Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Material Properties of Ferroelectric Liquid Crystals and Their Relevance for Applications and Devices

Sven T. Lagerwall [a] , Bengt Otterholm [a] & Kent Skarp [a]

[a] Departments of Physics and Organic Chemistry, Chalmers University of Technology, S-412 96, Göteborg, Sweden

Version of record first published: 13 Dec 2006.

To cite this article: Sven T. Lagerwall , Bengt Otterholm & Kent Skarp (1987): Material Properties of Ferroelectric Liquid Crystals and Their Relevance for Applications and Devices, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 152:1, 503-587

To link to this article: http://dx.doi.org/10.1080/00268948708070976

Mol. Cryst. Liq. Cryst., 1987, Vol. 152 pp. 503-587
Photocopying permitted by license only

Printed in the United States of America

MATERIAL PROPERTIES OF FERROELECTRIC LIQUID CRYSTALS AND THEIR RELEVANCE FOR APPLICATIONS AND DEVICES

SVEN T. LAGERWALL, BENGT OTTERHOLM and KENT SKARP

Departments of Physics and Organic Chemistry,
Chalmers University of Technology,
S-412 96 Göteborg, Sweden

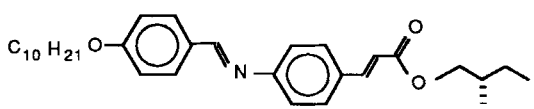
Abstract: Recent developments in understanding structural and material properties of ferroelectric liquid crystals are reviewed with emphasis on their relevance for electro-optic effects and device applications.

In only a few years the material situation has changed from one characterized by an almost complete lack of technically useful materials to one, not yet adapted to technical needs, but beginning to offer interesting, commercially available ferroelectric mixtures. The present device limitations can, however, be tracked down, not so much to the principal non-availability of materials as to the lack of understanding of which material properties are desirable and needed, in particular to permit simple and efficient matrix addressing. Thus we have centered our discussion to properties of prime importance for device dynamics in this review, which also contains a general discussion of material properties based on the molecular structure, as well as an assessment of the present industrial development.

FERROELECTRIC LIQUID CRYSTALS

Ferroelectricity has been known for crystals since 1921 when Valasek[1] investigated the C_2-symmetric crystal modification of Rochelle salt (potassium sodium tartrate). This crystal modification displayed a dielectric hysteresis indicating a spontaneous electrical polarization which is the characteristic feature of the ferroelectric state.

Ferroelectricity in liquid crystals, however, is a recently discovered phenomenon, first demonstrated 1975 in a paper[2] by the physicist R.B. Meyer together with the chemists L. Liébert, L. Strzelecki and P. Keller. Stating "...we show by symmetry that smectic C and H liquid crystals composed of chiral molecules must have a spontaneous polarization", they were able to show the presence of a spontaneous polarization by investigating the behaviour of DOBAMBC (decyloxybenzylideneaniline methylbutyl cinnamate, below), a material synthesized *ad hoc* to exhibit the above-mentioned properties in having a C* phase (and also a second tilted phase,[3] today designated I*).



DOBAMBC

Although earlier examples of materials showing a C* phase are known,[4] their ferroelectricity had never been recognized. DOBAMBC has therefore become a classic material in the field of ferroelectric liquid crystals and numerous papers dealing with it have since then appeared in the literature.

Symmetry arguments

Of the 32 crystal classes only 10 belong to point groups which permit the polarization to have a non-vanishing component, deduced by applying the pertinent symmetry operation, and thus allowing a spontaneous polarization.[5] These 10 crystal classes belong to the polar point groups C_1 (triclinic), C_4 and C_{4v} (tetragonal), C_6 and C_{6v} (hexagonal), C_2 and C_s (monoclinic), C_{2v} (orthorombic) and finally C_3 and C_{3v} (trigonal).

A close look at the point groups of the liquid crystal structures listed in *Table 1* reveals that C*, F*, G*, H*, I*, J* and K*, all of which belong to point group C_2, have the necessary properties to allow for a spontaneous polarization. Hence, all these phases are ferroelectric.

TABLE 1. Symmetries of the liquid crystal structures.

Achiral		Chiral	
N	$D_{\infty h}$	N*	D_{∞}
A	$D_{\infty h}$	A*	D_{∞}
B	D_{6h}	B*	D_6
C	C_{2h}	C*	C_2
E	D_{2h}	E*	D_2
F	C_{2h}	F*	C_2
G	C_{2h}	G*	C_2
H	C_{2h}	H*	C_2
I	C_{2h}	I*	C_2
J	C_{2h}	J*	C_2
K	C_{2h}	K*	C_2

It should be pointed out that the classification of the liquid crystal phases according to point groups is based on the time-averaged local symmetry of the phase in question. It should also be mentioned that regarding the smectic phases only the local symmetry (one layer) has been considered and

no attention has been paid to the normally present helicoidal structures of the C*, F* and I* phases. This means that the spontaneous polarization of these three phases is only a local property of each layer and that it is globally averaged to zero as the direction of the polarization changes with the helix.

Although C*, F* and I* normally have a helicoidal structure this is not necessarily the case, even in a pure compound. There are two kinds of molecular interactions involved in the helix formation. These give rise to two different effects: a spontaneous twist which is due to the molecular chirality and a spontaneous bend which is a result of the polar asymmetry. These effects may act in opposite sense and thus, in principle, a ground state helix-free C* (or F* and I*) can form (in a more or less narrow temperature interval) without a compensation of the polarization. The opposite situation, a helicoidal C* with zero polarization can, of course, also arise.[6] So far there is no reported evidence for either case whereas helix-compensated mixtures with non-vanishing **P** have been reported[7] and are easily prepared. It should be pointed out that unwinding of the helix, in whatever way, by no means makes the material non-chiral ("dechiralized"). Some authors[8] only refer to the helix-free chiral phases (G*, H*, J* and K*) as "ferroelectric" while they term the twisted phases "helielectric". With this narrowing and, in our view questionable, classification, true ferroelectricity would not have been demonstrated in liquid crystals until the advent of the surface-stabilized ferroelectric liquid crystal[9] in 1980 (*cf.* below). A further proposal has been made[10] to designate all these basic phenomena in smectics as "chiroelectric" rather than "ferroelectric". However, we think that little is gained but confusion by these distinctions. The more general distinction between proper and improper ferroelectrics may be more useful in certain circumstances, but cannot be subject to discussion in this article.

Direction of the polarization

To establish the relative direction of the spontaneous polarization, consider one isolated layer of a C* phase. The C* phase belongs to the point group C_2 (*cf. Table 1*) and consequently possesses a two-fold axis of rotation as its sole symmetry element. If the symmetry operation (rotation around the C_2 -axis) is applied to the medium, we can deduce that the polarization vector, **P**, can have a non-vanishing component only in the direction of the C_2 -axis, *i.e.* perpendicular to the direction of the tilt and to the director, **n**, see *Fig. 1*. This leaves us with two possibilities; the polarization can point in any of the two directions of the C_2 -axis. A distinction between the two situations has to be made in order to permit a complete description of the material properties. According to the most natural convention,[11] if **z**, **n** and **P** form a right-handed system the polarization is positive, should they form a left-handed system it is negative, *cf. Fig. 2*. From this discussion we can also conclude that the molecular contributions adding up to **P** are the dipole components directed along the C_2 -axis.

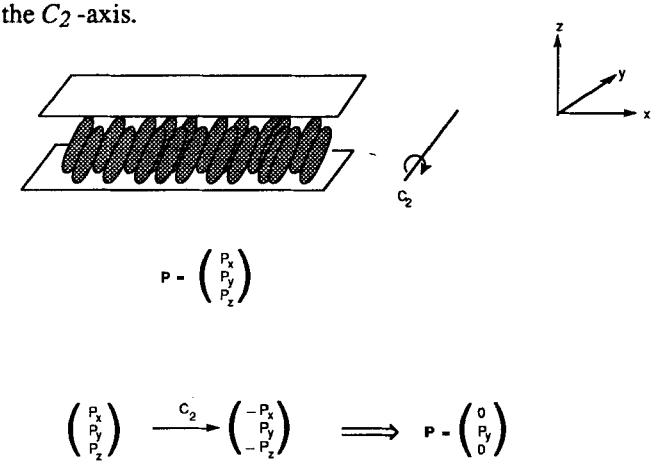


*FIGURE 1. C_2 - symmetry operation applied to a single layer C**

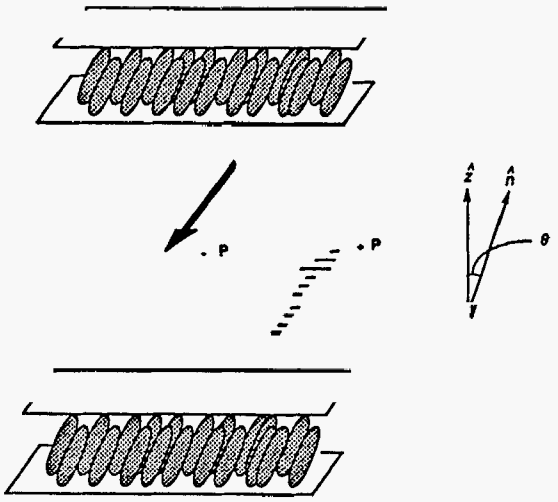


*FIGURE 2. The direction of the spontaneous polarization, **P***

Structural properties

In order to introduce the important macroscopic parameters in a more physical way, we will later outline some features of the currently used phenomenological description of the smectic C* phase.

In most experimental situations it is necessary for the evaluation to have a model for the structure of the sample. Such a model might be introduced on different levels: First it is necessary to discuss the physical properties in terms of macroscopically averaged quantities that are defined in the framework of a phenomenological theory. In the case of the chiral smectic C phase, the notations and ideas are often taken from statical and dynamical descriptions of nematics. We use the notion of a "nematic-like description" in order to emphasize this situation. A more complete, thermodynamic description, like the hydrodynamic description for nematics, is not yet established for the case of chiral smectics.

