possible to predict with any certainty the phases which will be exhibited by a new "liquid crystal-looking" compound. A knowledge of the structure and properties of known materials, coupled with intuition born of experience in the field, however, provides a powerful tool for design of new materials. The Orsay LC chemistry group, through its own work, knowledge of the literature, and daily interactions with the X-ray crystallographers and physicists at the Lab, had a considerable empirical knowledge base which allowed them to obtain a chiral smectic C

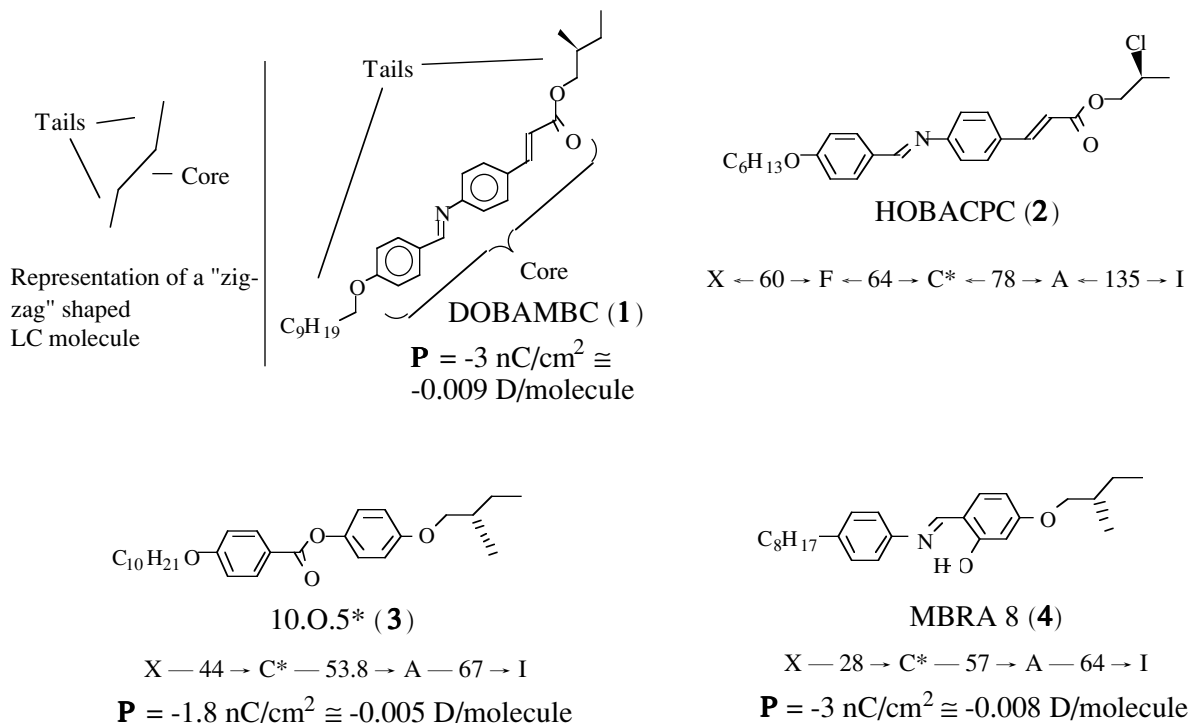


Figure 6. Classic FLCs reported prior to 1980.

material (DOBAMBC) on the first try!^{11,19} This classic piece of LC design work is exemplary of the powerful empirical approach still employed to a large degree.

In general, in 1975 known thermotropic liquid crystals possessed two basic structural features—a "rigid" core and one or two "floppy" tails. The core could be a steroid nucleus, or two or more aromatic or cyclohexyl rings joined by single bonds, or by two atom linking units such as imine or ester groupings. In addition to simple aryl and cyclohexyl cores, many other similar "rigid" polycyclic systems were also known to serve as liquid crystal cores.

Prior to the discovery of ferroelectricity in the chiral smectic C phase, almost all of the work on design and synthesis of liquid crystals was aimed at nematic and chiral nematic (cholesteric) materials. Indeed, the appearance of smectic phases in the phase sequence of a new compound was considered bothersome since such phases had no apparent utility, and simply lowered the stable temperature range of the desired nematic phases.

Even so, many compounds exhibiting smectic phases had been identified and catalogued,²⁰ and the smectic C phase was very well known to the Orsay group. From the information available, a set of empirical considerations for design of a smectic C mesogen could be listed as follows: 1) The core should be relatively long (> two rings); 2) There should be two tails, and both should be relatively long (> four atoms); and 3) The tails should be joined to the core by alkoxy or acyloxy linkages ("outboard dipoles"), and the central linkage of the core should possess a dipole moment normal to the director (such as ester or imine). As indicated in Figures 3 and 4, and in Figure 6, the structure of smectic C mesogens, with their core and two tails, is often represented as a zig-zag. This point is discussed in more detail below.

Ferroelectric Liquid Crystals

The DOBAMBC (**1**) structure (reproduced in Figure 6) was chosen because one required starting material, (S)-2-methylbutyl 4-aminocinnamate, was available in the Lab in connection with another project, and the p-decyloxybenzaldehyde was well known and readily available. Also, the target structure fit all the known empirical requirements for formation of a smectic C phase, and perhaps most importantly of all, the corresponding n-butyl 4-(4-decyloxybenzylideneamino)cinnamate and other homologues in the series had been shown previously to possess rich liquid crystal polymorphism, and in particular smectic phases (which had not, however, been identified as smectic C).¹⁹

Coupling of the aminocinnamate and benzaldehyde derivatives with formation of a Schiff base linkage led to DOBAMBC, which indeed exhibited a C* phase as mentioned above. With this material, Meyer was able to elegantly demonstrate the ferroelectricity of a C* liquid crystal. The polarization, however, was clearly quite low (later shown to be $\cong -0.009$ Debye/molecule), and immediately efforts aimed at synthesis of new FLC compounds with enhanced magnitude of the polarization began in the Orsay group.

In his 1975 paper, Meyer had considered factors which might affect the macroscopic polarization of FLCs, and had written "... if the chiral part of the molecule is only weakly coupled to the polar part, then internal molecular rotations may reduce the polarization." This suggested that direct attachment of an electronegative substituent at the stereocenter might lead to enhanced magnitude of **P**, and in 1976 the Orsay chemists published their synthesis of hexyloxybenzylideneamino chloropropyl cinnamate (HOBACPC, **2**).²¹ Prior to 1980, almost all of the experimental work on FLCs was accomplished with these two classic materials—DOBAMBC and HOBACPC.

Comparison of the polarization values exhibited for various different materials is extremely tricky. Thus, the observed polarization is dependent on the tilt angle, temperature of the measurement (both absolute, and relative to the temperature of the transition into the C* phase), the nature of the thermodynamic transition into the C* phase, the structure of the core (most importantly whether the core has 2 or 3 rings, but other factors can also affect **P**), and even the structure of the achiral tail. The values given in the Figures in this paper are chosen to be representative of the structural classes indicated.

Even given the caveats, it is clear as indicated in Figure 6 that HOBACPC exhibits enhanced polarization density relative to DOBAMBC (by about a factor of 3), in accord with the prediction. Indeed HOBACPC showed the highest polarization density and fastest electrooptic response of any known FLC until the 1980s. The invention of the SSFLC light valve by Clark and Lagerwall was reduced to practice using these materials, and the fast response achievable with HOBACPC provided an impressive lower limit on achievable SSFLC device performance (in particular a 500 nsec electrooptic response to a 50V/ μm driving pulse at 72°C), helping to stimulate interest in the new technology.^{14b}

Even so, the Schiff base LCs in general are well known for their hydrolytic instability, and DOBAMBC and HOBACPC are not exceptional in this regard (e.g. they cannot be purified by chromatography on silica gel, but instead hydrolyze to amine and aldehyde on the column). In addition, as indicated in Figure 6 both Orsay Schiff bases are ferroelectric only at elevated temperatures.

These problems with DOBAMBC and HOBACPC led to some classic work by a group of Russian scientists at Moscow State University and the State Committee of Standards of the USSR in Moscow, directed towards the synthesis of new FLCs with enhanced chemical stability and C*

phases at room temperature. Indeed, this work led to the first "chemically stable"²² FLC materials, and to the first FLCs with C* phases close to room temperature.²³

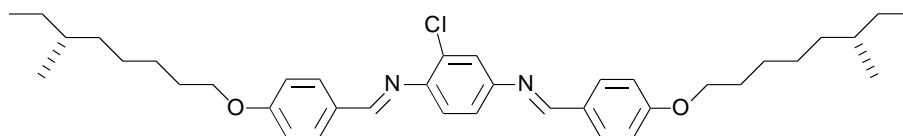
Thus, the bis-alkoxyphenylbenzoate system was well known to favor tilted smectic phases when the alkoxy tails possess more than four carbons.²⁰ This empirical result, when merged with the active amyl alcohol chiral unit long favored by liquid crystal chemists when chirality is required, led to the design of the classic "O.5*" phenylbenzoates exemplified by the 10.O.5* (**3**) structure shown in Figure 6.

In addition, the Russian group designed the 2-methylbutylresorcylicidene-4'-alkylaniline system (known as the MBRA series) based upon the desirable LC properties of the simple Schiff bases, in combination with greatly enhanced hydrolytic stability deriving from intramolecular H-bonding occurring in the MBRA core. As indicated by the phase sequences shown in the Figure, the homologue with an octyloxy achiral tail, MBRA 8 (**4**), shows a C* phase very close to room temperature.

3.2 Empirically designed FLCs reported between 1980 and 1985

The compounds listed in Figure 6 represent the basic FLC systems explored prior to the Clark-Lagerwall invention. Not surprisingly, with the disclosure of the SSFLC geometry, and the possibility of important device applications for FLC materials, a large effort aimed at design and synthesis of FLCs with improved properties (temperature range, polarization, response time, and others) was launched. A representative listing of the compounds reported during this exciting time of early empirical data-gathering is given in Figure 7.

In 1971, Helfrich and Oh had reported the synthesis and properties of a three-ring chiral C phase material possessing two 6-methyloctyloxy chiral tails (again prepared from active amyl alcohol), as shown below.¹² The successfully achieved goal of this work was to create a C phase possessing a helical twist, and the chiral material was designed by analogy to a known C phase compound possessing two n-nonyloxy tails.



Helfrich and Oh C* compound

In fact, this was the first single-component C* material ever reported, though at the time the idea of ferroelectricity in LCs had yet to develop. Of great interest to the FLC community was that the Helfrich compound possessed a C* phase between 29 and 94°C. Combining the MBRA core with the Helfrich tail gave the first enantiotropic room temperature ferroelectric liquid crystal material, MORA 8 (**5**), reported in 1982 by Bengt Otterholm and others at the Chalmers Technical Institute in Sweden working with Lagerwall.²⁴

While MORA 8 possesses an impressive C* temperature range, the polarization is so low it cannot be measured (its ferroelectric nature being simply a statement of the symmetry of the system). A comparison of the properties of MBRA 8 and MORA 8 (i.e. the polarization of MBRA 8 is larger than that of MORA 8) led to the empirical concept that polarization increases as the stereocenter is brought closer to the core.²⁵ This seemed reasonable based upon the well known fact that

Ferroelectric Liquid Crystals

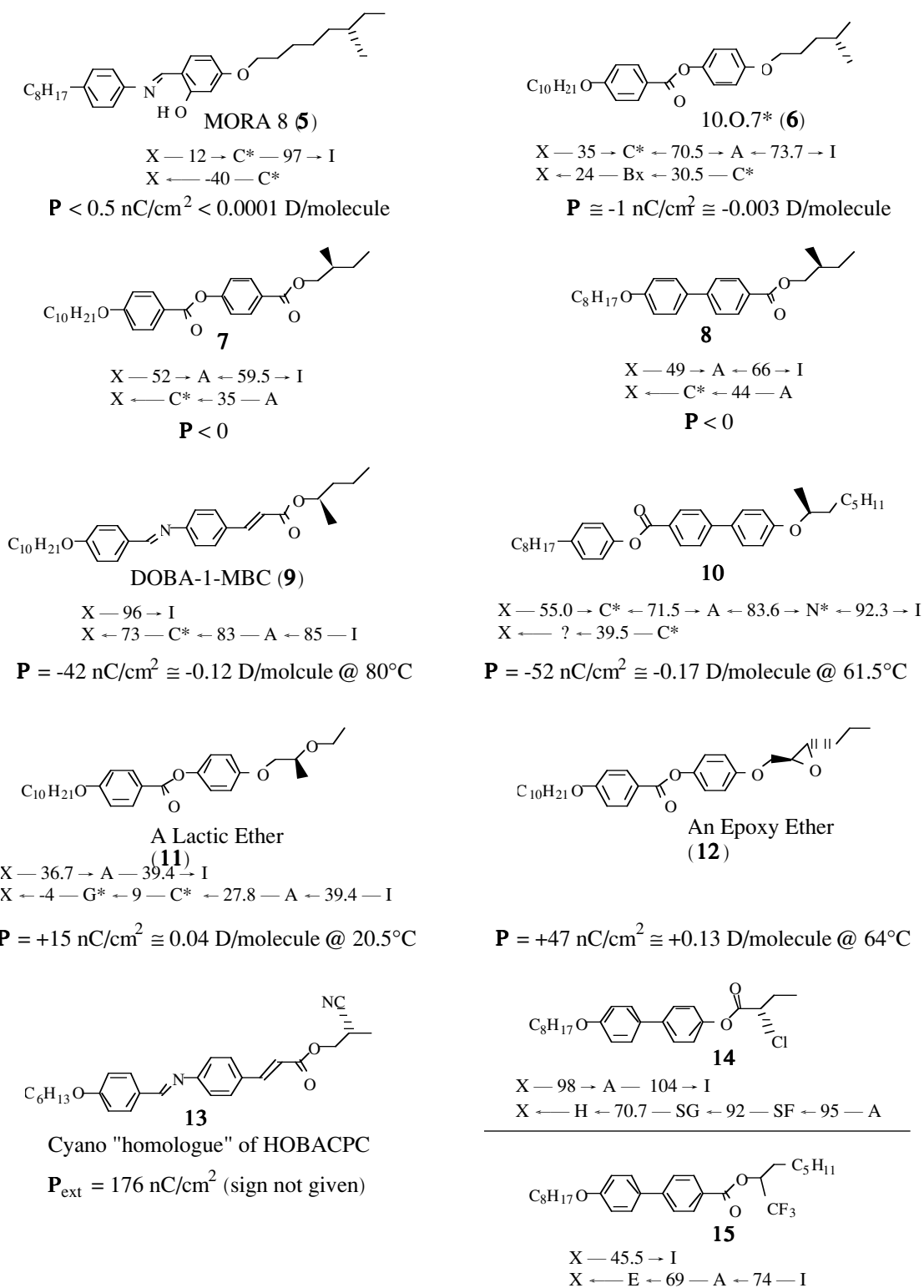


Figure 7. Representative empirically designed FLC materials reported between 1980 and 1985.

functional groups (experimentally determined for C—D bonds by NMR studies) in the tails of LC molecules become more isotropic in orientation upon moving out from the core.²⁶

During the next few years, several groups reported additional FLCs based upon the active amyl alcohol chiral unit. Interesting representative examples are given in Figure 7. Thus, Keller first

reported 10.O.7* (**6**), the 4-methylhexyloxy homolog of the Russian ester **3**.²⁷ This compound possesses a broad, stable C* temperature range, and as discussed below, has become important as a standard low polarization host in FLC host-guest studies.²⁸

Goodby and Leslie reported several ethers similar to compounds **3** - **6**, and also incorporated the 2-methylbutyloxy carbonyl chiral tail into biphenyl and phenylbenzoate cores, as illustrated for compounds **7** and **8**.²⁵ The biphenyl compound **8** is illustrative of an important class of materials, since Gray and Goodby had shown earlier that branching of the ester tail in this series favors C phase formation, though no discussion of the implications of the chirality of the tail was given in the early papers.²⁹ In any event, it now appears that methyl branching in general favors tilted phases—an important empirical correlation between structure and phase sequence.