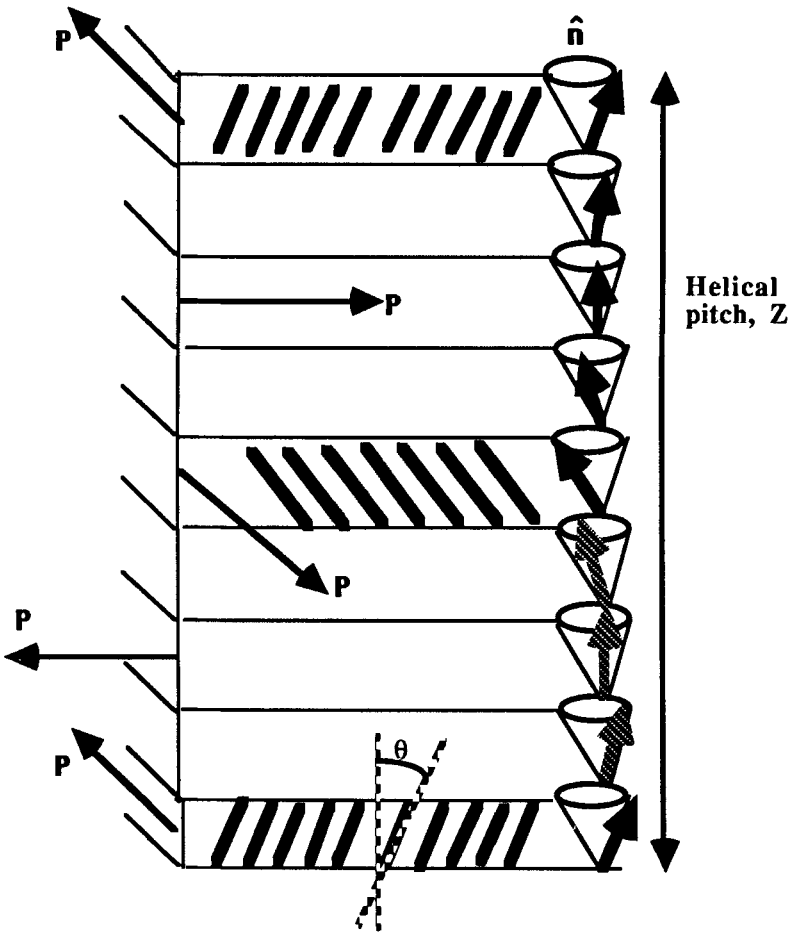


FIGURE 3a. Helicoidal smectic C structure.*

Referring to *Figs. 3a* and *3b*, one might consider the molecules in the smectic C* phase to form a layered structure, the thickness of one layer being typically of the order 20-30Å. From X-ray studies one concludes that the molecular centres are packed in a random way within the layers. The molecules tilt from the layer normal by the angle θ. As for nematics the

average direction of the molecular long axis is denoted the director, **n**. The spontaneous polarization **P** is given, for small tilt angles, by

$$\mathbf{P} = P_0 \mathbf{z} \times \mathbf{n}$$

As for most liquid crystalline phases, the variation in space of the vectors characterizing the structure at hand might be extremely complicated in a general case. For the object of studying physical parameters like dielectric constants and refractive indices, as well as the spontaneous polarization **P**, and pitch Z, it is of great importance to work with well-aligned samples in simple geometries. Two limiting cases with the layer normal uniform in the sample are shown in *Fig. 3*. In *Fig. 3a* the director spirals on a cone when moving in the **z**-direction so that a helicoidal structure with a characteristic pitch Z is formed. This structure is the "natural" one for the chiral smectic C phase, and is adopted when the liquid crystal is free from influences of body forces, external fields or surface conditions. The helical structure brings the otherwise created electric field outside a macroscopic sample to zero, thereby reducing its total free energy. It also means that there is almost no interaction between a macroscopic sample and an external field; more correctly the interaction is reduced to being dielectric and then changing character only by distorting the helix. The geometry in *Fig. 3a* is mostly used in helical pitch measurements, although also dielectric measurements have been performed in this geometry.

In *Fig. 3b* we illustrate the case when the helix is absent. For spontaneous polarization measurements, one might unwound the helix by a sufficiently large electric field, thereby orienting all dipoles and creating a structure with uniform **P** (and **n**). In this situation also θ can be measured. Alternatively, the boundary conditions of the cell are such that the helix is suppressed by surface stabilization (SSFLC-cell). In the simplest type of

such a cell we can have a uniform director and polarization vector also without an applied field.

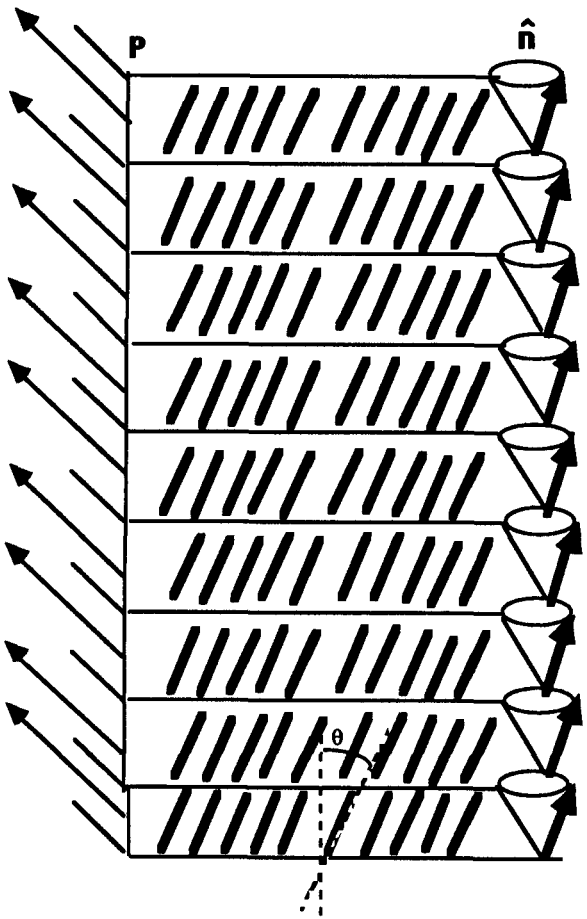


FIGURE 3b. Non-helicoidal smectic C structure.*

While the notions of layer normal, tilt angle, optic axis (in the approximation that the C*-phase can be considered uniaxial), helical pitch,

and even the spontaneous polarization, are rather straightforwardly given an intuitive, geometric interpretation, it is more difficult to have such an immediate understanding of the elastic, viscous and dielectric properties of ferroelectric liquid crystals. This is particularly true when size and boundary effects are considered. Sometimes it seems that the "bulk" properties, even for the simple parameters, are impossible-to-reach idealizations, that often function more as guiding lines than giving the ultimate physical description of the phase. One can think of the difficulties encountered when measuring the helical pitch (extreme surface condition sensivity), the tilt angle (strong electric field dependence near A-C transition where it is interesting to measure it accurately; possibility of layer tilt in samples), the spontaneous polarization (spurious current contributions, layer tilt), the dielectric properties (surface condition sensitivity, ionic conduction compensation, high-frequency cut-off in samples), the visco-elastic properties (tentative physical model, complicated experimental evaluation).

Thermodynamic model for the smectic C* phase

Thermodynamic properties of the smectic C* system are usually described by a phenomenological Landau free energy expansion, the first version given by Meyer.[6] By minimization of the free energy expression with respect to the introduced parameters (usually the tilt angle, polarization and helical pitch) it is possible to obtain the temperature dependence of these parameters. The Landau free energy density describing the SmA-SmC* transition is usually expressed as[12]

$$g(z)=\frac{1}{2}a(\xi_1^2+\xi_2^2)+\frac{1}{4}b(\xi_1^2+\xi_2^2)^2-\Lambda\left(\xi_1\frac{d\xi_2}{dz}-\xi_2\frac{d\xi_1}{dz}\right)+$$

$$+\frac{1}{2}K_{33}\left[\left(\frac{d\xi_1}{dz}\right)^2+\left(\frac{d\xi_2}{dz}\right)^2\right]+\frac{1}{2\chi}(P_x^2+P_y^2)-\mu\left(P_x\frac{d\xi_1}{dz}+P_y\frac{d\xi_2}{dz}\right)+C(P_x\xi_2-P_y\xi_1)$$

The order parameter is the two-component tilt vector $\xi=(\xi_1,\xi_2)$ describing the magnitude and the direction of the tilt of the long molecular axis from the normal to the smectic layers. The tilt of a molecule breaks the axial symmetry around its long axis inducing an in-plane polarization $\mathbf{P}=(P_x,P_y)$ perpendicular to the tilt. The vector ξ is the projection of the director $\mathbf{n}$ on the smectic planes. P_x and P_y are the components of the in-plane polarization, $a=\alpha(T-T_0)$, $b>0$, K_{33} is the elastic modulus, Λ the coefficient of the Lifshitz term responsible for the twist-bend modulation, μ and C are the coefficients of the "flexo-" and "piezo"- electric coupling between the tilt and the polarization. For small tilt angles θ we may write

$$\xi_1=n_zn_x\approx\theta\cos\varphi \quad ; \quad \xi_2=n_zn_y\approx\theta\sin\varphi$$

where $\varphi=\varphi(z)$ is the azimuthal angle determining the orientation of the molecular director $\mathbf{n}=(n_x,n_y,n_z)$ with respect to the normal $\mathbf{z}=(0,0,1)$ to the smectic layers. With the helicoidal ansatz ($q = 2\pi/Z$)

$$\xi_1=\theta\cos(qz) \quad ; \quad \xi_2=\theta\sin(qz)$$

$$P_x=-P\sin(qz) \quad ; \quad P_y=P\sin(qz)$$

substituted into the expression for g(z) we get

$$g(z)=\frac{1}{2}a\theta^2+\frac{1}{4}b\theta^4-\Lambda q\theta^2+\frac{1}{2}K_3q^2\theta^2+\frac{1}{2\chi}P^2-\mu qP\theta-CP\theta$$

Minimization of

$$F=\frac{1}{L}\int_0^L g(z)\,dz$$

with respect to θ, P and q yields the SmA-SmC* transition temperature T_C, the temperature dependence of the tilt angle and the pitch of the helix as well as the spontaneous polarization P:

$$\theta=\sqrt{\alpha/b}(T_c-T)^{1/2}$$

$$T_c=T_o+\frac{1}{\alpha}[\chi C^2+(K_{33}-\chi\mu^2)q^2]$$

$$Z=\frac{2\pi}{q}=2\pi\frac{K_{33}-\chi\mu^2}{\Lambda+\chi\mu C}$$

$$P=\chi(\mu q+C)\theta$$

In this model the pitch of the helix (Z) does not depend on temperature, and the polarization is proportional to the tilt angle. By including a field-term for the interaction with an external electric field in the free energy expression g(z), it is also possible to extract the temperature dependence of the dielectric constant ε. Below in *Fig. 4* is shown schematically the predictions of the Landau model given above, together with typical experimental results.

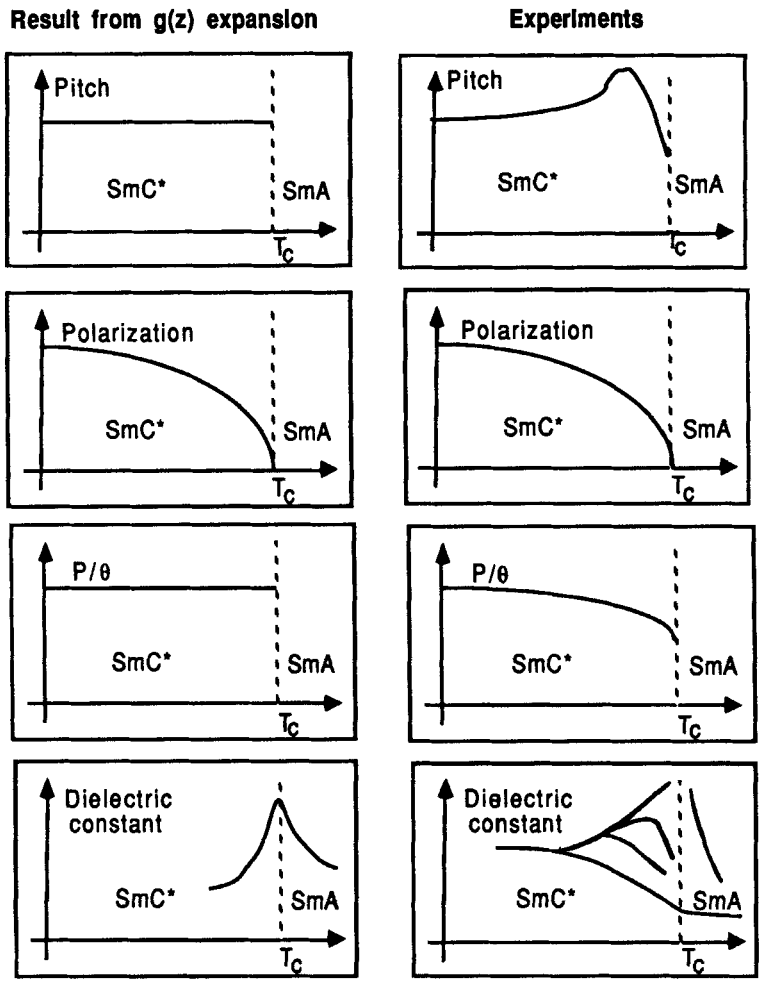


FIGURE 4. Comparison of predictions from the Landau expansion g(z) used above with typical experimental results.

The model is insufficient to accurately describe the temperature dependence of the pitch. More elaborate models have therefore been

suggested recently, adding additional terms in the Landau expansion.[13]

The experimental situation

In spite of considerable progress during the last years, the experimental situation is complicated. Partly this is due to the richness in the variety of phenomena and parameters encountered in ferroelectric liquid crystals. The presence of both smectic layers and chirality, of new electric and surface interactions, and of new defect structures add a new complexity even to some measurements which would seem fairly standard in non-ferroelectric liquid crystals. At the same time this is an extremely interesting challenge. To characterize the materials and their electro-optic behaviour, at least the following properties would be useful, in addition to thermodynamic phases and multi-component mixing behaviour of many of the parameters: polarization P(T), with sign, tilt angle θ, smectic pitch Z(T), with handedness, cholesteric pitch p(T), with handedness, refractive indices, $n_i(T)$, dielectric permittivities $\varepsilon_i(T)$, especially as a function of frequency, elastic, viscous, flexoelectric and electroclinic coefficients, surface polarity, and surface alignment properties. Already in view of the sheer number of involved parameters to measure, it is not surprising that we are far from having full control of measurement methods and problems. Seemingly trivial problems like measuring the smectic pitch Z, and even its handedness, present quite unexpected difficulties, to the point that nobody may be able to tell what is actually measured. A second example is the dielectric behaviour, where different geometries and approaches may seem to give conflicting results. Consequently, it is sometimes difficult to make a comparison between theory and experiment. A critical review of the behaviour of material parameters would therefore also have to include a critical discussion of various measurement methods, a task big enough to

be outside the scope of this article.

Often a polarization curve might seem to have a temperature dependence rather like that of *Fig. 5(b)*. An interpretation is not easy, but already a large value of the electroclinic coefficient (*cf.* below) would in principle be enough to deform the 2.order phase transition behaviour in (a) in the direction of (b). In such a case it is not clear which dielectric behaviour (χ) should be expected, and the transition temperature (T_C) will be affected by some uncertainty.

In view of the mentioned difficulties, we will limit ourselves to the discussion of a typical example, the temperature dependence of the pitch. This is a question of considerable current theoretical interest. According to classical Landau theory the pitch should be temperature-independent.[14] Experimentally, a strong temperature dependence is found, especially near T_{AC}. With the diffraction and direct microscopic observation methods one has experimentally in the vast majority of cases found a maximum in the pitch near T_{AC}, while very recent experiments with the Cano and selective reflection methods yield no such maximum,[15] but instead a very clear divergence at T_{AC} as already described. It has been known for a long time that the helical pitch is extremely sensitive to disturbances from the bounding surfaces, and already at thicknesses of hundred times the helical pitch might this influence be noticeable. The conclusion from such experiments is that measurements in the "bookshelf" geometry (with the smectic planes perpendicular to the glass slides) using *any* of the methods are likely to give a helical pitch somewhat shifted from the true bulk value. Thus, although recent Landau-theories, by including a biquadratic coupling term between P and q, seem to describe quantitatively the helical pitch behaviour near T_{AC} as observed in the bookshelf geometry, the newer observations of a diverging pitch, made in a geometry where the boundary influence is minimal, demonstrates that the theoretical attempts to describe

the temperature dependence of the helical pitch using various Landau expansions have to be reconsidered from new premises.

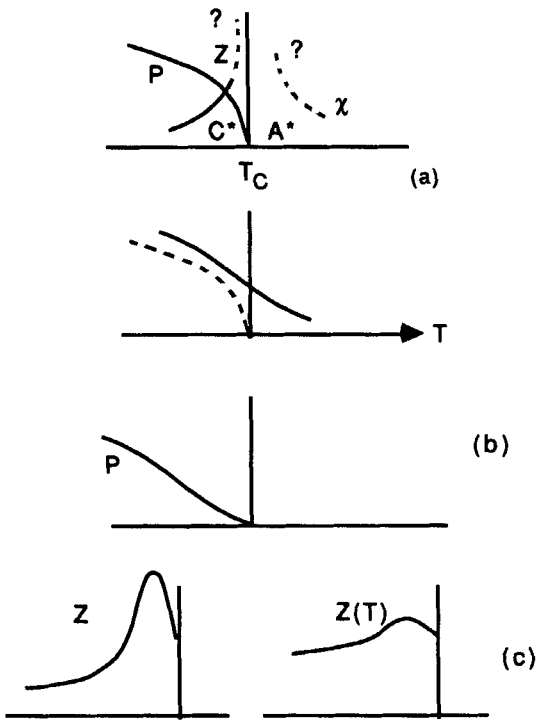


FIGURE 5. Ideal 2.order phase transition behaviour of P(T) at the A-C* transition (a). Experimentally, curves similar to the ones in (b) are often found. Common Z(T)-curves are shown in (c).*

THE ELECTRO-OPTIC EFFECTS

Just as the field of nematic liquid crystals experienced a boom concerning material development when promising applications emerged, interest in the synthesis of ferroelectric liquid crystals increased substantially when Clark

and Lagerwall[9,16] discovered a way of polarizing a ferroelectric liquid crystal (FLC), thereby developing a liquid crystal device with some remarkable features. They were able to demonstrate a symmetrically bistable fast-switching electro-optical device structure operating in the C* phase, or in any tilted chiral phase, for which the acronym SSFLC (Surface Stabilized Ferroelectric Liquid Crystal) was coined. Since the SSFLC provided the main impetus for the present activity in FLC research a short description of the principal features is given below.

Surface stabilization - The SSFLC concept

Consider two parallel glass plates, glued together, with appropriate spacers, and coated with a thin conductive layer, *e.g.* indium-tin oxide, and treated to ensure a planar orientation of the liquid crystal molecules, *i.e.* with the director parallel to the glass plates. The cell is filled in the isotropic phase, the director aligned in the nematic phase and, on cooling throughout the A phase, a uniform alignment can be obtained with the smectic layers standing perpendicular to the glass plates (the so-called "bookshelf geometry"). The alignment can be facilitated if an electric field is applied across the glass plates providing the material has a negative dielectric anisotropy. On further cooling, the material eventually enters the C* phase and the helicoidal structure characteristic of that phase normally develops. The helical pitch is in a direction parallel to the glass plates and the polarization is uniformly distributed around the helix and is consequently averaged to zero. At the boundaries (*i.e.* at the glass plates) however, the molecules are forced to lie in the plane of the glass plates and only two orientations are possible, *viz.* the tilt directions corresponding to the cross section between the plane of the glass plates and the cone as depicted in *Fig. 6*. The helix is still present in the bulk of the sample, but if

the cell is now made thinner (approximately to the order of the pitch, *i.e.* a few μm), the boundary conditions will suppress the helix and thus only the two orientations shown in *Fig. 6* are possible through the whole sample. Furthermore, in these two orientations the pertinent polarization vector is normal to the glass plates but opposite in direction (*cf. Fig. 6*). This is a somewhat idealized description of the cell state; in reality a number of features (like polarization direction *etc.*) will deviate from this simplest picture without altering the general device concept.

In essence one can say, and this is the crucial feature of the SSFLC device structure, that the boundary conditions are restrictive enough to suppress the helix formation while still allowing the two tilt directions.

Once this set-up is accomplished, an external electric field ,**E**, applied across the glass plates will switch the molecules collectively from one tilt direction to the other as the field is reversed. When the cell is sandwiched between crossed polarizers (one tilt direction is parallel to the direction of one polarizer), the optical effect is that the cell will switch from extinction (dark) to transmission (bright) corresponding to the UP and DOWN states depicted in *Fig. 6*. In addition to its high speed this device is the first liquid crystal device showing a linear electro-optic effect.

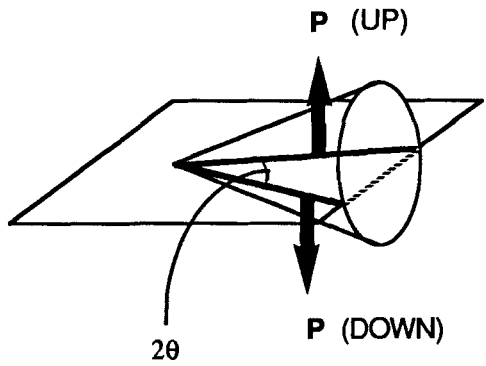


FIGURE 6. The two allowed molecular orientations in the SSFLC device

To conclude this section, the most salient features of the SSFLC device structure will be summarized:

i. The linear coupling between the polarization and the applied field makes the switching active in both directions on field reversal. Furthermore the switching is very fast, in the order of microseconds

ii. Bistability: The molecules will remain aligned in one direction until a reversed field is applied, thus giving a built-in memory effect

iii. Threshold behaviour: The switching has a sharp threshold, *i.e.* the change from no switching to full switching response is accomplished over a very small range of the amplitude and duration of the applied field

The SSFLC is also characterized by high optical contrast and an excellent viewing angle.