In 1984 Yoshino, at Osaka University, working with an excellent chemistry group at Ajinomoto Co. Inc. led by Sakamoto, reported a breakthrough in polarization with the characterization of DOBA-1-MBC (**9**).³⁰ This material, with a polarization density 3 times larger than the previous record holder (HOBACPC), exploited the empirical idea that the stereocenter should be close to the core for high polarization.

Shortly after the report of the high polarization observed for the 1-methylbutyloxycarbonyl chiral tail, the outstanding FLC synthesis group at Chisso Chemical Corporation disclosed its own work with FLCs possessing an alkoxy tail branched at the C-1 position, as exemplified by compound **10**.³¹ This structure is also illustrative of the important class of materials possessing the biphenylbenzoate three-ring core. Members of this large class generally possess excellent C phase properties (though the melting points tend to lie well above room temperature). Unfortunately, it also seems generally true that three-ring cores increase orientational viscosity, leading to slower response times relative to two-ring cores with similar polarization.

Our own work with empirically designed FLC materials began in 1981, at the behest of Clark, who like Lagerwall, was searching for organic chemists open to FLC involvements. The allure of this novel chirality phenomenon—ferroelectricity in liquids, in addition to a feeling that the phenomenon could somehow be understood in terms of molecular recognition, proved irresistible to a "chirophilic" stereochemist.

Based upon empirical design concepts by then well known, the lactic ethers^{28,32} and epoxy ethers,^{28,33} exemplified by compounds **11** and **12** shown in Figure 7, were prepared and characterized. As for the Russian group, we felt the phenylbenzoate core seemed a good choice due to the tendency for achiral bis-alkoxyphenylbenzoates to show smectic C phases, and also due to the ease of synthesis of LC mesogens possessing this core (the final step in the synthesis is generally coupling of a phenol with a p-alkoxybenzoyl chloride, imparting to the synthesis all the well known advantages of convergence).

While showing only moderate polarization density (similar to HOBACPC), several homologues in the lactic ether series showed monotropic C* phases at room temperature, and compound **11** exhibited the fastest room temperature response times reported at the time—less than 100μsec. This was an important result, since the faster response times reported for materials such as HOBACPC at elevated temperatures were clearly due in part to the greatly reduced orientational viscosity of FLC materials at high temperatures, and it was not known whether response times much faster than milliseconds (response times demonstrated for materials similar to 10.O.5*) could be achieved at room temperature in the SSFLC device.

Of course, for many physical studies a thermodynamically stable C* phase is required, and the tendency for compounds such as the lactic ether **11** to crystallize from the monotropic C* phase at inopportune moments was distressing to say the least. A solution to this problem, well known in the nematic LC area, is to broaden the thermodynamically stable liquid crystal temperature ranges by mixing several components to obtain a eutectic. This trick works since specific LC phases are typically miscible (indeed, miscibility is one of the tests often used to determine phases), while often the crystalline phases below the LC phases are immiscible. Thus, in mixtures the melting point is typically depressed relative to the pure components, while the LC transitions are not.

Lagerwall obtained a useful, stable room temperature mixture by combining equal parts of the Keller compound 10.O.7* with lactic ether **11**.^{32c} While the stable temperature range of this mixture was not large enough to be useful in commercial devices (C* from 20° to 40°C), many important experiments were accomplished with this material, including now classic X-ray scattering studies by the Clark group, which for the first time established the basic layer structure actually present in standard SSFLC cells (the chevron layer structure), and the origins of the famous zig-zag wall defects.^{34,35}

In addition to the lactic ethers, empiricism suggested that epoxy ethers of type **12** might possess large **P**. This, coupled with the recently reported Sharpless oxidation technology for synthesis of the required chiral epoxyalcohol starting materials,³⁶ led us to explore the system. At the time, more than thirty homologues of the cis and trans epoxy ethers in both the phenylbenzoate and biphenylcarboxylate series were prepared, and only one, compound (**12**), actually exhibited a C* phase.

The epoxy ethers were originally designed empirically, but at about this time the Boulder FLC group was in the midst of developing its molecular model for the origins of **P**, and compound **12** seemed an ideal test case. The polarization observed for this material, first measured in Chalmers by the Lagerwall group, was similar to that exhibited by the 1-methylheptyloxy compounds at 45 nC/cm², and the sign and magnitude of **P** were in fact in good agreement with expectation. This compound, and others in the series, are discussed in more detail below.

Finally, several additional interesting chiral tail units were investigated in the FLC context during this period, but no FLC properties were reported for pure compounds due to lack of the required C* phase in the phase sequence. Thus, the Russian group of Beresnev and Blinov et. al. was the first to our knowledge to report the synthesis of an FLC-type structure possessing a cyano substituent at the stereocenter (compound **13**).³⁷ This work was clearly an attempt to take advantage of the large C—CN bond dipole moment.

In their classic FLC papers of 1984,²⁵ Goodby and Leslie also were the first to report the synthesis and phase sequence of materials possessing the α -chloroester chiral tail, specifically a class of 2-chlorobutanoic acid derivatives exemplified by biphenyl **14**, and a single compound possessing the 1-trifluoromethylheptyloxycarbonyl chiral tail (**15**, apparently racemic). As indicated in the Figure, these materials also showed no C* phases.

The problem illustrated here—a new system, no matter how well conceived for inducing large polarization, could not be evaluated unless a C* phase could be obtained—was very common prior to 1985. Indeed, subsequent to the initial reports, it was shown that the compound classes represented by structures **13** and **14** are important FLC materials, as discussed in more detail below.

3.3 Breaking the 100 nC/cm² barrier—some modern high polarization FLCs

A priori, there is no method to reliably predict the maximum possible polarization of an FLC material. Thus, aside from practical considerations, synthesis of materials with very high polarization serves to define the limits in the FLC system, and provides important data for development of models for the molecular origins of **P**. Prior to 1986 no reports of FLCs with **P**>100 nC/cm² had been published, though it is now clear that such materials had been discovered in several laboratories during the period 1980-1985.

Specifically, the first materials with values of **P** measured to be over 100 nC/Cm² were α -chloroesters similar to the compounds reported by Goodby and Leslie, but not characterized by them with respect to polarization. Three groups independently reported FLCs possessing α -chloroester chiral tails, readily prepared from amino acids, at the 11th International Liquid Crystal Conference in 1986 (Figure 8). Thus, Demus, from the famous Halle liquid crystal school in East Germany, working with Lagerwall, described the valine-derived phenylbenzoate **16**, possessing a monotropic C* phase at room temperature, and a very fast electrooptic response time.^{28,38}

Both the group at Ajinomoto, working with Yoshino,³⁹ and the excellent FLC group of Heppke and Bahr at the Technical University of Berlin,⁴⁰ reported biphenyl α -chloroesters exemplified by the isoleucine derivative **17**. For several years materials similar to these exhibited the highest known polarizations, and due to their ease of synthesis, many important experiments were accomplished using them.

Several other empirically designed high polarization single component FLC materials are also listed in Figure 8. These compounds serve to illustrate the range of non-racemic structures explored in the context of FLC chemistry. Thus, the Boulder group has demonstrated that the epoxy ether tail can afford high polarization, as indicated for the very interesting phenylbenzoate **18**.⁴¹ In addition to the high polarization, compound **18** shows a strongly first order transition into the smectic C* phase, and a large tilt angle. Interestingly, mixtures of compound **18** with 10.O.7* exhibit a unique first order N-A-C tricritical point.⁴²

The lactate ester **19** is exemplary of a large class of lactic acid derivatives reported by the LC synthesis group at the University of Hull led by Gray, in collaboration with the physics and device groups at the Royal Signals and Radar Establishment and S.T.C. Technology Ltd. in England.⁴³ The interesting trifluoromethyl carbinol derivative **20** is a result of a collaboration between Yoshino and chemists at Daicel Chemical Industries Ltd. in Japan and the Department of Bioengineering at the Tokyo Institute of Technology, and represents a chiral unit prepared using biotechnological methods.⁴⁴ Finally, the axial cyano-cyclohexyl compound **21** is exemplary of several classes of LC materials prepared by the synthesis group at E. Merk, Darmstadt.⁴⁵

3.4 Smectic C hosts and chiral guests—evaluation of C* materials by mixing

As implied above, design of new FLC materials often proved frustrating since it was necessary to obtain a material possessing both the chiral tail under investigation, and a C* phase. The former was often achievable by synthesis, but the latter seemed more a matter of luck. Synthesis of a great many homologues, and incorporation of a new chiral tail into several different core systems provided one solution—if a C* phase was eventually found. But, this approach is quite tedious.

In fact, an elegant solution to this problem was already in the making in 1980. Thus, Kuczynski and Stegemeyer first reported that mixtures possessing C* phases could, in fact, be readily

Ferroelectric Liquid Crystals

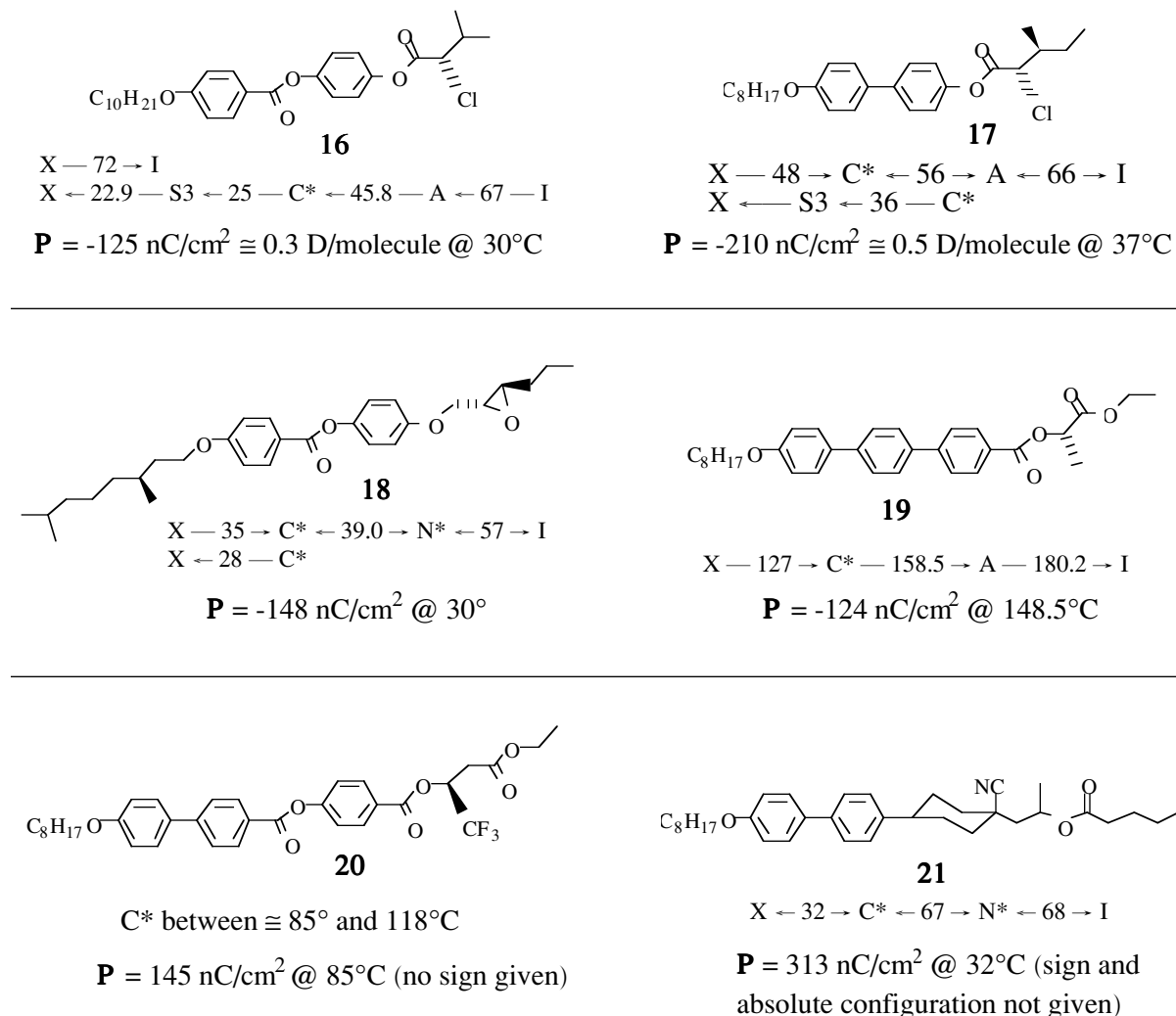


Figure 8. Some representative single-component FLCs with **P**>100 nC/cm².

obtained even when one of the components had no C* phase, or indeed no LC phases at all.⁴⁶ They showed that doping of the achiral C phase host **22** (Figure 9) with 1 mole % of such typical chiral compounds as 1-menthol or 8-methyl-5,6,7,8-tetrahydroindanedione gave a "switchable" C* phase whose polarization could be measured, though low values were obtained.

It is important to note here that upon doping with a chiral guest, the whole phase becomes ferroelectric, and upon reversal of the sign of an applied field, all the molecules in the phase switch by rotation about the tilt cone, not just the guests. This is basically because the coupling with the applied field is through the ferroelectric polarization, a property of the phase as a whole, not through coupling to any individual molecular dipoles.

In 1982, Beresnev and Blinov, et. al. published two important papers bearing upon this point.⁴⁷ Thus, using the prototypical phenylbenzoate **23** as host, the Russian group experimented with dopants which looked like C* mesogens, but possessed no C* phase. In this classic work, they showed that in general, the polarization of the mixtures was nearly proportional to the concentration of the chiral additive, and indeed, using the cyano "homologue" of HOBACPC (**13**) as guest in a concentration of 12.5% by weight, they obtained an FLC material which at the time showed the highest polarization known (22 nC/cm²; no sign of **P** given).

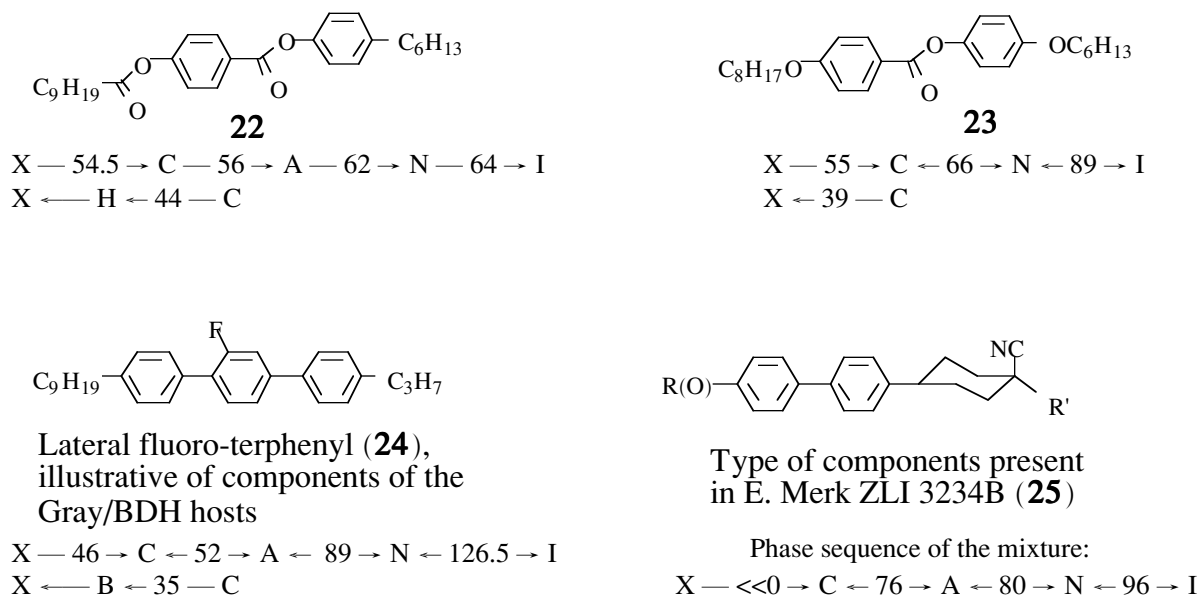


Figure 9. Some C Phase hosts used in mixing experiments.