Some peculiarities should also be mentioned. The threshold has a dynamic nature, *i.e.* it depends on pulse width as well as amplitude. This, together with the fact that no liquid crystal can support DC electric fields makes the electronic driving non-trivial. Finally, the helix-free state may be quite complicated and far from easy to achieve with standard, large-volume production methods, which presently makes the alignment problem a challenge.

The spin or Goldstone mode - The motion on the cone

One further idea with the SSFLC device can be traced back to the nature of the order parameter for the A-C* transition. It is that the collective molecular motion on the cone should have the lowest possible viscosity - even lower than for turning the director in a nematic - because only the phase angle in the order parameter is involved.[16] The order parameter is the two-component tilt vector $\xi = (\xi_1, \xi_2) = (\theta\cos\varphi, \theta\sin\varphi)$ as used above in the Landau free energy expansion (*cf.* page 11), but in this context it is more convenient to write it as $\xi = \theta e^{i\varphi}$. The motion on the cone keeps θ constant, only changing the gauge φ, if the motion takes place collectively, *i.e.* in the zero wave vector (Goldstone mode) limit. The situation is illustrated in *Fig. 7* where the conical motion around the molecular center of gravity is first shown together with its commonly used abbreviation and then, below, a comparison is made between the two limiting motions in the C phase and the one corresponding in the N phase. The characteristic viscosities for these three motions ought to be different: γ_φ, corresponding to the pure φ-motion ought to be lower than γ_θ, corresponding to a change in tilt. The θ-motion induces flow and is connected with a layer

compression or dilation; thus θ is a "hard" variable quite in contrast to φ.

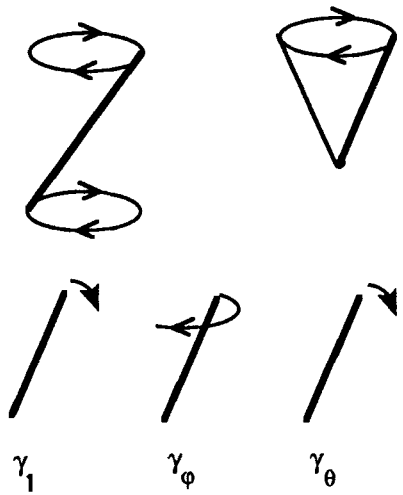


FIGURE 7. The motion on the cone. At the top is shown the molecule precessing around its center of gravity (θ=constant), symbolically abbreviated to the right. This is the phase angle motion at the bottom (γ_φ), as compared to the tilt motion (γ_θ) and the director motion in a nematic (γ_1).

On the other hand, there is a certain similarity between this motion and a rotation of the nematic director. Thus γ_θ should not be too different from γ_1, the nematic twist viscosity. In order to illustrate these ideas we have made some naive scetches in *Fig. 8*: (a) shows the situation when every molecule in a nematic is turning its axis, *e.g.* in accordance with a rotation of an external magnetic field, in fact a common method for measuring the rotational viscosity γ_1. A corresponding motion may be imagined for a smectic, involving γ_θ, in (b). This is the mode that softens at the C-to-A

transition (soft mode). In (c), finally, is shown the Goldstone mode for different values of θ. γ_φ ought to increase with increasing value of θ. It must be highest in the (unphysical) limit of $\theta \rightarrow 90°$, in which limit $\gamma_\varphi \rightarrow \gamma_\theta \rightarrow \gamma_1$. In the other limit, $\theta \rightarrow 0$, it reaches the general lower limit of the viscostiy in a liquid crystal, corresponding to the very fast rotational motion of the molecule around its long axis, the same in the smectic A phase as in the nematic phase (*Fig. 8c*, extreme right).

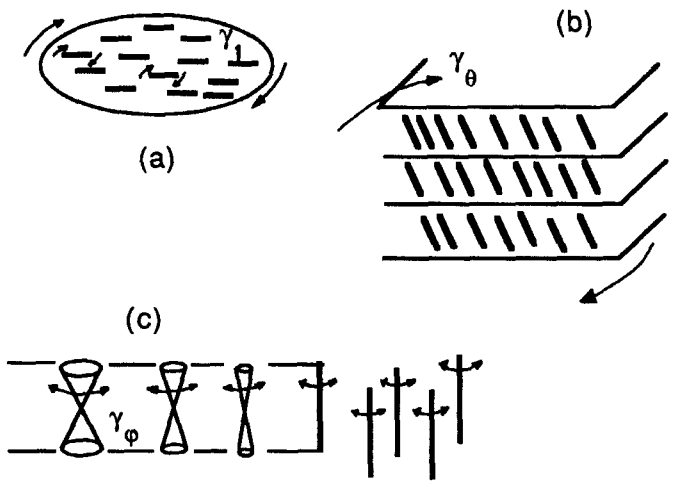


FIGURE 8. Collective motion turning the molecules around their centers of gravity in a nematic (a), for instance provoked by a rotating magnetic field; the corresponding tilt motion in a smectic C (b); the phase angle motion in a smectic C, degenerating into a smectic A ($\theta \rightarrow 0$) and a nematic (c). In the C phase two rotational viscosity modes exist, of which the Goldstone mode (γ_φ) vanishes at the C→A transition.

The first measurement of a viscosity in a smectic phase was reported by Meiboom and Hewitt in 1975.[17] The substance used is the (non-chiral) DHAB (di-heptyloxyazoxybenzene) which lacks an A phase and has a first-

order N-C transition at 94 °C. The method (torsional pendulum dissipation in a magnetically locked liquid crystal) rather measures a combination of γ_θ and γ_φ, but it is noticeable that a viscosity drop is observed on entering the C-phase, *cf. Fig. 9.*

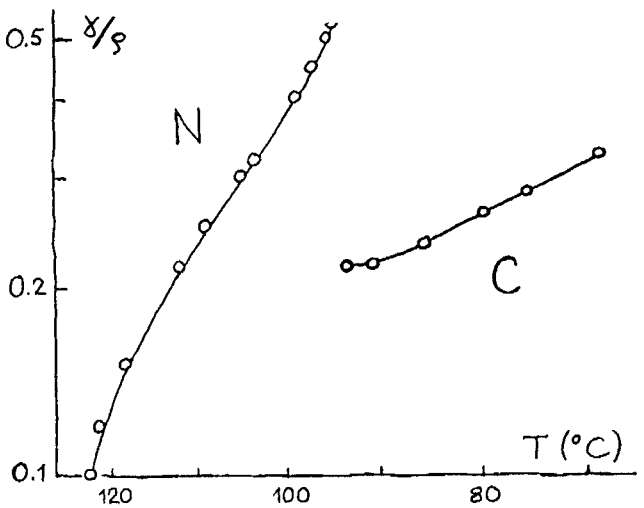


FIGURE 9. Arrhenius plot (on this scale almost linear in T) of the rotational viscosity measured in DHAB in the nematic and the smectic C phase. γ/ρ is the kinematic viscosity in cgs units (γ the viscosity in poise and ρ the density of the liquid). After Meiboom and Hewitt (Ref. 17).

One of the most interesting results from the last years regarding the viscosity - the least understood of the important parameters of ferroelectric liquid crystals - is that a Russian group has succeeded in measuring, for the first time, the different viscosities γ_φ and γ_θ separately.[18] In *Fig. 10* we show their results for DOBAMBC.[19]

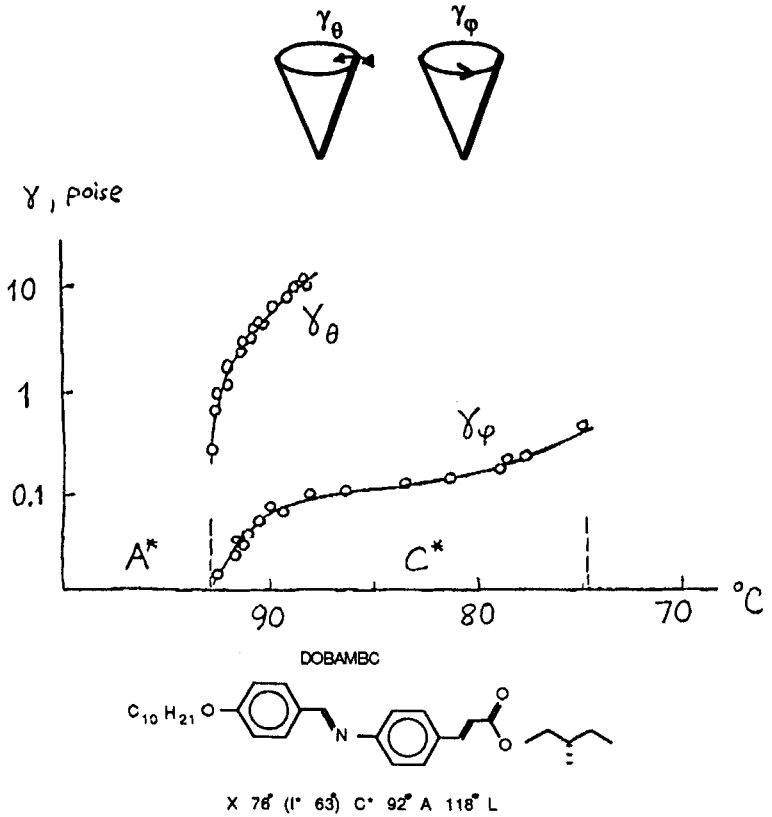


FIGURE 10. Arrhenius plot of the soft mode viscosity γ_θ and the Goldstone mode viscosity γ_φ in the C phase of DOBAMBC. Measurements by the Moscow group, cf. Ref. 19.*

In the presented range for γ_θ we see that it is a factor 30-100 larger than γ_φ, with the value 100 rather typical for the main part of the C* phase. Even more striking are their results on an N*-A*-C* mixture, presented in *Fig. 11*. As in the previous example, the Goldstone mode viscosity γ_φ is about 100 times lower than the soft mode viscosity γ_θ. Both of them diminish dramatically at the C*-A* transition, as does the nematic viscosity

γ_1 at the N*-L (isotropic liquid) transition. The twist viscosity γ_1 further diverges, as it should at the N*-A* transition. A remarkable feature is that γ_θ seems to extrapolate over, across the A* phase, into the γ_1 region in a natural way. This lends support to the idea discussed earlier (*Fig. 8*) that the nematic phase lacks a Goldstone mode, and that the nematic twist viscosity is rather comparable to the soft mode in the C phase. As for the orders of magnitude for the different viscosities, we will use them below in trying to make reasonably realistic estimations of device dynamics. One might point out that not only is it remarkable that γ_φ is two orders of magnitude lower than γ_θ but - perhaps even more against the habit of thinking - γ_φ in the smectic phase is at 50 °C still one order of magnitude lower than γ_1 in the nematic phase at 80 °C!

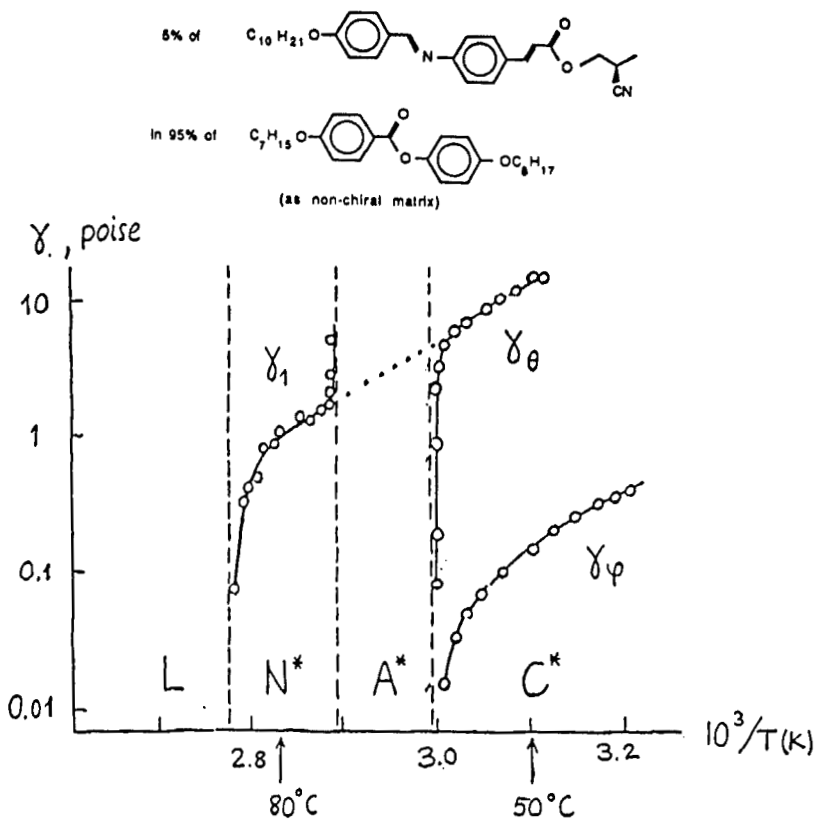


FIGURE 11. Arrhenius plot of the viscosity γ_1 in the nematic phase as well as soft mode and Goldstone mode viscosities γ_θ and γ_φ in the C phase of a two-component mixture. Measurements of the Moscow group, cf. Ref. 19.*

The soft-mode ferroelectric effect

The existence of a spontaneous polarization is possible only in chiral tilted smectic phases. However, in non-tilted smectic phases, like smectic A, built up from chiral molecules one observes an induced tilt on applying an external electric field. This so-called electroclinic effect was first

described by Garoff and Meyer[20] working with samples in which the smectic layers were parallel to the confining glass plates. In this geometry the effect is hard to detect and was studied as a probe for the A-to-C transition. In very thin samples of the bookshelf geometry typical of the SSFLC cell the effect is, however, easily and strikingly detectable at conveniently low applied fields, even in the CMOS-compatible and thus technically accessible range of 10 to 30 volts.

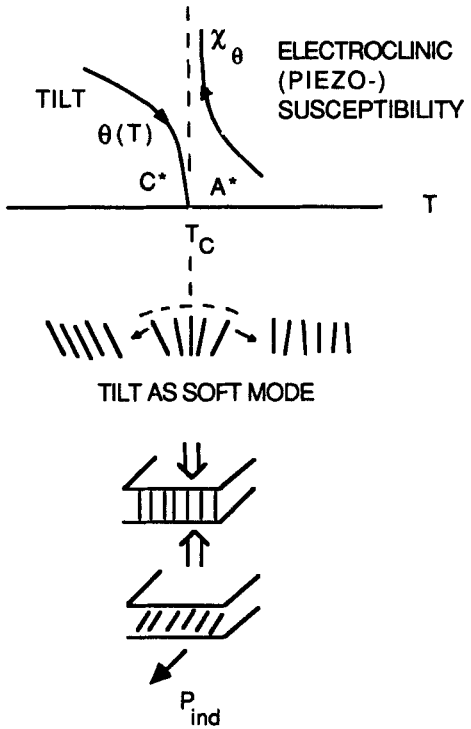


FIGURE 12. Critical divergence of the smectic layer compressibility related to molecular tilt in the A phase on approaching the A*-C* transition. A quite analogous relationship as between θ and χ_θ exists between polarization P and dielectric susceptibility χ_ε*

In order to introduce the effect we refer to the drawing in *Fig. 12*. On approaching the C* phase form above, the elastic constant controlling tilt fluctuations in the smectic A* layer has to soften. This pre-transitional effect can be expected to be small but should be detectable in a region near the transition. As the tilt is connected with a layer compression, also the layer has to soften in the sense that its compressibility increases, in fact diverges, on approaching the transition. The huge compressional fluctuations in the A* phase therefore induce fluctuations in polarization *via* the linear coupling between tilt and polarization. This is quite analogous to the piezoelectric effect in crystals, and in principle means that, on compression, a voltage would appear across the layer (*i.e.* between the glass plates in the bookshelf geometry). The reverse means that the molecules will tilt and compress the layers on application of an external electric field. We can also consider the electric field to induce a dielectric polarization which then couples linearly with the tilt. The pretransitional effect of course then means that this dielectric susceptibility also diverges on approaching the transition. Although the dielectric, the electroclinic and the ferroelectric changes in the molecular tilt may have several effects in common, their torques and dynamics are completely different. Because the first term in the Landau expansion is of dominating influence for the electroclinic response, the soft-mode switching might be very fast even if the viscosity involved is γ_θ and not the lower γ_φ. The application of the effect is shown in *Fig. 13*. Between crossed polarizers the bookshelf-aligned A* phase can be considered a retardation plate with a field-sensitive optic axis.[21]

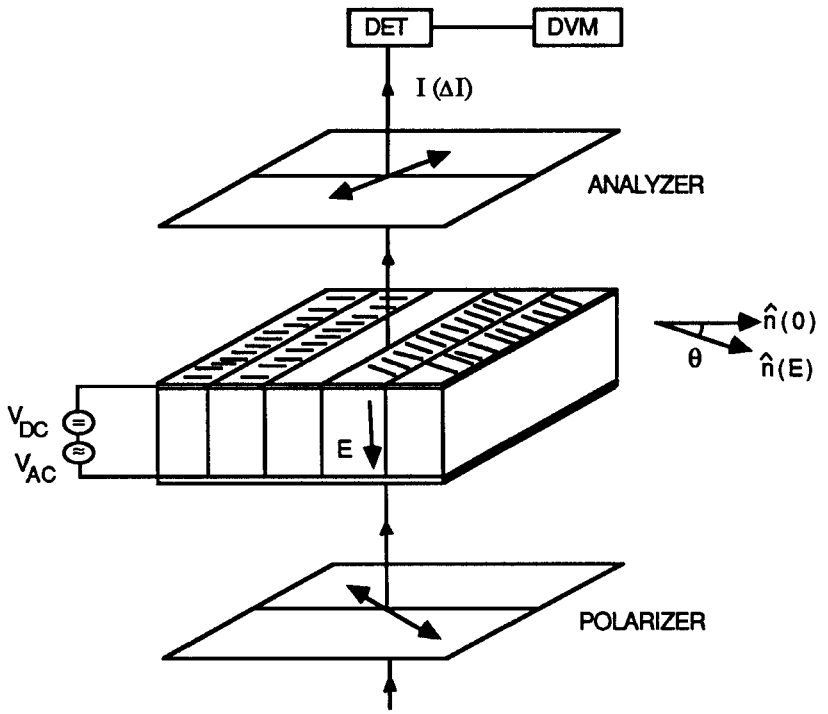


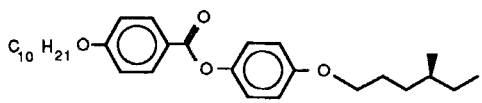
FIGURE 13. The A phase as a retardation plate with field-sensitive optic axis. The field-induced tilt θ(E) is shown as for a positive material ($\hat{n}(0) \times \hat{n}(E)$ parallel to E).*

The electro-optic characteristics can be used in several modes. With a polarizer setting symmetrical with regard to both tilt states there are two different optical extremum states corresponding to field off and maximum applied field, the effect being insensitive to the direction (+ or -) of the electric field and giving an optical modulation frequency of 2ω if a field of frequency ω is applied. With unsymmetric polarizer setting, the plus and minus field states correspond to different optical states; thus three device states, including the zero state, are attainable for every value of the voltage

amplitude.

With the crossed-polarizer setting $\phi = 22.5°$ the response is linear and the absolute value of intensity variation is maximized. If instead it is desirable to have a modulation around a high-extinction state and a higher modulation depth, a polarizer setting corresponding to $\phi = \theta$ should be used. At the cost of lower luminosity, any modulation depth could then be achieved.

The achievable speed is generally high with $\tau < 100$ ns common for a number of high-temperature compounds and $\tau < 1$ μs available at room-temperature.[22] For a given substance it is typically 10 to 100 times faster than the speed of the corresponding SSFLC mode. On approaching the C* phase, a characteristic critical slowing-down can be observed, *cf. Fig. 14*. On the other hand, the switching can be performed in the whole A* phase and not only near the A*-to-C* transition. The induced tilt angle (*cf. Fig. 15*) is still modest, less than 10°, but may raise as new materials are tested. It might be pointed out that the electroclinic coefficient is not simply related to the spontaneous polarization - it rather depends on the coefficients a and C in the Landau expansion used above - thus even compounds with very low P, like



might show quite pronounced soft-mode switching. The electroclinic coefficient is in fact a new independent material parameter to be added to the existing collection of data for promising ferroelectric device materials, *cf.* below.

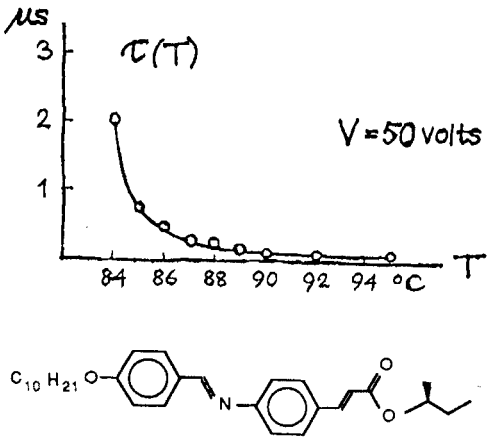


FIGURE 14. Critical slowing down of switching speed on approaching the A-C* transition. The material is DOBA-1-MPC, in the A* phase the range of which is from 83 °C to 102 °C. Sample thickness 2μm. Setup as in Fig. 13.*

In comparison with the surface-stabilized spin mode, the soft-mode has some characteristic similarities and differences: It is symmetric in the ON-OFF switching, has no bistability, has no threshold ("just grey-scale"), can be adapted to thicker cells and presents no manufacturing problems regarding alignment. It does not lend itself as easily to multiplexing.