This work leads directly to the idea that evaluation of new FLC components might be accomplished by doping the new material as a guest into a C phase host, and measuring the properties of the resulting mixture. This approach gains added importance given that all commercial FLC materials are mixtures, as mentioned above, and thus the properties imparted to a mixture by addition of a chiral component are actually more relevant to applications than its properties as the neat liquid. This approach to evaluation of FLC components has, in fact, become the standard, and it still seems generally true that the observed polarization is a linear function of concentration of the chiral component, and good data concerning the FLC properties of a new chiral tail may be obtained in this way without the necessity of obtaining a sample of C* material possessing that tail. A more detailed description of this technique is given below in connection with the Boulder Model for the molecular origins of **P**.

In the early doping experiments, single compounds possessing a smectic C phase typically served as host. In our own work, and that of others, the chiral phenylbenzoate 10.O.7* (**6**) has served as an excellent standard C* host. Though this compound is ferroelectric itself, the polarization is very small, and the advantage of a very broad C* temperature range (an example of the empirical rule that methyl branching in the tail favors the C phase) outweighs the slight inconvenience of a chiral host with non-zero **P**.

Given the commercial importance of C* materials, and the ability to impart useful ferroelectricity upon a broad temperature range C phase host by adding small quantities of chiral dopant, it is not surprising that a considerable effort has been devoted to the development of commercial smectic C host mixtures.

For example, Gray and his group at Hull have put great effort into development of effective smectic C host materials, which are incorporated into C phase mixtures commercially available from BDH in Britain. While the exact composition of the multicomponent hosts resulting from this work are not public, particularly interesting achiral components which have been reported are the "lateral fluoro-terphenyls" illustrated by structure **24** in Figure 9.⁴⁸ This material is particularly

interesting since it possesses no alkoxy tails, and no branching in the tails, yet shows an enantiotropic C phase. Also exemplary of useful C phase hosts is the multicomponent mixture ZLI-3234B developed by the FLC group at E. Merk, with composition indicated by structures **25**. The true enantiotropic X \rightarrow C transition is difficult to measure, since the mixture is very difficult to crystallize, instead simply cooling into a glass at temperatures far below 0°C.

Using hosts such as those indicated in Figure 9, many high polarization FLC dopants (of "high polarization components") have been characterized—some designed empirically, and some in a more directed way. Generally, the polarization of these guests is presented as an extrapolated value, assuming a linear relationship between \mathbf{P} and concentration of the guest. These \mathbf{P}_{ext} values are then often normalized for tilt angle θ , since polarization is a strong function of θ , and different mixtures possess different values of θ . For the purposes of this paper, the unnormalized \mathbf{P}_{ext} value will generally be presented, along with the temperature of the measurement.

Several representative high polarization components are listed in Figure 10.^{49,51} It should be pointed out in this context that the cyano compound **13** first reported by Beresnev and Blinov in 1982 exhibits $\mathbf{P}_{\text{ext}} = 176 \text{ nC/cm}^2$. Finally, the cis-epoxyester phenylpyrimidine **31**, prepared by Scherowsky at the Technische Universität Berlin using Sharpless asymmetric epoxidation technology, apparently exhibits the highest extrapolated polarization density observed to date,⁵² though the same chiral tail in combination with other cores apparently affords extrapolated polarization densities on the order of 300-400 nC/cm². Unfortunately, these results have never been published, though similar results with the cis-epoxyester tail have been disclosed in the context of FLC polymers.⁵³ In the following sections, a description of the Boulder model for the molecular origins of \mathbf{P} , and our own results in FLC component design, are presented.

4 Early Models for the Molecular Origins of the Polarization in FLCs

From the beginning, of course, chemists in the FLC field were working towards development of a molecular level model for the origins of the polarization. Specifically, such a model should state which molecular dipoles are oriented in a polar fashion leading to the observed macroscopic polarization, and allow prediction of the sign of \mathbf{P} given the absolute configuration of the FLC component. This is a tall order—consider the well known lack of "chirality phenomena" for which a simple, direct connection between the "handedness" of the observable macroscopic property and the absolute configuration of the molecules exists.^{1b}

Early consideration of the origins of \mathbf{P} in FLCs were based upon important models for the achiral smectic C phase—specifically, models for explaining the observed director tilt. The first such model, proposed by McMillan in 1973,⁵⁴ suggested the attractive idea that the tilt in smectic C phases was due to a dipole-dipole interaction between the "outboard" dipoles connecting the tails to the core. This model grew out of the empirical fact that all known C phases at the time possessed such dipoles. However, it was later found that LCs with two alkyl tails could show C phases,⁵⁵ (also, see structure **24**) implying that the outboard dipole-dipole interactions could not be the only contribution to C phase order.

In 1978, Bartolino, Doucet, and Durand published a classic paper describing a steric model for the origins of the smectic C phase.⁵⁶ This paper suggested that the tilt was a result of the "zig-zag" shape of the LC molecules. Thus, examination of molecular models suggests that when two alkyl or alkoxy tails are joined to an aromatic core, then one favorable conformation has geometry such that the axis of minimum inertia (the "long axis") of the core is not colinear with the axis of minimum inertia of the two tails, and the overall structure forms a zig-zag as indicated in Figure 6.

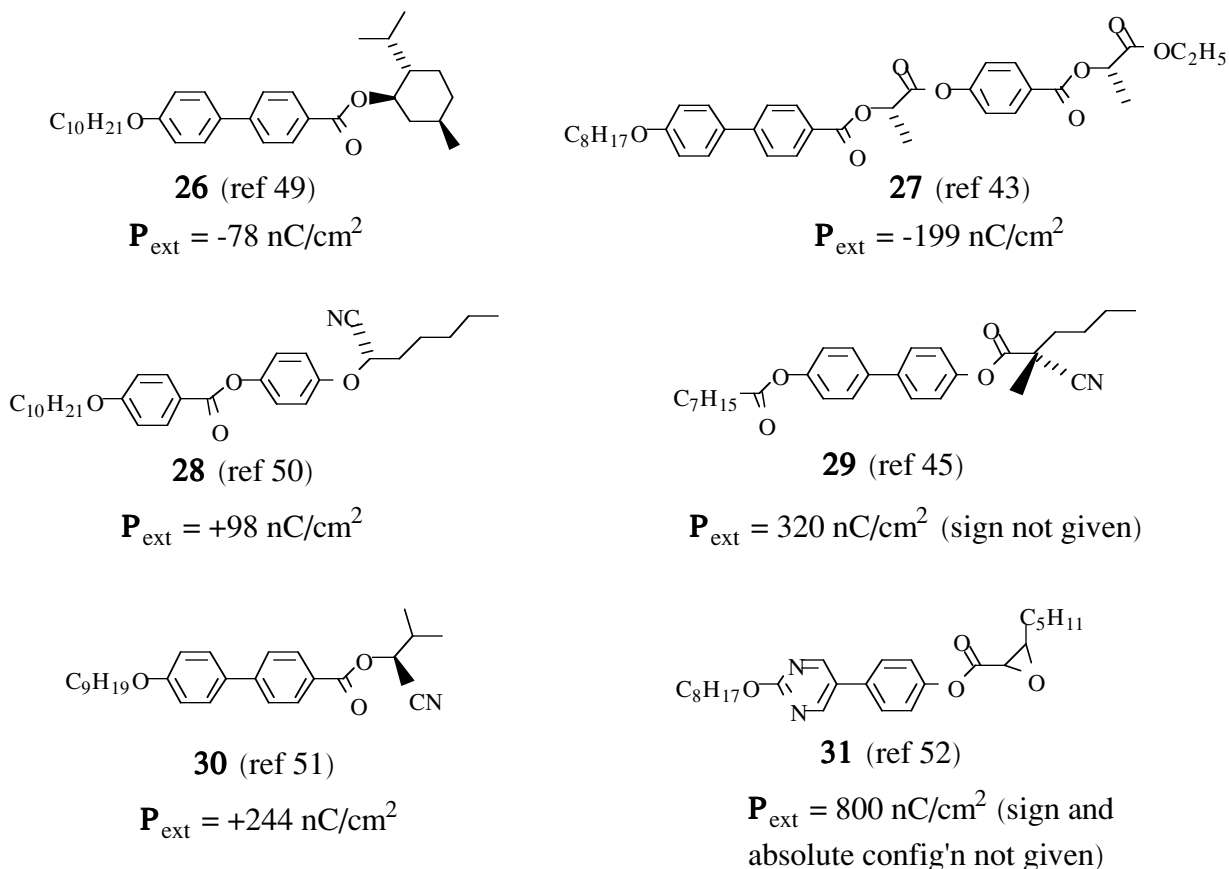
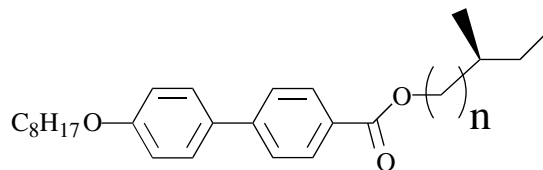


Figure 10. Some modern high polarization dopants evaluated in mixtures containing 10% by weight of the chiral component.

Furthermore, the French group suggested that since the cores were relatively rigidly packed, while the tails were essentially melted (i.e. taking up more volume) in the LC phase, a preferred packing arrangement would have the overall molecular director tilted relative to the layer normal, with the tails less tilted than the core, leading to the experimentally observed smectic C order.

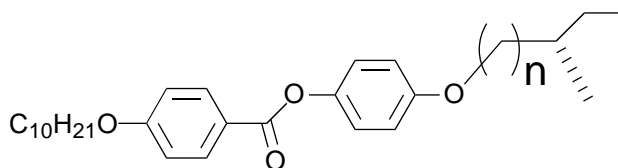
It now appears that this basic model is essentially correct, though the detailed origins of the C phase structure are still not understood. Thus, for example, a recent high resolution X-ray scattering study of the prototypical mesogen 4'-butoxyphenyl-4-decyloxybenzoate show that for this material at least, the tails are indeed less tilted than the core in the C phase.⁵⁷

Based upon the zig-zag model, Goodby and Leslie in 1984 suggested that the observed polarization of many active amyl alcohol derivatives, such as compounds **32** with $n=0-2$, was due to orientation of the methine-methyl dipole at the stereocenter.^{25,58} This proposal suggests that when the stereocenter for each homologue has the same absolute configuration, then the sign of P should alternate, as is indeed observed (the magnitude of P was not given).



32 $n=0$; $\mathbf{P}>0$
 $n=1$; $\mathbf{P}<0$
 $n=2$; $\mathbf{P}>0$

As was later discussed by Goodby, however, this correlation does not always hold.⁵⁹ For example, we have shown that the sign of \mathbf{P} for members of the prototypical homologous series of phenylbenzoates **33** are all negative.⁶⁰ Note also that \mathbf{P} does not decrease monotonically, as expected based upon the simple empirical rule that \mathbf{P} should decrease as the stereocenter is moved away from the core. Goodby qualitatively interpreted "anomalous" results of the this type as indicating that in FLCs sometimes the tails are less tilted than the core, and sometimes the tails are more tilted than the core.



33 $n=1$; $\mathbf{P} = -1.8$
 $n=2$; $\mathbf{P} = -4.0$
 $n=3$; $\mathbf{P} = -1.0$

5 The Boulder Model for the Molecular Origins of \mathbf{P}

Clearly, the polarization of FLC phases may be considered as a manifestation of the "crystal" packing forces in the medium, as suggested by the "steric model" of Durand for the tilt. That is, the molecules of the phase are oriented with respect to the tilt plane and layer normal by interaction with their neighbors. This interaction is responsible for the polar orientation of molecular dipoles which is manifested as the ferroelectric polarization of the phase.

If one could simply minimize using empirical force fields a cubic volume of, perhaps, 10,000 FLC molecules with respect to all inter- and intramolecular degrees of freedom, then presumably the FLC phase would exist in a free energy minimum at some temperatures, and the tilt and polarization of the phase could be calculated. Unfortunately, such a minimization is not possible given the computing power available today, partly due to the slow reorientation times associated with rotation of rod shaped molecules about their short axis.

In our own attempt to devise a predictive model for the origins of \mathbf{P} , we are developing an approach where the polarization is considered as a manifestation of a form of molecular recognition occurring in the liquid phase.^{32b,61} More specifically, the time average orienting affect of the "crystal lattice" upon each individual molecule is modelled qualitatively by a van der Waals surface, or surface of constant molecular mean field. This surface behaves like the "binding site" typically considered in organic host-guest chemistry or biochemistry to explain specificity in 1:1 complexation. In an isotropic fluid, this binding site takes the shape of a sphere on the time

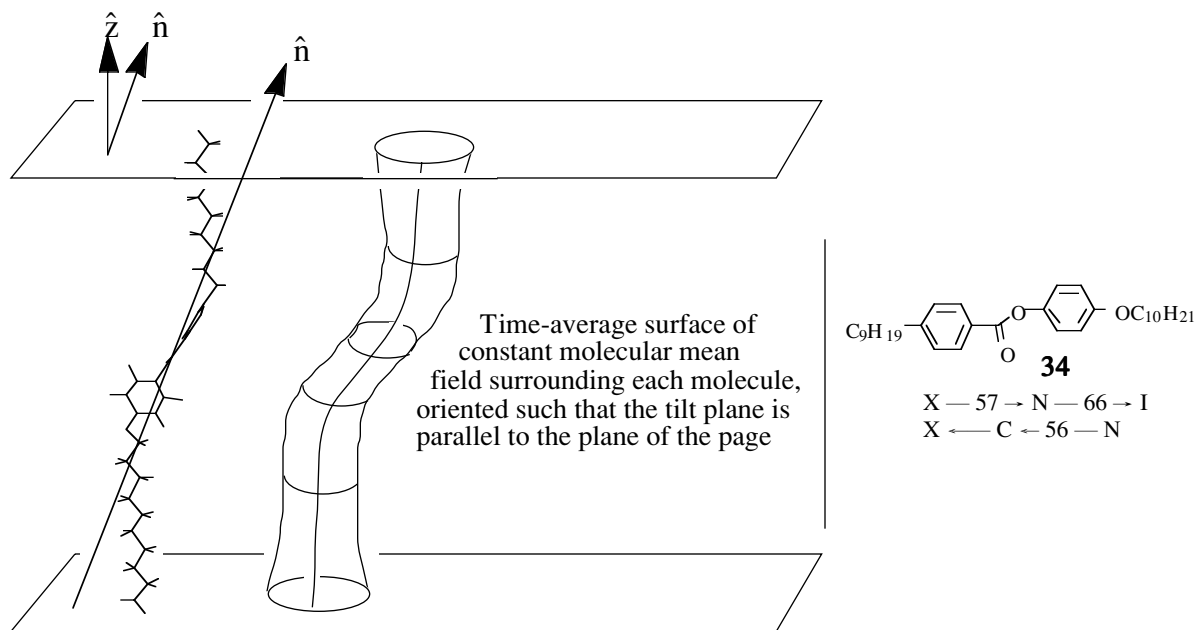


Figure 11. Proposed shape of the C phase "binding site" for simple p-p' disubstituted phenylbenzoates—the "bent cylinder".

average, such that all orientations, relative to the lab frame, of bound "guest" molecules are degenerate.

In a nematic, smectic A, or any other untilted LC phase, the time average binding site takes the shape of a cylinder (relative to the lab frame), giving rise to the observed orientational order. For a molecule bound in such a surface, rotation about the director gives rise to degenerate rotational states, affording the time average C_∞ axis of symmetry along the director empirically observed for all untilted LC phases (chiral and achiral). This cylindrical "binding site" model has in essence been discussed in the literature as an approach for modelling nematic tail conformational order by Samulski.⁶²

In the smectic C phase, however, this hypothetical cylindrical binding site does not simply tilt over. Intuition and examination of space filling models suggested to us that the appropriate binding site shape for the C phase is a bent cylinder, illustrated in Figure 11 relative to the smectic layers and tilt plane (plane of the page) of a C phase. Note that according to the model, achiral C phases possess this binding site. In the Figure, a zig-zag MM2 minimum of the achiral C phase mesogen 4-n-decyloxyphenyl-4'-n-nonylbenzoate (**32**), with the tails less tilted than the core, is used to illustrate a molecule in the phase.