On the other hand, one should not forget that the soft-mode might be a useful addition to the spin-mode *in the C* phase* - because it is always present. It has essentially the same important characteristics in the C* phase as in the A* phase, only that the susceptibility below T_C is half that above ($\chi_C = 1/2\ \chi_A$). It therefore cannot, and should not, be neglected in the device physics. We will return to these questions below.

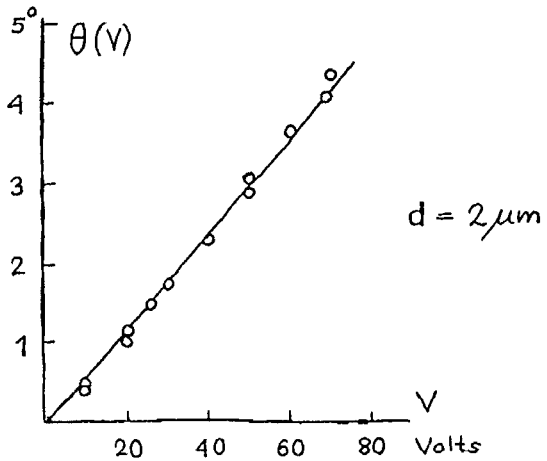


FIGURE 15. Linearity in the tilt angle response versus applied voltage in DOBA-1-MPC at 86 °C.

Finally, the presence of the electroclinic effect has to be taken into account in connection with the interpretation of some parameter combinations like P/θ. The electroclinic switching may also give rise to considerable perturbation already in the shape of the polarization curve. An example is seen in *Fig. 16*. Clearly no useful estimation of critical behaviour can be made at all, at the C*-A* transition, when the electroclinic coefficient is large, which is indeed very often the case.

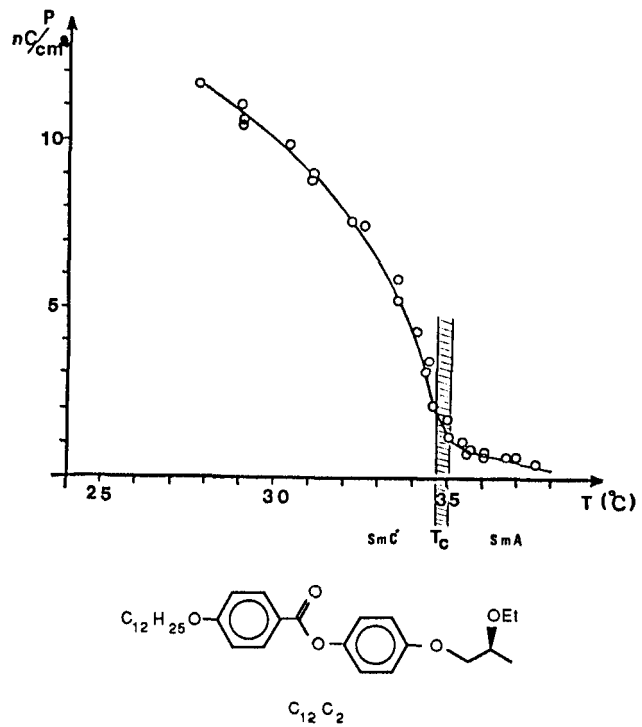


FIGURE 16. Measured polarization for the substance $C_{12}C_2$ as a function of temperature. The strong deviation from ideal power law behaviour is here mainly caused by the electroclinic effect

SSFLC device dynamics

In order to get a feeling for what requirements will be set on material parameters by the device applications, it is illustrative to make some simple estimations of dynamic quantities. We will primarily be interested in the ferroelectric torque, the dielectric torque and the available speed for switching the optic axis, using realistic values for applied field, for polarization and viscosity, and for dielectric anisotropy. The geometry for

switching the optic axis around the cone is shown in *Fig. 17* where the molecular pretilt is described by the azimuthal angle ϕ. As the experience shows, the switching from the DOWN state to the UP state, or vice versa, is not really a Frederiks type instability, *i.e.* not fluctuation-controlled (this would lead to much longer switching times than those actually involved, *cf.* Ref. 23), hence there is always a small pretilt, at least at the surface.

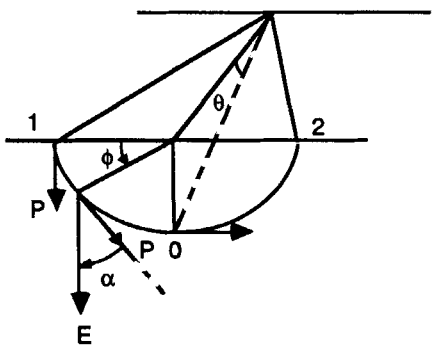


FIGURE 17. Switching the optic axis around the cone. In positions 1 and 2 there is no torque from an applied vertical field E. The torque is maximum in neutral position 0.

Comparison of torques

In magnitude, the ferroelectric torque (per unit volume) is

$$\Gamma^P = |\mathbf{P} \times \mathbf{E}| = PE\sin\alpha = PE\sin\phi \approx PE\phi$$

or, in addition per unit angle

$$\Gamma^P/\phi = PE$$

If we apply a field E of 10 V/μm = 10^7 V/m and take P to 10 nC/cm^2 = 10^{-4} C/m^2 we obtain for the torque a value of Γ^P/ϕ = 1000 N/m^2.

The dielectric torque is quadratic in the field E and, per unit angle φ (*cf. Fig. 18*) approximately equal to

$$\Gamma^\varepsilon/\varphi = (-)1/2\varepsilon_a\varepsilon_0 E^2$$

where $\varepsilon_0 = 8.85 \cdot 10^{-12}$ As/Vm and ε_a is the dielectric anisotropy. If $\varepsilon_a > 0$ the dielectric torque always wants to force the molecule into the $\varphi = 0$ position which disfavours the positions 1 and 2 (*Fig.17*) and counteracts any switching threshold between them, hence destroys the bistability. For a material with $\varepsilon_a < 0$, on the other hand, the dielectric torque is beneficial, stabilizing positions 1 and 2 and reinforcing the threshold. Assuming a value of $\varepsilon_a = -1$, and with E = 10^7 V/m as before, we obtain for the dielectric torque a value $\Gamma^\varepsilon/\varphi = 1/2 \cdot 8.85 \cdot 10^{-12} \cdot 10^{14} \approx 500$ N/m^2.

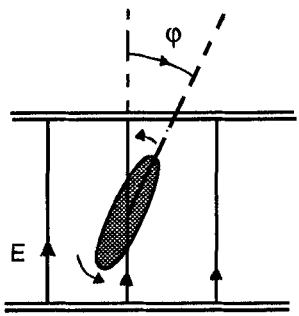


FIGURE 18. The dielectric torque acting on a molecule making the angle φ with the applied field. The indicated direction corresponds to $\varepsilon_a > 0$.

As the example shows the ferroelectric and dielectric torques may be fairly equal in magnitude. At sufficiently low voltages the ferroelectric

torque will always dominate, because it is linear in the field, whereas at sufficiently high voltages the dielectric torque will always dominate, because it is quadratic in the field. In our numeral example we have used quite typical values for all quantities involved. Consequently there will be an important domain where the torques more or less balance and this is probably the most important question in device performance. Ironically, this has not been generally understood until lately, and consequently, the important information on the dielectric anisotropy $\varepsilon_a \equiv \varepsilon_{//} - \varepsilon_{\perp}$ (at the relevant frequencies) for available ferroelectric materials is practically non-existent.

The presence of the dielectric torque naturally influences the switching dynamics. In the case of $\varepsilon_a < 0$ it counteracts and slows down the first half of the cone swing ($1 \rightarrow 0$ in *Fig. 17*) but speeds up the second half ($0 \rightarrow 2$). For $\varepsilon_a > 0$ we have the opposite behaviour. In any case ($\varepsilon_a > 0$ or $\varepsilon_a < 0$) the total result, as was shown by Xue, Handschy and Clark,[24] is a slowing down of the switching process. An ideal situation would therefore be to switch a material around its cross-over frequency (where ε_a changes sign from positive to negative) with a switching pulse shaped such that its frequency change turns $\varepsilon_a > 0$ into $\varepsilon_a < 0$ after half its duration. Such a material could be designed, but would have to have its cross-over frequency matched to the device pulse frequency and would show the usual complicating temperature drift of the cross-over frequency typical for two-frequency materials. It therefore presently seems a little exotic, and one has to make the best out of the situation using a material with $\varepsilon_a < 0$.

AC stabilization

One of the large potentials of the SSFLC device is its applicability to large screens in multiplex drive. The addressing is performed by scanning

one row at the time while so-called data pulses are applied to the columns. The superposition of these waveforms is one of two-binary coded pulses telling wether a certain picture element has to switch or not. In this somewhat simplified description every switching pulse is polar whereas the totality of pulses felt by any element is a flow of AC voltage of slightly irregular character and with a much lower average than the switching voltage. Except when being in the actually addressed line (which happens only a small fraction of time for a large matrix) any one pixel (picture element) thus only feels this AC "data background" or "cross-talk" pulse stream, which then has to be designed in such a way that a pixel never (even partly) switches but instead is stabilized in its rest position. Some common addressing schemes are characterized by having a background voltage of at most V/3 if we designate the switching voltage by V. In our numerical example above with a ferroelectric torque of 1000 N/m^2, the dielectric torque is now insignificant, having diminished to about 50 N/m^2 (a factor three-squared less than before). This means that there is no more "AC stabilization" which may be detrimental for the contrast of the matrix. Thus the overall voltage has to be raised in order to restore the dielectric-ferroelectric torque balance, or the P-ε_a value combination has to be changed. We will come back to these questions below, in connection with the discussion of device characteristics and electronic driving.

Switching times

When an external field is applied as in the previous section, the torque exerted by it will in general try to turn the optic axis into a new position. The liquid reacts with a damping viscous torque Γ^v, directed so as always to reduce any existing angular velocity

$$\Gamma^{v} = -\gamma d\phi/dt$$

where the proportionality constant is a phenomenological viscosity. Beginning again with the ferroelectric case, and neglecting elastic effects, the motion of the director is given by the torque balance

$$\Gamma^{P} + \Gamma^{v} = 0$$

With reference again to *Fig. 17* the ferroelectric torque will be directed to diminish the initial angle ϕ_0 between P and E, *i.e.* with sign $\Gamma^{P} = -PE\sin\phi$. The torque balance then reads

$$PE\phi + \gamma_C\phi = 0$$

where we assumed ϕ to be small and introduced the subscript C to indicate smectic C cone motion. With

$$\tau^{-1} = PE/\gamma_C = \lambda$$

the equation simply reads

$$-\phi = \lambda\phi$$

with the solution

$$\phi = \phi_0 e^{-\lambda t} = \phi_0 e^{-t/\tau}$$

Thus the characteristic switching time τ is given by

$$\tau_P = \gamma_C/PE$$

in the ferroelectric case. Inserting the values for P (10 nC/cm^2) and E (10 V/μm) already used above and with a γ_C-value of 0.1 poise = 10^{-2} kgm^{-1}s^{-1} (*cf. Fig. 11*) we obtain $\tau_P = (10^{-2}/1000)$s = 10 μs, which is a fairly realistic value under the given assumptions.

For the dielectric case we obtain in complete analogy, the torque equation

$$1/2|\,\varepsilon_a\,|\,\varepsilon_0 E^2\varphi + \gamma_N\dot{\varphi} = 0$$

with the corresponding solution

$$\varphi = \varphi_0 e^{-t/\tau_\varepsilon}$$

$$\tau_\varepsilon = \frac{\gamma_N}{1/2|\,\varepsilon_a|\,\varepsilon_0 E^2}$$

With γ_N = 10 poise (*cf. Fig. 11*; the subscript indicates the nematic-like viscosity in this case) and the same values (ε_a = -1, *etc.*) as in the previous section, we obtain for the characteristic time $\tau_\varepsilon \approx 1/(4.5\cdot 100)$ s ≈ 2 ms, again a quite realistic value. Had we chosen a field strength more typical for nematic devices, like 1 V/μm, then the characteristic times would have been 100 μs and 200 ms, respectively, for the ferroelectric and dielectric case. Going in the other direction, if we raise E to 100 V/μm, this would yield τ_P = 1 μs and τ_ε = 20 μs. It is clear that, owing to the quadratic field dependence of the dielectric torque, the dielectric switching will ultimately

be, in principle, as fast and faster than the ferroelectric switching. In order to qualify as a switching time, the measured time should however correspond to a useful electrooptic effect. The relevant question to be addressed is thus what optical changes and electrooptic characteristics can be connected with switching at a given speed (contrast, viewing angle, ON-OFF symmetry, bistability, multiplexibility, device flexibility). This is not always made clear[25], and it is a rather trivial fact that, in principle, all common nematic (and smectic) electro-optic effects based on dielectric torques can, in principle, be made faster than the ferroelectric effects, especially with the extremely high dielectric anisotropies available today in many materials.

Finally, we calculate the critical field for unwinding the helix present in a thick sample, using our earlier value for the polarization. The expression is[6]

$$E_C = \frac{\pi^4}{4} \frac{K}{PZ^2}$$

where we set the elastic constant K equal to 10^{-11} N and assume a fairly hard-twisted material with Z = 1 μm. We then find E_C to be in the region 1 to 10 volts per μm. At the lower end, *i.e.* for materials with slightly weaker twist, the field is just sufficiently low to neglect the dielectric torque and the above formula could be used without modification in order to determine P, if K were known, which is, however, essentially never the case. At the higher end E_C is of the same order of magnitude as SSFLC switching fields and materials with such a hard twist cannot, *a fortiori*, be used in SSFLC devices.

Slightly outside of these numerical estimations, an important question for the device dynamics is the scaling of the viscosity with the tilt angle θ. We know that K scales as θ^2 and P as θ. How about viscosity? Is it a linear or

quadratic function in θ? Intuitively it is clear that a small value of θ would lead to a more rapid switching than a larger θ, other factors being equal. The θ-dependence also leads to a certain part in the temperature dependence of the viscosity, a part that ought to be scaled out when comparing and judging the viscosity for different materials and material classes.

Experimentally the situation is, as usually, unclear. Early light scattering measurements on free-standing films[26] seemed to favour a quadratic dependence, $\gamma = \gamma_0 \sin^2\theta$. This proportionality has also been concluded from a molecular statistical model.[27] Some Russian work[18] seems to show, however, that both $\sin\theta$ and $\sin^2\theta$ might be applicable. We will address this question from a consistent phenomenological point of view in the next section. Before doing so, we might just briefly take a second look on our expression for the ferroelectric switching time

$$\tau = \gamma/PE$$

If $\gamma \sim \theta$ just as P then $\tau \sim 1/E$. If $\gamma \sim \theta^2$, then $\tau \sim \theta/E$. It is clear that the second expression is more in agreement with experience than the first one, even if the strong T-dependence of γ_0 persists in both expressions and tends to mask the particular dependence on θ.

Viscous torque and rotational viscosity in the smectic C* phase

The rotational viscosity in the smectic C* phase is presently not as firmly based on a continuum theoretical description as is the case for the corresponding quantity γ_1 for nematics. It is nevertheless possible to introduce a term of the form

$$-\gamma_1 \frac{d\phi}{dt}$$

with a dissipative coefficient γ related to the gradients $d\phi/dt$, in order to describe the viscous torque always acting to reduce an existing angular velocity. This is also the way one usually introduces the time-dependence in order to describe dynamical switching in FLC cells.[28-34] In the nematic case it is today established, through the Leslie-Ericksen continuum description, how this director torque is coupled to other director torques (*e.g.* of surface or external field origin), and also how it in general couples to the velocity field to introduce a flow in the liquid crystal. The present situation for smectic C* liquid crystals is not equally well developed, but in order to describe *e.g.* switching phenomena caused by the application of an external electric field, a description neglecting material flow effects and thus involving only the director equation is often employed, as we have done above. Moreover, one often studies the smectic far from phase transitions, so that the tilt angle θ is considered constant; further the smectic layers are considered to be parallel. Even with these simplifying assumptions, the correct continuum description of the smectic C* phase becomes complicated, especially when polar surface effects are included. The other common phenomenological description, the Landau-type expansion for the smectic A- smectic C phase transition, has been pursued more extensively when discussing both static and dynamic properties of the smectic C* phase.[20,35-37] A more "classical" continuum mechanical description, involving parameters such as elasticities and viscosities whose temperature dependence is not explicitly appearing in the dynamical equations, has only been attempted more recently.[38]

Scaling rule for the rotational viscosity

Referring to *Fig. 19* below, let us discuss the rotational viscosity in the smectic C* phase as related to the rotational viscosity in the nematic phase. In addition to **n** it is convenient to introduce a vector **c** being the unit vector along the projection of **n** in the layer plane.

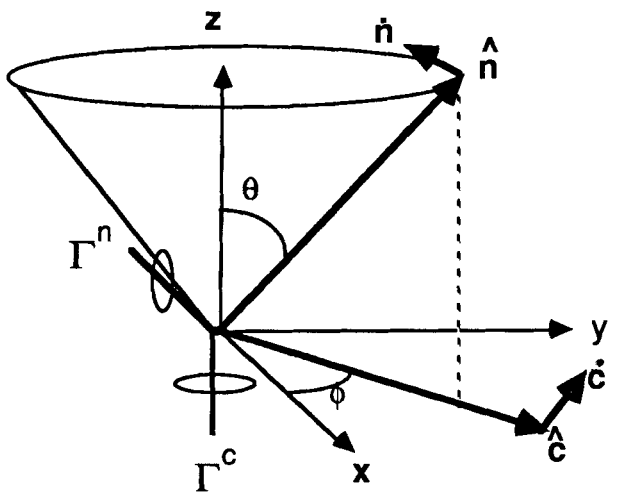


FIGURE 19. Definition of angles and vector notation in the smectic C phase.

One model that might be used is to consider the director in the smectic C* phase to be dynamically similar to a nematic director constrained to the cone θ=constant. By dynamically similar we mean that the smectic **c**-director will be damped by a viscous torque that is just the **z**-component of the viscous torque acting on the **n**-director. The viscous torque on the n-director is given from the hydrodynamics of nematics as

$$\Gamma^{n} = -\hat{n} \times \gamma_1 \dot{n}$$

where γ_1 is commonly called the rotational viscosity, and **n**-dot is the angular velocity of the director. The direction of this torque is such that it always tends to diminish a director angular velocity that has been introduced by *e.g.* an application or removal of a shear flow or an external magnetic or electric field. Let us now calculate this torque for the conically constrained nematic director of *Fig. 19*. The director may be expressed in polar coordinates as

$$n_x = \sin\theta \cos\varphi$$
$$n_y = \sin\theta \sin\varphi$$
$$n_z = \cos\theta$$

For the calculation of the viscous torque we take the time derivative of **n**

$$\dot{n}_x = -\dot{\varphi} \sin\theta \sin\varphi$$
$$\dot{n}_y = \dot{\varphi} \sin\theta \cos\varphi$$
$$\dot{n}_z = 0$$

The z-component of the torque Γ^{n} is calculated to be

$$\Gamma^{n}_{z} = - \dot{\varphi} \gamma_1 \sin^2\theta$$

If now the viscous torque on the smectic **c**-director is introduced in formal analogy with the definition of the viscous torque in nematodynamics, we may write

$$\Gamma^{c} = - \hat{\mathbf{c}} \times \gamma_c \dot{\mathbf{c}}$$

where γ_c is the rotational viscosity for the **c**-director. Proceeding as for the **n**-director, we get for the time derivative and **z**-component of the torque

$$c_x = \cos\varphi$$
$$c_y = \sin\varphi$$
$$c_z = 0$$

$$\dot{c}_x = -\dot{\varphi} \sin\varphi$$
$$\dot{c}_y = \dot{\varphi} \cos\varphi$$
$$\dot{c}_z = 0$$

$$\Gamma^{c}_{z} = -\gamma_c \dot{\varphi}$$

If we now compare the expressions for the **n**-director and the **c**-director,

we can infer the relation

$$\gamma_c = \gamma_1 \sin^2\theta$$

As mentioned above the proportionality of the rotational viscosity γ_c to $\sin^2\theta$ has also been concluded from a molecular statistical model.[27] The experimental material is at present not large enough to enable a verification of the scaling rule given above, although some experiments independently determining γ_c and θ have been reported.[18] However, these results do not allow a discrimination between $\sin\theta$ and $\sin^2\theta$, but if we go back to the naive picture discussed in connection with *Figs. 8* to *11*, we see that only a quadratic term could eventually account for the correct order of magnitude. With $\theta = 10°$ we find γ_c to be a factor of 33, with $\theta = 5°$ a factor of 130 smaller than the nematic viscosity ($\theta = 90°$). For $\theta = 22.5°$ it would be smaller only by a factor of 7. Thus the measurements still indicate a somewhat larger difference than the model.

SSFLC APPLICATIONS

The SSFLC devices can be used in a number of modes,[39] the most important of which are the birefringence mode and the guest-host mode. Several other electro-optic effects involving ferroelectric liquid crystals have been reported, *e.g.* the scattering modes,[40] and applications are being filed for new effects and applications. However, the prototypes presented so far concern the typical SSFLC situation and in the following general discussion we will have this in mind.