The C phase binding site must possess several specific features in order to correctly capture the symmetry of the phase. Thus, the binding site must possess a C_2 axis normal to the tilt plane—otherwise a C phase could have non-zero polarization along the director, which has never been observed. Also, for similar reasons, in an achiral C phase the binding site must possess a σ plane congruent with the tilt plane. Aside from these symmetries, a priori the binding site could take up any shape, including a cylinder. The importance of the bent cylinder shape, and our interpretation of the fundamental basis of ferroelectricity in chiral C phases, is illustrated in Figure 12.

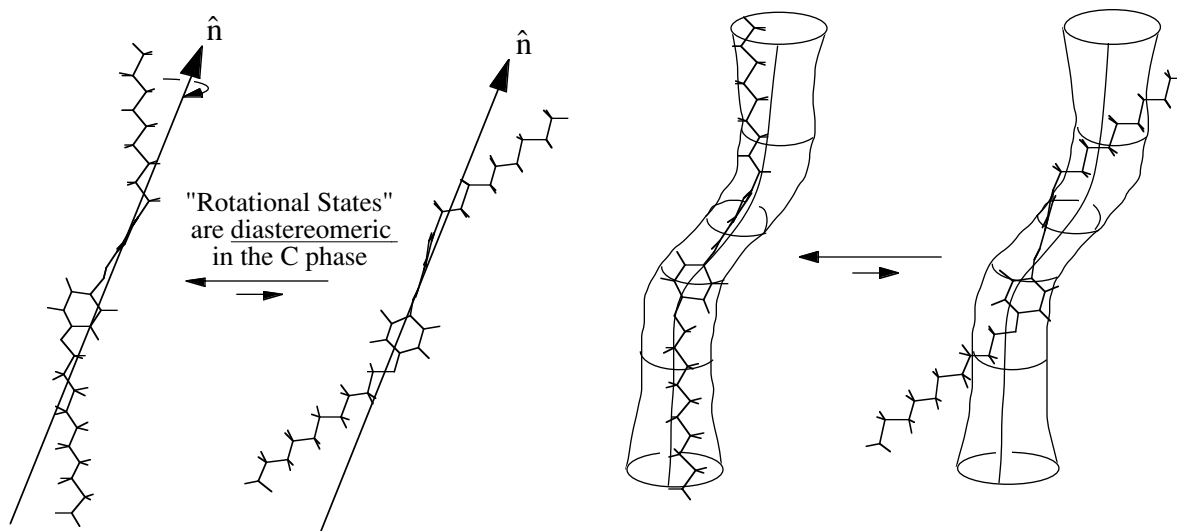


Figure 12. Proposed preferred rotational and conformational orientation for compound **34** in the C phase.

Thus, in an achiral C phase rigid rotation of a single conformation about the director gives rise to diastereomeric rotational states relative to the lab frame (the glass substrates of the cell and buffing direction in the case of an aligned sample). According to the Durand zig-zag model, and experimental results, the tails are less tilted than the core, as indicated on the left in the Figure. The bent cylinder binding site takes these concepts and experimental facts into account. Thus, as indicated on the right in Figure 12, it can easily be seen that docking the MM2 minimum into the bent cylinder effectively models the diastereomeric nature of the rotational states in the phase.

While this rotational order occurs in achiral C phases, due to the symmetry of the binding site, no macroscopic polarization (i.e. net polar orientation of molecular dipoles on the time average) can occur unless the "docked" molecules are chiral. The observed polarization is given by equations 2 and 3, where D_i is the number density of the i th conformation present in the phase, \mathbf{P}_i is the contribution to the polarization from the i th conformation, $\vec{\mu}_{\perp i}$ is the component of the molecular dipole normal to the tilt plane when the molecule is oriented in the rotational minimum in the binding site for the i th conformation, ROF_i is the "rotational orientation factor", a number from zero to one reflecting the degree of rotational order for the i th conformation, and ϵ is a dielectric constant of the medium.^{32b}

$$\mathbf{P} = \sum_{\text{over all } i \text{ conformations}} D_i \cdot \mathbf{P}_i \quad \text{equ 2}$$

$$\mathbf{P}_i = \vec{\mu}_{\perp i} \cdot \text{ROF}_i \cdot 1/\epsilon \quad \text{equ 3}$$

When the molecules are achiral, or in a better illustration, the phase is racemic, the ROF_i , and ϵ for each conformation need not change relative to the chiral case, but for each conformation contributing a positive \mathbf{P}_i , there is an equal number density of the enantiomeric conformation contributing an equal magnitude but negative \mathbf{P}_i (i.e. with equal magnitude but opposite sign of $\vec{\mu}_{\perp i}$), leading to a zero net polarization.

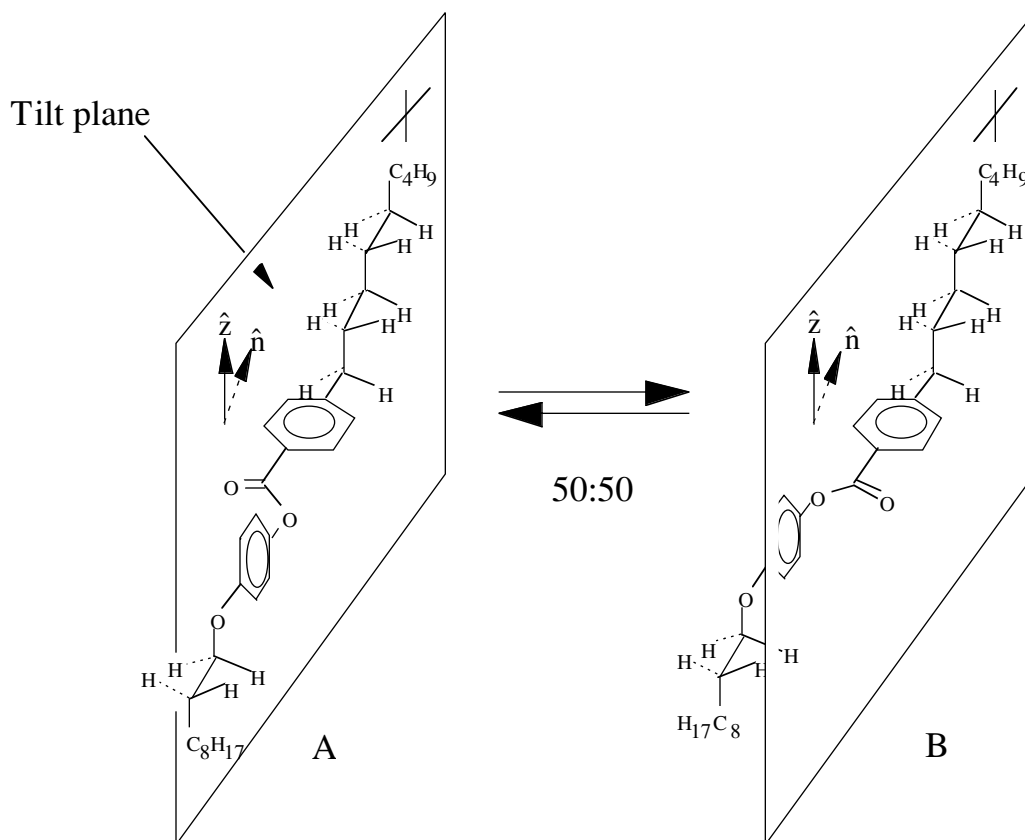


Figure 13. Proposed preferred rotational and conformational orientation for compound **34** in the C phase, viewed from a point almost in the tilt plane.

Even when applied qualitatively, we find this model much more useful than simply stating that the tails are less tilted than the core. The basic paradigm of the binding site model as an approach for thinking about order occurring in FLC phases is that all C phases, chiral or achiral, possess the same basic binding site shape, as illustrated in Figures 11 and 12. This is another way of stating that the "crystal lattice" of all thermodynamic C phases is the same. While this is a very crude first order version of our model, we have found it to be quite useful. Several illustrations of the power of this molecular recognition approach for interpretation and prediction of properties of FLC materials are given in the next section.

First, however, our method for graphically illustrating conformation and rotational orientation in C phases must be introduced. Thus, it became clear early on that a way of showing molecular conformations of mesogens emphasizing the orientation of molecular dipoles normal to the tilt plane would be very useful. The projections shown in Figures 11 and 12, viewing the mesogens along the polar axis, is not appropriate since it is difficult to visualize dipoles projecting in front of, or behind the plane of the page. Thus, the most useful projection for our purposes would be viewing the molecules from a point nearly in the tilt plane. Such a projection is illustrated in Figure 13 for the nonylbenzoate **34**. Note that the viewer is positioned close to the tilt plane (not actually in it), at a point to the left of, and somewhat in front of the plane of the page in Figure 12.

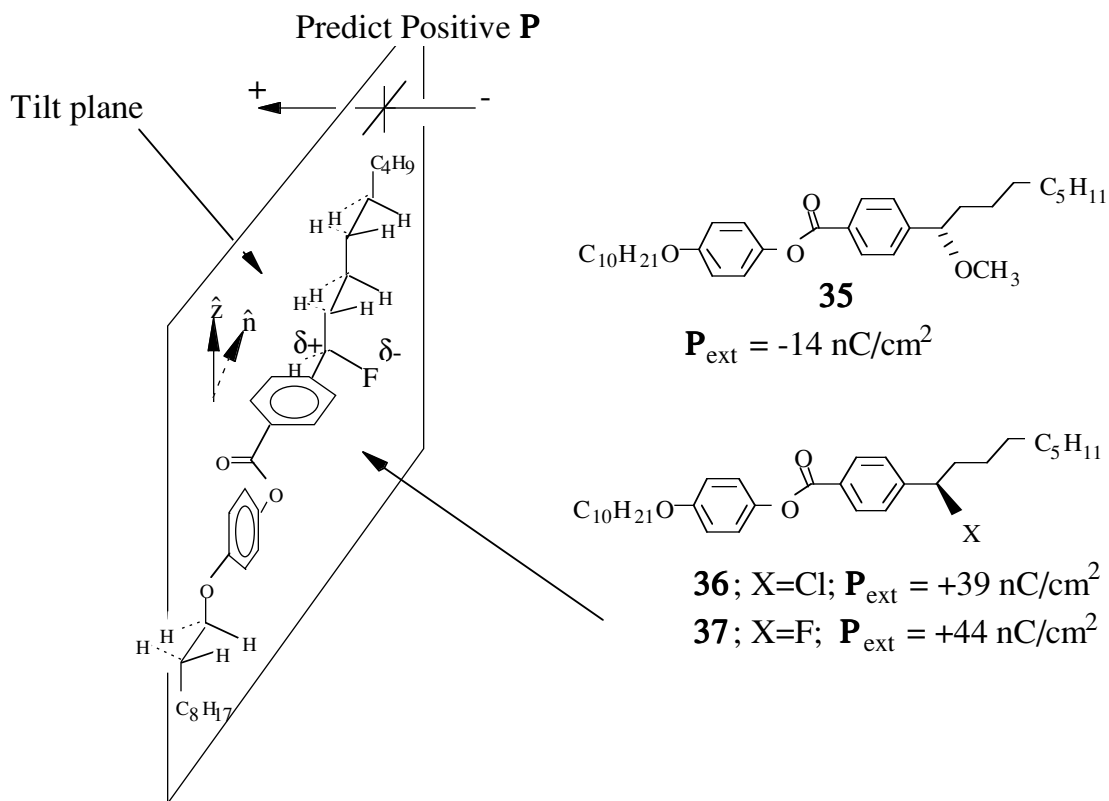


Figure 14. Properties observed for some substituted nonylbenzoates, and the prediction according to the Boulder Model for the 1-fluorononyl compound **37**.

Unfortunately, geometrically accurate molecular conformations in diagrams such as those shown in Figure 13 are not as useful as might be imagined. Therefore, throughout the rest of this paper, drawings meant to represent actual conformations are used. These drawings are not geometrically correct, but serve the purpose of illustrating functional group orientation in C phase mesogens relative to the tilt plane of the phase.

Aside from introducing the projection we will be using, Figure 13 also illustrates an important point. That is, for a given conformation of phenylbenzoate **34**, e.g. conformation A, oriented according to our model, there is a substantial component of the carbonyl dipole normal to the tilt plane. However, there is an equal number density of conformations B in the phase, such that the net polarization of a sample of the material would be zero. This is the empirical fact, and is captured by our model since the binding site is achiral, therefore conformations A and B when docked into the binding site form enantiomeric objects, and must possess equal free energy, and exist in equal number density.

6 Tests of the Boulder Model

6.1 Nonylbenzoates substituted with dipoles on the alkyl tail.

Mental docking of chiral molecules such as 10.O.5* or the lactic ethers into the bent cylinder binding site leads to polar orientation of dipoles in the phase. But, as we pointed out in our original paper describing the Boulder model,^{32b} the magnitude of **P** observed for materials of this type is very small (< 0.1 D/molecule), and there are several important conformations which must

be considered, each of which will possess subtleties of rotational orientation. Therefore, it is simply not possible to interpret the polarization exhibited by these materials without a much more sophisticated treatment (if at all). Our efforts were directed towards design of new materials with large polarization of predictable sign according to the model.

The proposal for conformational and rotational orientation of an alkylbenzoate occurring in C phases, as indicated in Figure 13, suggested the design of a series of substituted alkylbenzoates as a critical test of the model. Thus, as indicated in Figure 14, several nonylbenzoates possessing polar substituents at C-1 of the alkyl tail were prepared and characterized.^{61a}

Unfortunately, none of these materials possessed a C* phase. But, the mixing approach to evaluation of C* materials is perfectly consistent with the Boulder model. The host used for evaluation of compounds **35** - **37** was 10.O.7* (**6**), whose binding site is expected to possess the shape indicated in Figures 11 and 12. The polarizations shown in Figure 14 were extrapolated from 1:1 mixtures of host and guest. When a chiral guest is added to the host, the guest molecules are expected to be oriented by the binding site according to the model, leading, for example, to the prediction indicated in Figure 14 for the 1-fluorononyl homologue.

Specifically, doping the (R) fluoride **37** into 10.O.7* is expected to afford to a preferred orientation of the guest molecules relative to the tilt plane and C phase layers as indicated in Figure 14. As described above, the carbonyl dipole is not considered to contribute to the net polarization, since while the conformations indicated in Figure 13 are now diastereomeric with the stereocenter at C-1 on the tail, we feel they will still be present in equal number density in the C* phase. The C-F dipole, however, is clearly expected to be oriented in a polar fashion, since reversal of the direction of this dipole leads to a conformation or rotational orientation which does not "fit" in the host matrix.

The prediction is indicated on the drawing. That is, the polar orientation of dipoles from - to +(!) should be in the direction of $\hat{x}\hat{x}$ (right to left in the Figure), leading to a positive macroscopic polarization.

As indicated, the prediction for the sign of **P** is consistent with the observed properties of all three compounds **35** - **37**. Note that the sign of **P** for the methoxy compound is negative because the absolute configuration of this material is (S). Indeed, the quantitative magnitude of **P** observed for these compounds is surprisingly consistent as well, given that the dipole moment of a C—O bond is about 1/2 that of a C—F or C—Cl bond.

In order to test the validity of the extrapolation technique in our system, the polarization observed for six mixtures of the 1-fluorononyl benzoate **37** were measured, as shown in Figure 15. As indicated by the plot, the observed polarization of mixtures of the fluoro compound **37** in host 10.O.7* are linear in concentration of the components, and serves to illustrate the small scatter which can be obtained in the experimental measurement of **P**. Also, the extrapolated polarization of the sample of compound **37** used in the concentration study is +30 nC/cm². The discrepancy between this value and that shown in Figure 14 lies in the fact that the sample used for the mixing experiment was not enantiomerically pure. It is useful to point out here that we feel the enantiomeric excess as measured by the FLC polarization technique (68% ee) is much more accurate than that obtained by optical activity measurements (53±17% ee).

While the results obtained with molecules possessing a single stereocenter and one large dipole certainly are consistent with the concept that the tails are less tilted than the cores in FLC

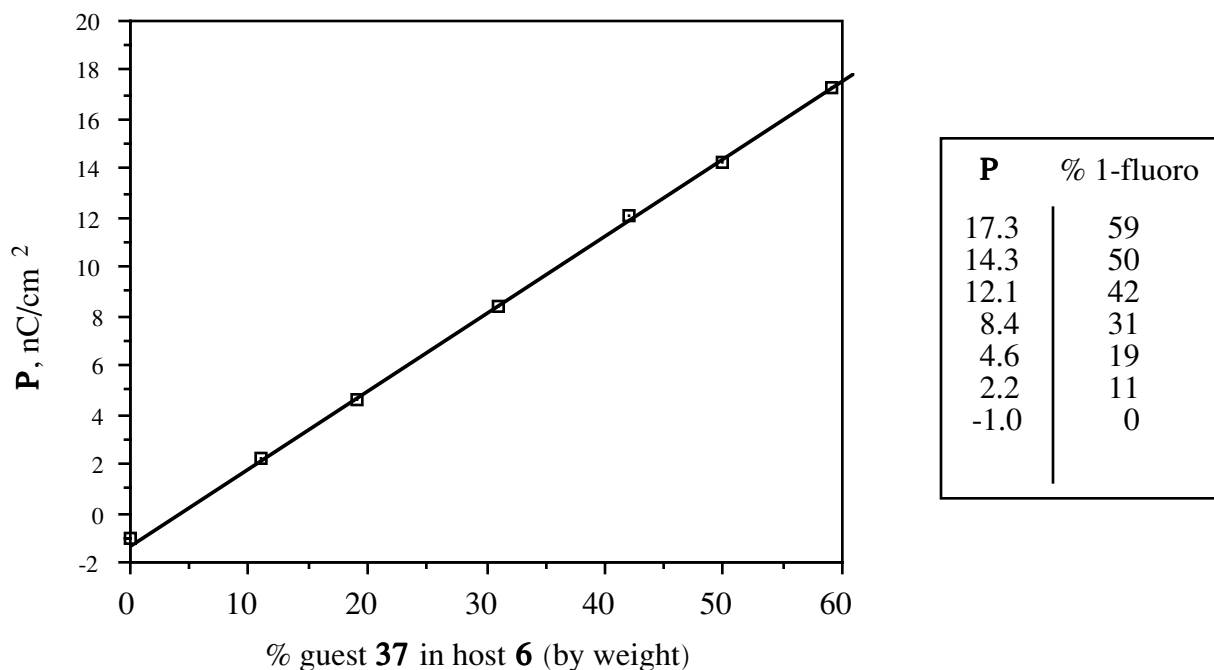


Figure 15. Polarization observed for mixtures of fluorononyl benzoate **37** in host **6** as a function of concentration of **37**.

mesogens, we felt that a much stronger test of the model would derive from examination of molecules possessing multiple dipoles. In this case, it is possible to evaluate pairs of diastereomers, for which the model makes very different predictions for very similar stereoisomeric compounds.

Thus, as indicated in Figure 16, the series of epoxides **38** - **41** were prepared and evaluated as guests in host 10.O.7* (due to low solubility of these compounds in host **6**, mixtures with 10% by weight of guest were evaluated).^{61b,c,63} Again, the results were in good agreement with the predictions of the model.

Note specifically the anti and syn fluoroepoxides **39** and **41**, indicated in the drawings oriented relative to the tilt plane. The observed proton and ¹⁹F NMR spectra of these diastereomeric compounds in CDCl₃ solution indicate that the conformations shown in the Figure are not the only important, or even the most important conformations in isotropic solution (Anti diastereomer **39**: ¹H NMR δ 5.41 (d of d, 1H, J=4.3, 46.9 Hz, ArCHFR); ¹⁹F NMR δ -185.73 (d of d, J=11.4, 47.4 Hz, ArCHF). Syn diastereomer **41**: ¹H NMR δ 5.27 (d of d, 1H, J=6.0, 47.4 Hz, ArCHF); ¹⁹F NMR δ -188.42 (d of d, J=9.31, 47.1 Hz, ArCHF). Indeed, it is expected that the epoxide and C—F dipoles would be opposed in the minimum energy conformation for both diastereomers due to unfavorable dipole-dipole repulsions in the conformation indicated in the Figure for the syn diastereomer **41**.

By our model, however, it is the binding site which forces the syn diastereomer to orient with the dipoles aligned, while the anti diastereomer is free to adopt the conformation shown wherein the dipoles are opposed. Thus, the syn diastereomer is expected to possess a large negative polarization, while the anti diastereomer is expected to show small **P**, as is indeed observed. In fact, quantitatively the syn fluoroepoxide shows a polarization remarkably close to the sum of polarizations observed for the 2,3-epoxynonyl (**38**) and the 1-fluorononyl (**37**) compounds,

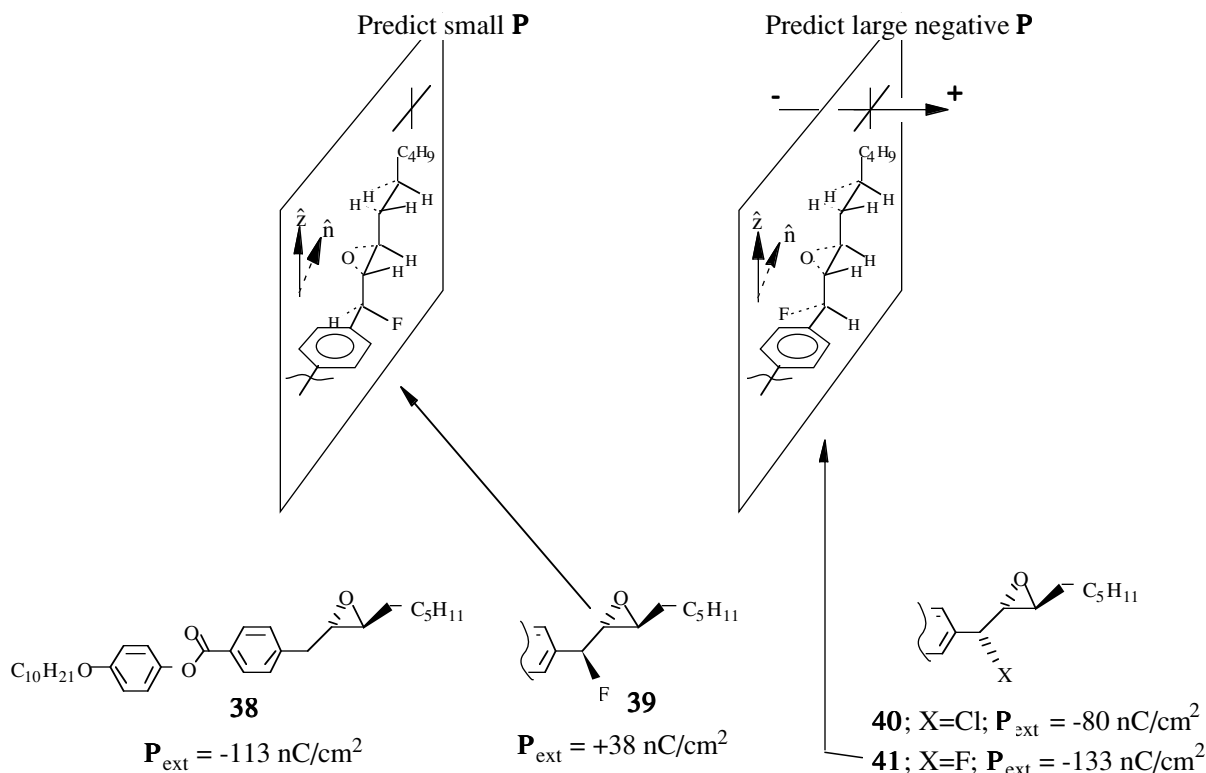


Figure 16. Further studies on substituted nonylbenzoates, and tests of the Boulder Model using diastereomeric pairs (all values of \mathbf{P} extrapolated from 10% mixtures in host **6**).

adjusting for the absolute configurations of the materials used in the experimental measurements and the different tilt angles of the mixtures (normalized $\mathbf{P}_{\text{ext}}/\sin\theta$ for **37** = 46 nC/cm²; $\mathbf{P}_{\text{ext}}/\sin\theta$ for **38** = 101 nC/cm²; and $\mathbf{P}_{\text{ext}}/\sin\theta$ for **41** = 139 nC/cm²). Such quantitative correlations must be made with care, however—note the anomalously small polarization of the 1-chloroepoxide **40** relative to epoxide **38**.

Even given the caveats, the agreement between the predictions of the Boulder Model, and observations for the compounds illustrated in Figures 14-16 is remarkable. Thus, as illustrated in Figure 17, a system is in hand where there exists a direct connection between an easily observable macroscopic chirality phenomenon (the measured sign and magnitude of \mathbf{P} in an FLC thin film), and the microscopic relative and absolute configuration of the molecules comprising the film.

While it is impossible to obtain an actual crystal structure showing the location of the atoms of the molecules in an FLC phase, we have recently obtained an interesting crystal structure relevant to this discussion. Thus, in connection with studies aimed at design of FLCs possessing cyano substituents on alkyl tails, the racemic 2-cyanoalkylphenyl benzoate **42** (Figure 18) was prepared.⁶⁴ This material fortuitously gave X-ray quality crystals, and exhibited the novel crystal packing shown in the Figure. Compound **42** crystallizes in the monoclinic space group Pn, with a single mirror plane of symmetry (actually a glide plane). In the crystal, the molecules self-assembled into homochiral layers, with an easily defined "director" tilt and layer normal.

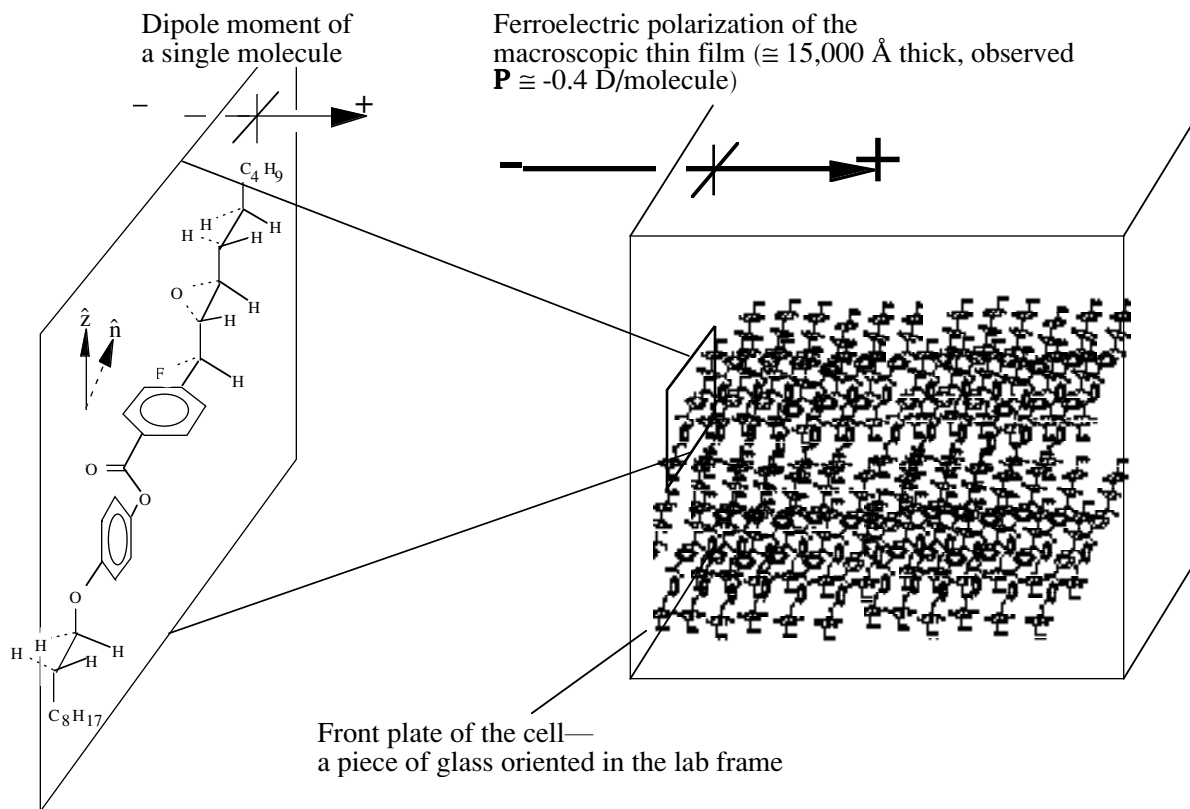


Figure 17. A direct connection between macroscopic polarization (a "chirality phenomenon") and microscopic relative and absolute configuration.

It is evident that the molecules pack in an "anti-clinic" manner, such that the tilt direction alternates from layer to layer. Thus, as is shown in the view on the right (with the crystallographic mirror plane congruent with the plane of the page), the (R) molecules in the top layer tilt back, while the (S) molecules tilt forward. It is obvious that the crystal is polar—representing the class of achiral polar materials (indeed, every direction in the plane of the page in the right hand view is a polar axis—naturally there can be no non-zero component of the polarization normal to the mirror plane). If one imagines that the cyano and the benzoate carbonyl dipoles are the only important molecular dipoles (not true here, given the polar orientation of the nitro groups), it is quite easy to give a sign of \mathbf{P} to each layer, as indicated, by assuming the cyano dipole is the larger. It is interesting to note that the packing in this crystal is similar to the first-order prediction of the Boulder Model for an FLC phase of such molecules!

There are, however, important differences. Thus, there is a gauche bend at the C2-C3 bond, such that the C4-C9 n-hexyl grouping is anti to the cyano group at C2. Due to this conformational preference, the tails are not really "less tilted" than the core, as indicated in the orthogonal view of the crystal structure shown on the left in the Figure (viewing the crystal down the "polar axis" of the cyano groups). This is quite reasonable, since a priori, in a crystal, the tails might be expected to take up less volume than the core (since they're not melted, as in an LC phase), and therefore be more tilted than the core. In this crystal the cyano groupings seem to dominate the tail packing—nuzzling into a cavity formed by the gauche bend, and forming a close contact (H-bond or dipole-dipole interaction) with the methine hydrogen α to the cyano group on an adjacent molecule.

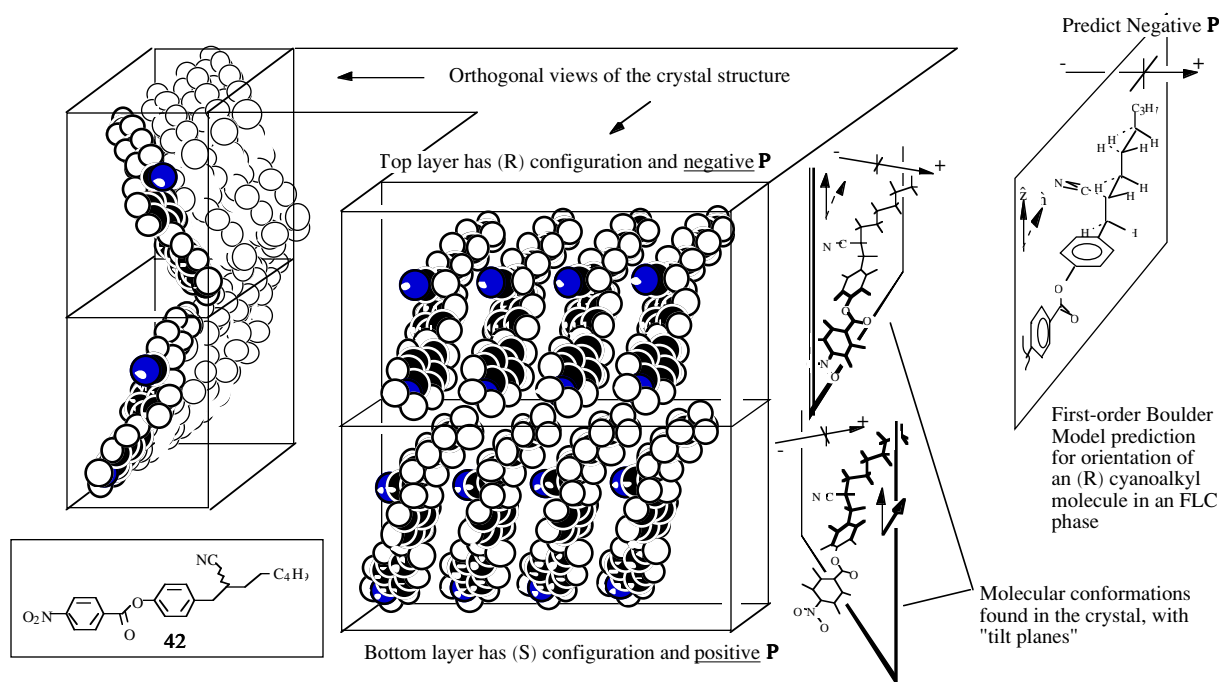


Figure 18. Crystal structure of a racemic 2-cyanoalkylphenyl benzoate.

Studies aimed at elucidating the behavior of enantiomerically enriched cyanoalkylphenyl benzoates in FLC hosts are in progress, and it will be interesting to determine whether the sign of **P** for the FLC phases possessing these units will be the same as that observed in the homochiral layers of the racemic crystal.

6.2 An interpretation of the polarization of alkoxyphenylbenzoates

Bis-alkoxyphenylbenzoates represent an important FLC class, but as mentioned above, properties of the prototypical active amyl alcohol derivatives or the lactic ethers synthesized in our group could not be interpreted using the Boulder Model. However, before the polarization was measured, we had predicted the sign and qualitatively the magnitude of **P** for the trans epoxy ethers represented by compound **12** based upon the model shown in Figure 19.

Thus, assuming the alkoxy tail prefers a conformation wherein the C1 carbon is in the plane of the aromatic ring (a reasonable assumption allowing the well known "anisole" resonance stabilization of this type of conformation) we had proposed the preferred conformation and rotational orientation shown in the drawing on the left for the (S,S) epoxy ether **12**. This orientation suggests that the polarization of the epoxy ether should be large and positive, in good agreement with experiment (Figure 7). The assumption regarding the preferred conformation for compound **12** in the C* phase gets some support from the experimentally observed conformation of epoxy ether phenylbenzoate **43** occurring in single crystals by X-ray diffraction,⁶⁵ as shown in the Figure.

The orientational preferences indicated in Figure 19, however, are insufficient to interpret results observed for the well known methyl substituted alkoxy compounds. The problem is illustrated by the properties of the 1-methylheptyloxyphenylbenzoate **44**, shown in Figure 20 along with the classic homologous series of compounds **33**. If the conformation and rotational orientation of

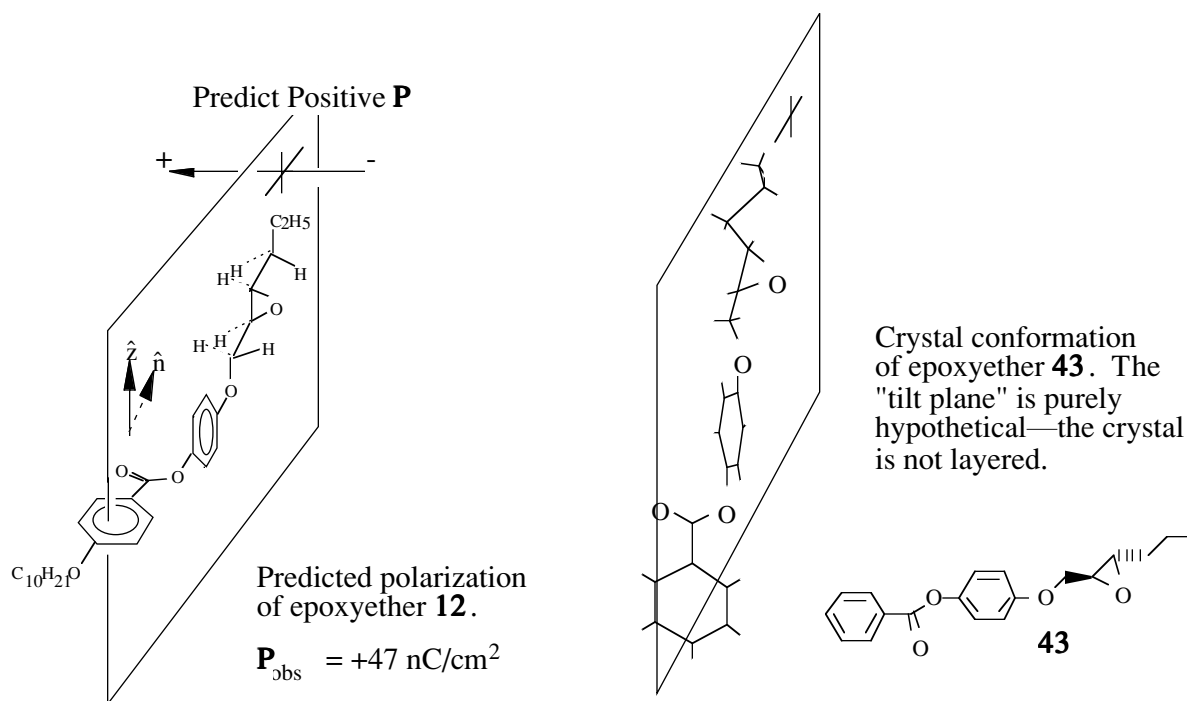


Figure 19. Proposed preferred conformation and rotational orientation of epoxy ether **12** according to the Boulder Model, and the conformation observed for a crystal of epoxyether **43**.

these materials were similar to that shown in Figure 19, then the alkoxy dipole would be in the tilt plane, and therefore would not contribute to \mathbf{P} ! Thus, one would expect all members of the series to possess small polarization density, with alternating sign of \mathbf{P} , deriving from orientation of the methyl-methine dipole as proposed by Goodby et. al.

As mentioned above, those authors discussed the lack of sign alternation as indicating a dramatic difference in the rotational orientation of the members of the series (tails more tilted than the core for some homologues), and while discussing the anomalously high polarization observed for the 1-methyl substituted compounds, gave no proposed explanation.

While we feel the factors involved in dipole orientation of the low- \mathbf{P} members of the series are too subtle to interpret at this time, we have developed a simple, attractive model for the properties of the 1-methylheptyloxy compounds illustrated by compounds **10** and **44**.

Thus, while many systems are apparently understandable in terms of a single major conformation and rotational orientation in the FLC phase, in many important cases it will be necessary to consider several such molecular states, as suggested by equations 2 and 3. From the beginning, it seemed likely that the properties of the methyl substituted alkoxy compounds were related to a contribution to the polarization from the alkoxy dipole. This means that in some important molecular states, the alkoxy dipole must be oriented normal to the tilt plane, and that this orientation is handed, such that summing over all conformations does not average the net orientation to zero.

Experimentally, to our knowledge every known FLC mesogen possessing the 1-methylheptyloxy tail pioneered by the Chisso group (many of which possess enantiotropic C^* phases) shows

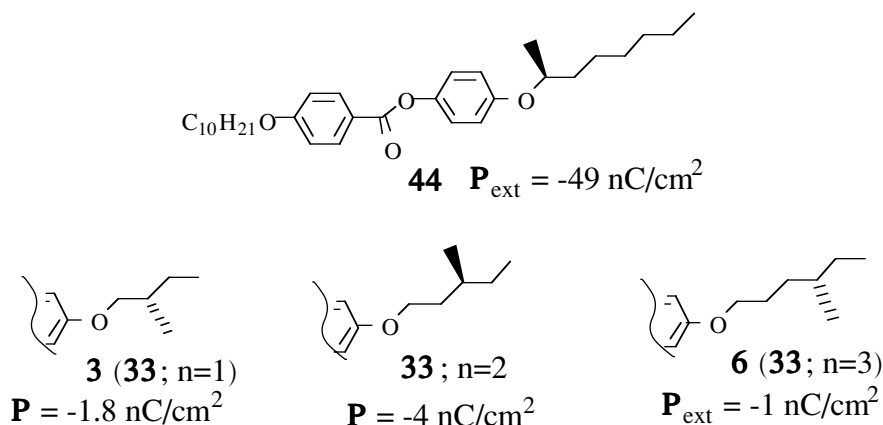


Figure 20. Properties of some classic methyl-substituted phenylbenzoates.

negative P when the tail has the (S) absolute configuration. The sign and magnitude of P of this large class of mesogens is nicely exemplified by the properties of the (S) phenylbenzoate **44**, measured in our own labs using 10.O.7* as host.

Figure 21 illustrates our interpretation of the observed polarization of this important class of FLC materials. Thus, in imagining how compound **44** would dock into the bent cylinder binding site, it seems clear that a family of three important conformations must be considered, as indicated. Conformation B is similar to that shown in Figure 19 to interpret the sign of P for the epoxyether **12**, but no large polarization would be expected from this orientational state since the alkoxy dipole is in the tilt plane.

For the two likely conformational and rotational states A and C, however, the alkoxy dipole has a large component oriented normal to the tilt plane as shown. Note that these conformations possess a "gauche bend" at the C1-C2 bond in order to keep the tail in the binding site. If there were no stereocenter in the tail, conformations A and C would be enantiomeric, and exist in equal number density, destroying the polar orientation of dipoles. However, given the stereocenter, these conformations are in fact diastereomeric, and should have significantly different steric strain energies, and therefore different number densities in the phase.

Specifically, conformation C has a gauche interaction between the methyl substituent and the methylene grouping at C4 on the tail which is lacking in conformation A. The bottom of Figure 21 illustrates three molecular mechanics minima in orthographic projection, representing the drawings shown at the top of the Figure. Also given are the relative MM steric strain energies (MMXE) calculated for conformations A, B and C in isotropic medium (gas phase). While clearly the FLC phase is anything but isotropic, it seems reasonable that the intermolecular interactions in the phase would not perturb the relative strain energies of the three conformations shown, specifically since they were already screened to "fit" in the binding site.

If conformation and rotational orientation A were indeed favored over C in the FLC phase, with conformation B also present, then a negative net polarization would be expected. Indeed, the simple picture given in Figure 21 nicely explains the observed results for all known FLCs possessing the simple 1-methylalkoxy chiral tail.

In order to further probe this system, and provide additional tests for the model illustrated in Figure 21, the diastereomeric pair of epoxyethers **45** and **46** were prepared and characterized as guests in

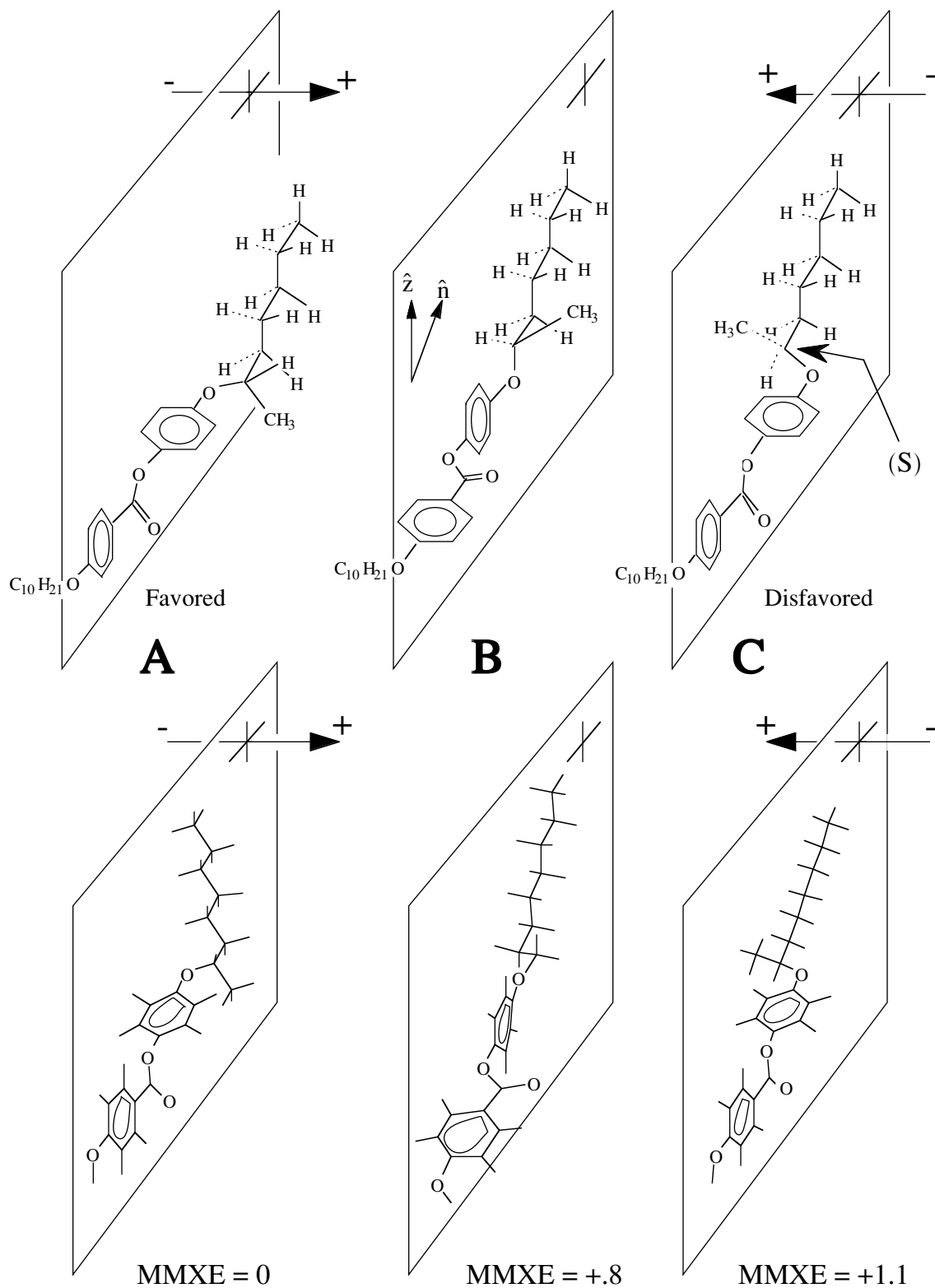


Figure 21. Interpretation of the polarization of compound **44** according to the Boulder Model. the host 10.O.7*, as shown in Figure 22. As indicated in the Figure, the Boulder model suggests that the 1-(R)-2,3-(S,S) epoxide **45** should exhibit a large, positive **P**, since in the preferred

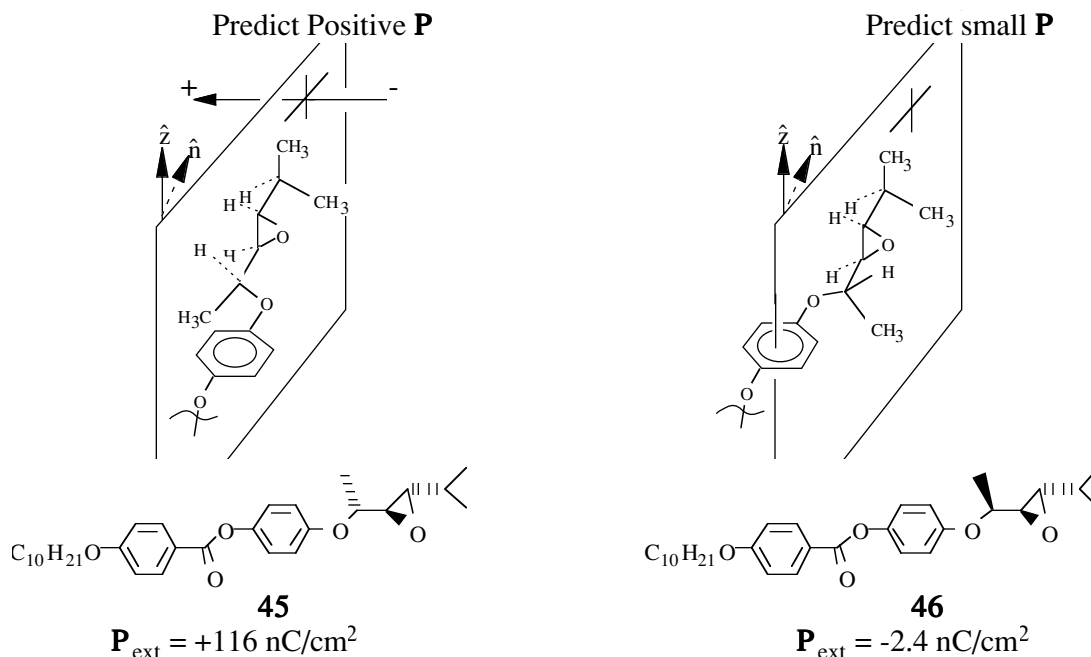


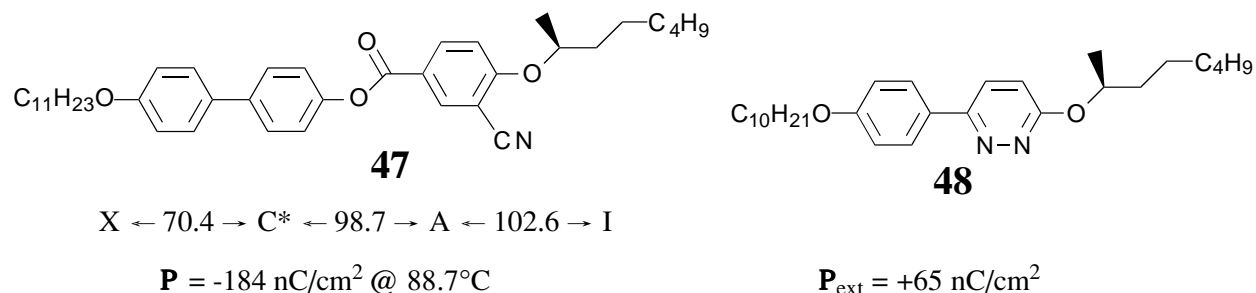
Figure 22. Proposed single most preferred conformational and rotational orientation for the diastereomeric pair of epoxyethers **45** and **46**, and observed polarization for each component.

orientation, the alkoxy and epoxy dipoles are aligned, while the diastereomeric material **46** should show small **P** since these dipoles are opposed relative to the tilt plane. As indicated, these expectations were met, and indeed to our knowledge this pair of diastereomers shows the largest difference in magnitude of **P** yet found for any stereoisomeric pair of FLC components (almost a factor of 50, and of opposite sign).

The Chisso group has also reported results quite consistent with the model illustrated in Figure 21. Thus, the Chisso chemists proposed that substitution of the aryl ring bearing their chiral tail with an electronegative substituent at the ortho position should increase the magnitude of the molecular dipole moment along the axis of the alkoxy dipole. They felt this should increase the magnitude of **P**, implying that the alkoxy dipole must be oriented normal to the tilt plane, though no discussion of the origins of the observed sign of **P**, or illustration of the actual molecular orientation relative to the tilt plane in the FLC phase, was given.

In this beautiful example of FLC design, the Chisso group reported a large class of compounds exemplified by the biphenylbenzoate **47**, possessing substituents ortho to the chiral tail. Indeed, normalizing for temperature and tilt angle, materials such as these possess among the largest polarization densities known. In addition, the Chisso group reported the highly interesting observation that the pyridazine compound **48** shows positive extrapolated **P** for the (*S*) alkoxy tail. The latter result was interpreted in terms of a ring orientation where the nitrogen lone pair is syn-periplanar to the stereocenter, such that the heterocycle dipole and alkoxy dipole are opposed. Both the sign and magnitude of **P** for these Chisso compounds are nicely rationalized by the model shown in Figure 21.

Ferroelectric Liquid Crystals



In order to further probe this fascinating and potentially very useful aromatic ring orientation in FLC phases, we have prepared and obtained preliminary data on a series of nicotinic acid derivatives, as illustrated in Figure 23. Thus, as Chisso proposed for the pyridazine compound **48**, we expected the pyridine nitrogen atom of compound **49** to prefer a conformation syn periplanar to the stereocenter on the alkoxy tail, as indicated in the Figure. This assumes that the lone pair on nitrogen is less sterically demanding than an aromatic C-H bond—a reasonable hypothesis.

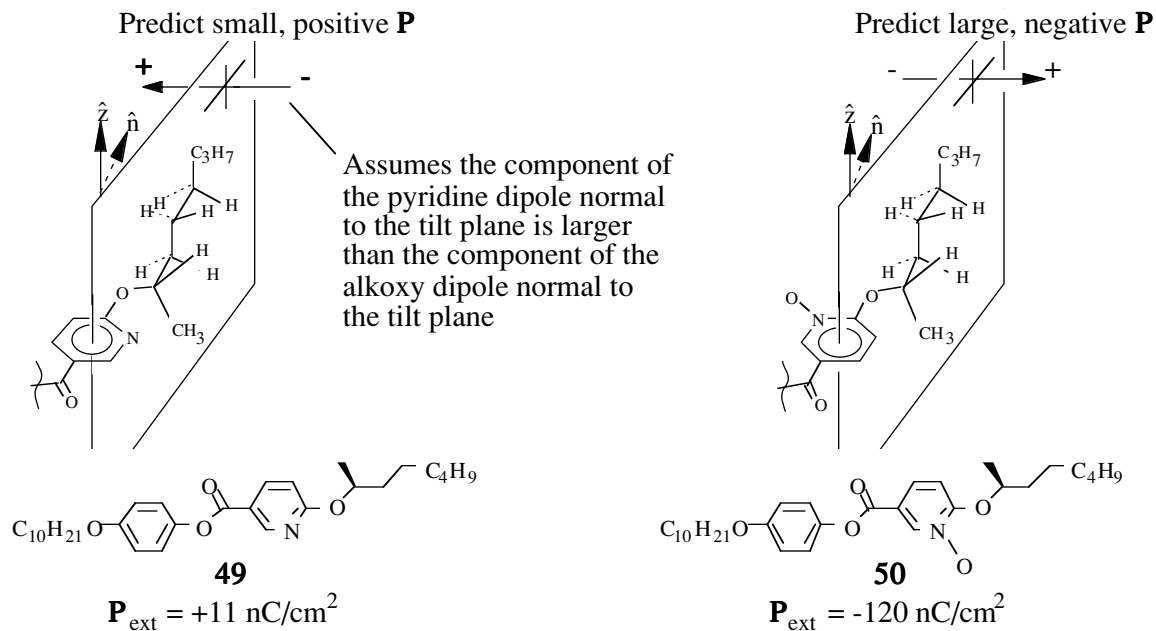


Figure 23. Proposed single most preferred conformational and rotational orientation for the nicotinic acid derivatives **49** and **50**, and observed polarization for each component.

Since the dipole moment of pyridine ($> 2D$)⁶⁶ is larger than the dipole moment of a C-O bond ($\cong 1D$) it was expected that the sign of **P** for compound **49** would be positive, and of smaller magnitude than the non-heterocyclic analogue. But, upon oxidation of the pyridine to the N-oxide **50**, the model suggested that the aromatic ring should "flip" relative to the chiral tail in the preferred orientation, as indicated in the Figure. Assuming that the dipole moment of the N-oxide is negative on oxygen, and of large magnitude (the dipole moment of pyridine N-oxide $\cong 4D$),⁶³ the model predicts a negative polarization for compound **50**, with magnitude enhanced relative to the non-heterocyclic compound. Again, as indicated in the Figure, these expectations were indeed met.

Thus, in summary, we feel the basic interpretation of functional group orientation in FLCs possessing alkoxy chiral tails given in Figure 21 has considerable merit. Further work aimed at probing aromatic ring orientation in FLCs is in progress in our laboratories.

6.3 FLC Polymers

For many interesting applications, FLC thin films are useful. However, for other applications it is convenient or necessary that polar functional group orientation occur in a solid rather than a liquid. For this reason, a large effort has recently been launched in various groups directed towards the synthesis and characterization of ferroelectric liquid crystal polymers (FLCPs).^{67,68} Indeed, in accord with the general fact that when mesogenic molecules are attached to a simple polymer backbone, LC phases are very likely to occur (most LC phases known to occur in low molecular weight materials have also been identified in LC polymers), many FLCPs have been observed.

Due to the small magnitude of **P** measured for these materials, and difficulty in obtaining well aligned samples for characterization, however, it has not been previously possible to interpret the sign or magnitude of **P** in these polymer films on a molecular level. Thus, for example, polyacrylate and polymethacrylate FLCPs have been prepared incorporating mesogens similar to 10.O.7* (with the 4-methylheptyloxy chiral tail), and measured polarization densities on the order of 1 nC/cm² have been observed.

Given the great potential importance of FLCPs, we recently began a program aimed at studying these materials and determining whether controlled polar orientation of functional groups in non-crystalline solids could be achieved. For the polymer backbone, the well known polysiloxane chain was chosen since it is known that this side chain liquid crystalline polymers possessing this backbone often give tilted phases. For the chiral mesogen, the epoxy ether system of compound **12** was chosen due its ready availability, the expected stability of the epoxide unit under the conditions required to attach the mesogen to the polymer backbone, and our high degree of understanding of functional group orientation in this system.

Thus, the side FLCP **51**, indicated in Figure 24, was prepared and characterized.⁶⁹ To our delight, the neat polymer actually possessed a very broad temperature range, stable C* phase as shown in the Figure. This is in complete agreement with expectation, since as mentioned above, the presence of the polymer backbone has a strong tendency to broaden the LC phases observed for the corresponding low molecular weight mesogenic units.

Using a novel combination of surface conditions, and physical manipulation, it proved possible to obtain well aligned samples of the FLCP **51** between glass plates. While switching of the FLCP was slow (\cong msec), it was still quite possible to accurately measure the polarization of the ferroelectric polymer film by the standard polarization reversal method. As shown in the Figure, the neat polymer exhibited a polarization of **P** = +60 nC/cm², in good agreement with that observed for the monomer FLC material **12** (**P** = +45 nC/cm²).

When the FLCP is cooled below about 85°C, switching stops, indicating that the polymer has "frozen" into a glass. While in the bulk the material is crystalline at room temperature, the glass obtained in a thin film has never been seen to crystallize, even after many months at room temperature. This polymer glass is electrically polar at room temperature, as indicated by experimental measurements of the static polarization.

It is well known in the LC polymer field that a glass resulting from the "freezing" of an LC polymer film retains the order present in the LC phase. The measurements on the glass of polymer

molecular orientation occurring in the polymer film. That is, the observed polarization is a result of polar orientation of the epoxide dipole, and the overall molecular order is similar to that proposed for the low molecular weight compound **12**, but with the siloxane chain present in the layers as indicated.

This model suggests that, contrary to the general rule with polymers, the FLC should be soluble in low molecular weight C phase hosts, and the polarization observed for the mixtures should be a linear function of the concentration of the guest (in this case the polymer side chain mesogens). Indeed, polymer **51** is miscible in all proportions with host 10.O.7*, and as shown in the Figure, the polarization obtained for mixtures containing 20% and 50% by weight of guest, as well as the neat guest, are linear with concentration of the guest. To our knowledge this is the first example of host-guest mixing experiments using a low molecular weight C phase host, and FLC guest. The nicely consistent results obtained seem to support the basic proposed model for functional group order in the polymer film, and further studies aimed at characterizing and utilizing these highly unusual materials are in progress.

7 Conclusion

The experimental study of ferroelectricity in fluids is but fifteen years old, yet already there are important potential applications of the unique materials exhibiting this property, and considerable progress in the development of a molecular level understanding of the phenomenon has been made. Even so, there are many mysteries on the scientific front, and many new applications under development and perhaps even more yet to be conceived.

We hope that FLC materials will help strengthen the bridge between electronics and organic stereochemistry—an exciting future awaits.

8 Acknowledgements

The author would like to thank the following agencies for funding the FLC chemistry work occurring in his labs, and for supporting the task of writing this manuscript: The Office of Naval Research, the NSF Engineering Research Center program (Optoelectronic Computing Systems Center, Grant # CDR-8622236), and the National Science Foundation (Grant # DMR-8611192). In addition, the invaluable contributions of Professor Noel Clark to the FLC chemistry effort in Boulder cannot be overstated. Finally, the author wishes to thank Dr. Mark Handschy and Dr. Michael Wand, of Displaytech, Inc., for their great help in preparing this manuscript.

9 Reference

- ¹ Two outstanding recent reviews describing aspects of the properties of polar organic crystals are given in: a) Paul, I. C.; Curtin, D. Y. "Gas-Solid Reactions and Polar Crystals," in *Organic Solid State Chemistry*, Desiraju, G. R. (Ed.); Elsevier, Amsterdam, 1987; pp 331-370. and b) Addadi, L.; Berkovitch-Yellin, Z.; Weissbuch, I.; Lahav, M.; Leiserowitz, L. "A Link Between Macroscopic Phenomena and Molecular Chirality: Crystals as Probes for the Direct Assignment of Absolute Configuration of Chiral Molecules," in *Topics in Stereochemistry*, Eliel, E. L.; Wilen, S. H. Allinger, N. L. (Eds.); John Wiley & Sons, Inc., 1987; pp 1-85

- ² Hahn, T.; Klapper, H. "Point Groups and Crystal Classes," in *International Tables for Crystallography*, Hahn, T. (Ed.); D. Reidel Publishing Company, Dordrecht, Holland, 1983; pp 745-786.
- ³ Williams, D. J. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 690-703.
- ⁴ Leslie, T. M.; Demartino, R. N.; Choe, E. W.; Khanarian, G.; Haas, D.; Nelson, G.; Stamatoff, J. B.; Stuetz, D. E.; Teng, C.-C.; Yoon, H.-N. *Mol. Cryst. Liq. Cryst.* **1987**, *153*, 451-477.
- ⁵ Popovitz-Biro, R.; Hill, K.; Landau, E. M.; Lahav, M.; Leiserowitz, L.; Sagiv, J. *J. Am. Chem. Soc.* **1988**, *110*, 2672-2674.
- ⁶ Tillman, N.; Ulman, A.; Schildkraut, J. S.; Penner, T. L. *J. Am. Chem. Soc.* **1988**, *110*, 6136-6144.
- ⁷ a) de Gennes, P. G. *The Physics of Liquid Crystals*; Oxford U.P.: London, 1974. b) Chandrasekhar, S. *Liquid Crystals*; Cambridge University Press: Cambridge, 1977.
- ⁸ Blinov, L. M.; Davidyán, S. A.; Petrov, A. G.; Todorov, A. T.; Yablonski, S. V., "Manifestation of Ferroelectricity in a Lyotropic Liquid Crystal with a Chiral Additive: A Structure Analogous of a Biomembrane," Abstracts of the Second International Conference on Ferroelectric Liquid Crystals, Göteborg, Sweden; Abstract Number O 31, (1989).
- ⁹ Saupe, A. *Mol. Cryst. Liq. Cryst.* **1969**, *7*, 59-74.
- ¹⁰ Meyer, R. B. "Structural Problems in Liquid Crystal Physics," in *Molecular Fluids*, Balian, R. Weill, G. (Eds.); Gordon and Breach, London, 1976; p 272. This paper presents a written account of work presented at the "Summer School of Theoretical Physics," held in Les Houches, France, August, 1973. Meyer also presented this idea, along with preliminary experimental results, in a famous talk at the Vth International Liquid Crystal Conference in Stockholm, in 1974.
- ¹¹ Meyer, R. B.; Liebert, L.; Strzelecki, L.; Keller, P. *J. Phys., Lett. (Orsay, Fr.)* **1975**, *36*, L-69-L71.
- ¹² Helfrich, W.; Oh, C. S. *Mol. Cryst. Liq. Cryst.* **1971**, *14*, 289-292.
- ¹³ Clark, N. A.; Lagerwall, S. T. *Appl. Phys. Lett.* **1980**, *36*, 899-901.
- ¹⁴ a) Handschy, M. A.; Clark, N. A. *App. Phys. Lett.* **1982**, *41*, 39. b) Clark, N. A.; Handschy, M. A.; Lagerwall, S. T. *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 213-234. c) Xue, J.-Z.; Handschy, M. A.; Clark, N. A. *Ferroelectrics* **1987**, *73*, 305. d) Xue, J.-Z.; Handschy, M. A.; Clark, N. A. *Liquid Crystals* **1987**, *2*, 707-716.
- ¹⁵ Handschy, M. A.; Johnson, K. M.; Moddel, G.; Pagano-Stauffer, L. A. *Ferroelectrics* **1988**, *85*, 279-289.
- ¹⁶ a) Moddel, G.; Johnson, K. M.; Handschy, M. A., *Optical and Digital Pattern Recognition*, Liu, H.-K. Schenker, P., Editor, Proc. SPIE 754, 207 (1987). b) Pagano-Stauffer, L. A.; Handschy, M. A.; Moddel, G., "High Speed High Resolution Optically Addressed Spatial

- Light Modulator," *Optical Information Processing Systems and Architectures*, Javidi, B., Editor, Proc. SPIE 1151, (in press).
- ¹⁷ Clark, N. A.; Lagerwall, S. T. *Ferroelectrics* **1984**, *59*, 25-67.
- ¹⁸ a) Martinot-Lagarde, P. *J. Phys., Colloq. (Orsay, Fr.)* **1976**, *37*, 129. b) Martinot-Lagarde, P. *J. Phys., Lett. (Orsay, Fr.)* **1977**, *38*, L-17.
- ¹⁹ Keller, P.; Liebert, L.; Strzelecki, L. *J. Phys., Colloq. (Orsay, Fr.)* **1976**, *37*, 27 - 33.
- ²⁰ Demus, D.; Demus, H.; Zasche, H. *Flüssige Kristalle in Tabellen*; VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, 1974.
- ²¹ Keller, P.; Juge, S.; Liebert, L.; Strzelecki, L. *C. R. Acad. Sc. Paris* **1976**, *282 C*, 639-641.
- ²² Chemical stability is always relative. For example, while the phenylbenzoates typified by 10.O.5* are very stable thermally and with respect to visible and IR light, they are apparently unstable with UV irradiation, and decompose after long periods of time in sun light.
- ²³ a) Loseva, M. V.; Ostrovskii, B. I.; Rabinovich, A. Z.; Sonin, A. S.; Strukov, B. A.; Chernova, N. I. *Pis'ma Zh. Eksp. Teor. Fiz.* **1978**, *28*, 404-409 (English translation: *JETP Lett.* **1978**, *28*, 375. b) Ostrovskii, B. I.; Rabinovich, A. Z.; Sonin, A. S.; Sorkin, E. L.; Strukov, B. A.; Taraskin, S. A. *Ferroelectrics* **1980**, *24*, 309-312.
- ²⁴ Hallsby, A.; Nilsson, M.; Otterholm, B. *Mol. Cryst. Liq. Cryst.* **1982**, *82*, 61-68.
- ²⁵ a) Goodby, J. W.; Leslie, T. M. *Mol. Cryst. Liq. Cryst.* **1984**, *110*, 175-203. b) Goodby, J. W.; Leslie, T. M. *Liq. Cryst. Ordered Fluids* **1984**, *4*, 1-32.
- ²⁶ Samulski, E. T.; Dong, R. *J. Chem. Phys.* **1982**, *77*, 5090-5096.
- ²⁷ Keller, P. *Ferroelectrics* **1984**, *58*, 3.
- ²⁸ The Keller compound 10.O.7* (4-[(S)-(4-methylhexyl)oxy]phenyl 4-(decyloxy)benzoate), the lactic ether **11** (4-[(S)-2-ethoxypropoxy]phenyl 4-(decyloxy)benzoate), the epoxy ether **12** (4-[(S,S)-2,3-epoxyhexyloxy]phenyl 4-(decyloxy)benzoate), and the α -chloroester **16** (4-[(S)-2-chloro-3-methylbutyryloxy]phenyl 4-(decyloxy)benzoate) and the (R) enantiomer of the latter, are commercially available from Aldrich.
- ²⁹ Gray, G. W.; Goodby, J. W. *Mol. Cryst. Liq. Cryst.* **1976**, *37*, 157-188.
- ³⁰ a) Yoshino, K.; Ozaki, M.; Sakurai, T.; Sakamoto, K.; Honma, I. M. *Jpn. J. Appl. Phys.* **1984**, *23*, 175-177. b) Sakurai, T.; Sakamoto, K.; Honma, M.; Yoshino, K.; Ozaki, M. *Ferroelectrics* **1984**, *58*, 21-32. c) Sakurai, T.; Mikami, N.; Yoshino, K. *Jpn. J. Appl. Phys.* **1985**, *24*, 56-58.
- ³¹ a) Inukai, T.; Saitoh, S.; Inoue, H.; Miyazawa, K.; Terashima, K.; Furukawa, K. *Mol. Cryst. Liq. Cryst.* **1986**, *141*, 251. b) Furukawa, K.; Terashima, K.; Mitsuyoshi, I.; Saitoh, S.; Miyazawa, K.; Inukai, T. *Ferroelectrics* **1988**, *85*, 451-459.
- ³² a) Walba, D. M.; Vohra, R.; Slater, S.; Clark, N. A.; Supon, F.; Handschy, M. *Bulletin of*

- the American Physical Society* **1985**, *30*, 330. b) Walba, D. M.; Slater, S. C.; Thurmes, W. N.; Clark, N. A.; Handschy, M. A.; Supon, F. *J. Am. Chem. Soc.* **1986**, *108*, 5210-5221. c) Lagerwall, S. T.; Wahl, J.; Clark, N. A., "Ferroelectric Liquid Crystals for Displays," *1985 International Display Research Conference*, Editor, Cat. No. 85CH2239-2, 213-221 (1985).
- ³³ Walba, D. M.; Vohra, R. T.; Clark, N. A.; Handschy, M. A.; Xue, J.; Parmar, D. S.; Lagerwall, S. T.; Skarp, K. *J. Am. Chem. Soc.* **1986**, *108*, 7424-7425. See also reference 32c.
- ³⁴ a) Rieker, T. P.; Clark, N. A.; Smith, G. S.; Parmar, D. S.; Sirota, E. B.; Safinya, C. R. *Phys. Rev. Lett.* **1987**, *59*, 2658. b) Clark, N. A.; Rieker, T. P. *Phys. Rev. A* **1988**, *37*, 1053.
- ³⁵ Clark, N. A.; Rieker, T. P.; MacLennan, J. E. *Ferroelectrics* **1988**, *85*, 79-97.
- ³⁶ Katsuki, T.; Sharpless, B. K. *J. Am. Chem. Soc.* **1980**, *102*, 5974-5976.
- ³⁷ a) Beresnev, L. A.; Pozhidaev, E. P.; Blinov, L. M.; Pavlyuchenko, A. I.; Étingen, N. B. *JETP Lett.* **1982**, *35*, 531-534. b) Beresnev, L. A.; Blinov, L. M.; Baikalov, V. A.; Pozhidayev, E. P.; Purvanetskas, G. V.; Pavluchenko, A. I. *Mol. Cryst. Liq. Cryst.* **1982**, *89*, 327-338.
- ³⁸ Mohr, K.; Köhler, S.; Worm, K.; Pelzl, G.; Diele, S.; Zschke, H.; Demus, D.; Andersson, G.; Dahl, I.; Lagerwall, S. T.; Skarp, K.; Stebler, B. *Mol. Cryst. Liq. Cryst.* **1987**, *146*, 151-171.
- ³⁹ a) Ozaki, M.; Yoshino, K.; Sakurai, T.; Mikami, N.; Higuchi, R. *J. Chem. Phys.* **1987**, *86*, 3648-3654. b) Yoshino, K.; Ozaki, M.; Kishio, S. I.; Sakurai, T.; Mikami, N.; Higuchi, R. I.; Masao, H. *Mol. Cryst. Liq. Cryst.* **1987**, *144*, 87-103. c) Sakurai, T.; Mikami, N.; Higuchi, R.; Honma, M.; Yoshino, K. *Ferroelectrics* **1988**, *85*, 469-478.
- ⁴⁰ Bahr, C. H.; Heppke, G. *Mol. Cryst. Liq. Cryst. Letters* **1986**, *4*, 31-37.
- ⁴¹ Compound **18** was prepared by M.D. Wand, R.T. Vohra and D.M. Walba, and the polarization was measured by R. Shao, D.S. Parmar and N.A. Clark in Boulder.
- ⁴² Parmar, D. S.; Clark, N. A.; Walba, D. M.; Wand, M. D. *Phys. Rev. Lett.* **1989**, *62*, 2136-2139.
- ⁴³ Bone, M. F.; Bradshaw, M. J.; Chan, L. K. M.; Coates, D.; Constant, J.; Gemmell, P. A.; Gray, G. W.; Lacey, D.; Toyne, K. J. *Mol. Cryst. Liq. Cryst.* **1988**, *164*, 117-134.
- ⁴⁴ Yoshino, K.; Ozaki, M.; Taniguchi, H.; Ito, M.; Satoh, K.; Yamasaki, N.; Kitazume, T. *Jap. J. Appl. Phys.* **1987**, *26*, L77-L78.
- ⁴⁵ Geelhaar, T.; Kurmeier, H.-A.; Wächtler, A. E. F. We thank Dr. Geelhaar for providing a preprint of this work prior to publication.
- ⁴⁶ a) Kuczynski, W.; Stegemeyer, H. *Chem. Phys. Lett.* **1980**, *70*, 123. b) Kuczynski, W. *Ber. Bunsenges. Phys. Chemie* **1981**, *85*, 234.

- 47 a) Beresnev, L. A.; Pozhidaev, E. P.; Blinov, L. M.; Pavlyuchenko, A. I.; Étingen, N. B. *JETP Lett.* **1982**, *35*, 531-534. b) Beresnev, L. A.; Blinov, L. M.; Baikalov, V. A.; Pozhidayev, E. P.; Purvanetskas, G. V.; Pavluchenko, A. I. *Mol. Cryst. Liq. Cryst.* **1982**, *89*, 327-338.
- 48 The synthesis is given in: Chan, L. K. M.; Gray, G. W.; Lacey, D.; Toyne, K. J. *Mol. Cryst. Liq. Cryst.* **1988**, *158B*, 209-240. The phase sequences shown in Figure 8 were presented in a seminar by G. Gray, Chalmers Technical Institute, Göteborg, Sweden, May, 1987.
- 49 Bone, M. F.; Coates, D.; Gray, G. W.; Lacey, D.; Toyne, K. J.; Yound, D. J. *Mol. Cryst. Liq. Cryst. Letters* **1986**, *3*, 189-195.
- 50 a) Eidman, K.; Walba, D. M.; Parmar, D. S.; Clark, N. A., Abstracts of the 11th Int. Liq. Cryst. Conf., Berkeley, California, 0-040-FE (1986). b) Walba, D. M.; Eidman, K. F.; Haltiwanger, R. C. *J. Org. Chem.* **1989**, in press.
- 51 Sage, I.; Jenner, J.; Chambers, M.; Bradshaw, M. J.; Brimmell, V.; Constant, J.; Hughes, J. R.; Raynes, E. P.; Samra, A. K.; Gray, G. W.; Lacey, D.; Toyne, K.; Chan, L.; Shenouda, I.; Jackson, A. *Ferroelectrics* **1988**, *85*, 351-359.
- 52 Personal communication with G. Scherowsky.
- 53 Scherowsky, G.; Rhode, E.; Schliwa, A.; Sprnger, J.; Trapp, W. Presented at the 2nd International Ferroelectric Liquid Crystal Conference, Göteborg, Sweden, June 1989.
- 54 McMillan, W. L. *Phys. Rev. A* **1973**, *8*, 1921-1929.
- 55 Goodby, J. W.; Gray, G. W.; McDonnell, D. G. *Mol. Cryst. Liq. Cryst.* **1977**, *34*, 183-188.
- 56 Bartolino, R.; Doucet, J.; Durand, G. *Ann. Phys.* **1978**, *3*, 389-396.
- 57 Keller, E. N.; Nachaliel, E.; Davidov, D. *Phys. Rev. A* **1986**, *34*, 4363-4369.
- 58 Goodby, J. W.; Chin, E.; Leslie, T. M.; Geary, J. M.; Patel, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 4729-4735.
- 59 Goodby, J. W.; Chin, E. *J. Am. Chem. Soc.* **1986**, *108*, 4736-4742.
- 60 Compound **33**, n=1, is the Russian ester 10.O.5* (**3**); Compound **33**, n=2, 10.O.6*, was first reported in: Decobert, G.; Dubois, J.-C. *Nouv. J. Chim.* **1986**, *10*, 777-782. The polarization of 10.O.6* = -4 nC/cm²; unpublished results from our laboratories. Compound **33**, n=3, is the Keller compound 10.O.7*, with a polarization estimated in our labs to be -1 nC/cm².
- 61 a) Walba, D. M.; Clark, N. A., "Model for the Molecular Origins of the Polarization in Ferroelectric Liquid Crystals," *Spatial Light Modulators and Applications II*, Efron, U., Editor, Proc. SPIE 825, 81-87 (1988). b) Walba, D. M.; Clark, N. A. *Ferroelectrics* **1988**, *84*, 65-72. c) Walba, D. M.; Clark, N. A.; Razavi, H. A.; Parmar, D. S. "A Novel

Application of the Host-Guest Paradigm: Design of Organic Optoelectronic Materials," in *Proceedings of the 5th International Symposium on Inclusion Phenomena and Molecular Recognition*, Atwood, J. L. (Ed.); Plenum Publishing Corp, in press.

- ⁶² Samulski, E. T.; Toriumi, H. *J. Chem. Phys.* **1983**, *79*, 5194 and references therein.
- ⁶³ Walba, D. M.; Razavi, H. A.; Clark, N. A.; Parmar, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 8686-8691.
- ⁶⁴ Walba, D. M.; Clark, N. A.; Razavi, H. A.; Eidman, K. F.; Haltiwanger, R. C.; Parmar, D. S., "A Novel Application of the Molecular Recognition Paradigm: Design of Ferroelectric Liquid Crystals," *Liquid Crystal Chemistry, Physics, and Applications*, Doane, J. W. Yaniv, Z., Editor, Proc. SPIE 1080, 115-122 (1989).
- ⁶⁵ The unpublished crystal structure of epoxyether phenylbenzoate **43** was determined by R. Curtis Haltiwanger, University of Colorado Department of Chemistry and Biochemistry X-ray Laboratory.
- ⁶⁶ McClellan, A. L. *Tables of Experimental Dipole Moments*; W.H. Freeman and Company: San Francisco, 1963.
- ⁶⁷ a) Shibaev, V. P.; Kozlovsky, M. V.; Beresnev, L. A.; Blinov, L. M.; Plante, N. A. *Polym. Bull.* **1984**, *12*, 299. b) Decobert, G.; Soyer, F.; Dubois, J. C. *Polym. Bull.* **1985**, *14*, 179. c) Decobert, G.; Dubois, J. C.; Esselin, S.; Noel, C. *Liquid Crystals* **1986**, *1*, 307. d) Zentel, R.; Reckert, G.; Reck, B. *Liquid Crystals* **1987**, *2*, 83. e) Esselin, S.; Bosio, L.; Noel, C.; Decobert, G.; Dubois, J. C. *Liquid Crystals* **1987**, *2*, 505. f) Uchida, S.; Morita, K.; Miyoshi, K.; Hashimoto, K.; Kawasaki, K. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 93-102.
- ⁶⁸ a) Keller, P. *Ferroelectrics* **1988**, *85*, 425-434. b) Suzuki, T.; Okawa, T. *Makromol. Chem., Rapid Commun.* **1988**, *39*, 755.
- ⁶⁹ Walba, D. M.; Keller, P.; Parmar, D. S.; Clark, N. A.; Wand, M. D. *J. Am. Chem. Soc.* **1989**, in press.
- ⁷⁰ a) Moussa, F.; Cotton, J. P.; Hardouin, F.; Keller, P.; Lambert, M.; Pépy, G.; Mauzac, M.; Richard, H. *J. Physique* **1987**, *48*, 1079-1083. b) Hardouin, F.; Noirez, L.; Keller, P.; Lambert, M.; Moussa, F.; Pépy, G. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 389-397.