The FLC device potential

Fairly logically, the first commercial device on the market was a small, low-cost, noise-free and large aperture shutter-modulator capable of giving a continuous grey level transmission by time modulation.[41] The extension of this to printheads for fast printers in office automation and general printing technology is obvious and only awaits simpler and more convenient addressing schemes than those presented (*e.g.* Hitachi, NEC) for its full exploitation. It should be pointed out that bistability in many cases is not necessary *e.g.* in some modulator and optical engineering applications. Then the highest speeds in both C* phase and A* phase are available. In terms of speed it may further be noticed that not only are the ferroelectric liquid crystals interesting for being outside competition in the μs regime; equally remarkable from a performance point of view is the result achieved by Merck[42] in 1986 of 2 ms switching time for 15 volts/μm at minus 20 °C. (A very advanced nematic would have a switching time around 1 s at this temperature.)

The direction of high spatial resolution is also particularly interesting in connection with high switching speed. The Boulder group, in collaboration with 3M, has demonstrated a small high resolution matrix, where the pixels (ITO on glass electrodes) are 17 μm x 17 μm with 5 μm between pixels. At this resolution (which is quite practical from a manufacturing point of view) a normal 35 mm projection slide would have about 1000 x 1500 pixels and could be multiplexed at video rates. The market for liquid crystal projection devices is rapidly developing and the SSFLC/soft mode devices are certainly extremely promising in this area, as they are for three-dimensional television.

Laser deflectors and switches for optics communication also merit a mentioning. An SSFLC laser deflector with a very large deflection angle

has recently been demonstrated.[43]

Optical engineering and computing

Before going on to the presently most important area of display applications, which will be the topic in the following sections, we finally want to draw attention to the renewed interest in the very powerful domain of optical engineering and even optical computing, brought about by the emerging SSFLC technology.

The first liquid crystal device in optical engineering was the spatial light modulator or liquid crystal light valve (LCLV) developed by Hughes[44] and consisting of a liquid crystal sandwiched onto a photoconductor. The original motivation was to transform information carried by light (images) from incoherent to coherent. Another possibility is to display computer-generated information (text, graphics, pictures) directly as a projected image or to read in graphic data directly into a computer. The name "light-valve" also evokes a further major use: to amplify the intensity of an image. A low-intensity picture is focussed on the back side photoconductor which addresses the optically shielded liquid crystal on the front side. Light from a powerful source is then reflected off the front side, intensity-modulated according to the incoming picture. For the first-mentioned application incoherent incoming and coherent outgoing light replaces the low and high power light, respectively. This type of light valve is a typical example where bistability is not required, nor even desirable. In addition to being photo-addressed, as described above, the device could also be matrix-addressed, although photo-addressing is clearly desirable in all situations of light-light coupled architecture, when closed light-loops could be built, coupled to or integrated in other light-loops.

The original light-valves commercialized by Hughes, were quite

powerful but limited by the response time 10-100 ms of the utilized nematics. They were therefore unable to work in real time, which is, however, highly desirable in some of their most important applications, involving decision-making steps, where the outcome of one operation influences the nature and sequence of the following ones. Real time in this connection usually means that a number of steps have to be performed within, say, at most 1/100 of a second. Thus the speed requirements, although not fantastic, are slightly outside the reach of nematics.

In optical or optoelectronic computing the required speed may be somewhat higher but, again (except for supercomputers), not higher than what is achievable today. A reasonable assessment is that a pixel speed allowing operation at $\geq$ 10 kHz is desirable. If sufficiently many gate elements can be processed simultaneously and in parallel, which they can in a two-dimensional array, then very high computing speeds (GHz region) can indeed be achieved. A simple example of a device using a 2D switching array is the optical crossbar switch[45] which can be described as a kind of optical switchboard. Already a 32 x 32 matrix array is of great technical interest and a 256 x 256 array is an advanced project for reconfiguring interconnections in VLSI computers. Another highly interesting application of the 2D array is in matrix-matrix multiplication using incoherent light, for instance in the RUBIC calculator cube (involving two light valves) configuration,[46] and in logic operations in general.

Knowing that intense research is going on in non-linear elements and optical bistability, one could raise the question whether ferroelectric liquid crystals would at all be able to compete with some of these fancy picosecond switches. The answer is yes, because if the same problem (and many problems are of this kind) can be solved with a liquid crystal system, it would be pointless to mobilize the quite more complex and formidable picosecond systems, which furthermore suffer from severe problems in

heat dissipation. To cite one of the experts in optical computing on what is needed[47]: "Number one is inexpensive, large, low-loss, low-power dissipation, room temperature, manufacturable, transparent materials and structures with very large interaction coefficients". Ferroelectric liquid crystals having strong interaction with both light and with electric fields, are indeed among the most interesting optoelectronic materials in this regard and strong attention should now be attached to them also in connection with optoelectronic computing.

DEVICE DEVELOPMENT

The industrial FLC device development has so far almost uniquely been directed towards displays, mostly even at once towards the very largest displays, a task much more complicated than for any of the applications mentioned above. One might say that, in this first phase, all fundamental understanding problems, all material problems, all basic technical problems and all manufacturing problems had to be attacked simultaneously for this new liquid crystal technology, very substantially different from the earlier ones.

Device manufacturing problems

The first unconventional problem is the cell thickness, d. In order to avoid splay structures, d should be typically 1-3 μm. This leads to problems in applying the spacers and in filling, although it seems that both of these can be overcome. Chromatographic effects on filling leading to a spatially varying composition along the surface have been observed and is of some concern to material suppliers. Commonly spacer spheres are sprayed on to the glass although printing techniques may ultimately be used

(perhaps also for filling). Rubbing to influence alignment is a much more delicate operation than for nematics. Any one combination of FLC material and bounding surface may prefer, more or less strongly, a certain surface state with $\mathbf{P} \cdot \mathbf{s} > 0$ or $\mathbf{P} \cdot \mathbf{s} < 0$ ($\mathbf{P}$ polarization, $\mathbf{s}$ the surface normal).[48] If this interaction is strong, it means a strong tendency for splay state, if both surfaces are equal or equally coated and rubbed. In this case the splay can be reinforced or weakened if a rubbing direction is chosen[39] corresponding to the same sign in $\mathbf{P} \cdot \mathbf{s}$ or opposite to it. For the material/surface combination any rubbing direction may also be characterized as positive or negative, according to whether it provokes $\mathbf{P} \cdot \mathbf{s} > 0$ or $\mathbf{P} \cdot \mathbf{s} < 0$.

A large variety of surface states are possible and many of them do, in fact, work quite well. Thus even if there is much more to be learned on SSFLC alignment techniques, viable solutions begin to emerge to the alignment-addressing problem which has to be considered together, *cf.* below.

Mechanical shock

An early observation was that mechanical deformation of an SSFLC display may lead to the appearance of milky, dead areas, *e.g.* when exerting a local pressure on the front plate. Microscopic inspection showed that these areas are characterized by a very pronounced invasion of zig-zag defects, destroying the layer structure and rendering the material non-switchable. As any vibrations of the bounding glass plates relative to each other are fatal to the ordered layer structure (which has to be restored by going up to the isotropic state) the glass plates have to be glued together to a rigid non-vibrating and non-deformable structure, preferably by using as thin plates as possible or a thin bottom plate glued onto a thicker top plate.

Photoresist printing might be a good way to achieve this but epoxy distance spheres were used by Seiko I&E in the first successful attempt to overcome this problem.[49] The very characteristic zig-zag defects, appearing under conditions which still have to be cleared, have been analyzed recently by the Boulder group and traced back to the existence of layer tilt and a chevron-like layer structure, in which an abrupt jump in chevron direction is mediated by a new kind of liquid crystal defect.[50,51]

Thermal stability of the material

For severe storage, transport and application conditions the useful temperature range of the C* phase has to be reasonably broad. It is fairly obvious that this requirement has been very difficult to fulfill during the very short period of active material development so far. No doubt has this also hindered commercialization to some small extent. However, essentially the same problems are involved in developing a broad-band mixture whether it is the question of smectic or nematic and there is no reason to believe that C* problem would be essentially more difficult to solve, but just a matter of (reasonable) time. The chemical suppliers are now opting for materials with custom designed parameter values while keeping a useful temperature range from at least -30 °C to +70 °C. Thus, we do not think that materials, as little as alignment and cell thickness will limit the present development. In spite of the mentioned problems one should not forget that, in many aspects and especially in the long run, FLC technology offers simpler and cheaper solutions to manufacturing than other advanced liquid crystal technologies. It is our feeling that the essential present problems are not so much in manufacturing as in electronic addressing.

Addressing FLC devices

The switching process, in the details, sensitively depends on FLC parameters like θ, P, ε_a and on device parameters like cell thickness, layer tilt, molecular surface pretilt and defect structure. In a complicated way these features together influence threshold, speed, static and dynamic contrast and memory properties. Oblique evaporation of SiO has been observed to induce a very homogeneous alignment with a low density of defects (almost no zig-zags); however the switching can tend to be a little slow in these structures. This might be explained if the switching process, in this case, has to be nucleated at one of the surfaces, whereas a chevron cell behaves nearly as two independent cells clamped together[51] with the extended 2D defect in the middle always mediating an efficient bulk switching. If then also nucleation has to be considered in an advanced analysis, simple considerations are presently sufficient to show that rapid progress in device performance will be possible if careful attention is paid to the interplay between material properties and addressing cycles.

Bistability with dynamic memory

Consider a cross section of the thin (splay-free) electro-optic cell with the optic axis direction and the corresponding polarization vector given at different depths as depicted in *Fig. 20*. In this figure the layer is thought to be in the plane of the paper and the molecular directions are represented by the field of **c**-directors. The polarization **P**, as in *Fig. 17*, has the relation to **n** and **c** valid for a positive material (P>0). To the left is shown the state (1) corresponding to the application of a high electric field in the downward direction. This might be the situation immediately after a strong latching pulse, E DOWN. When the field is taken away, the transmission will

generally fall off, more or less rapidly, as indicated in the lower part of the figure. The important question is how rapidly. This depends on the stabilizing dielectric torques ($\varepsilon_a<0$) from the data signal background that the picture element feels between successive addressing periods. If these torques are efficient they support the high contrast states (1) and (2) and suppress the states (1') and (2') characterized by lower contrast. The ideal multiplexing is clearly such that the transmission falls off unnoticeably slowly between addressing periods (dashed lines in *Fig. 20*), in which case we may say that we have achieved a perfect dynamic memory. The goal for every addressing scheme must therefore be to supply a voltage train whose rms value is as high as possible (for good dielectric stabilization) at the same time as keeping as high a discrimination as possible (in order to prevent non-addressed pixels from flickering by full or partial switching). Such an inherent ("AC")-stabilization does not involve any "holding" voltage in addition to the addressing voltage but has nevertheless a decisive influence on the threshold behaviour, and on the contrast, for which no variations related to the driving process itself should be noticeable at any time.

In an earlier section we compared numerically the dielectric torque $\Gamma^{\varepsilon}\sim\varepsilon_a\varepsilon_0E^2$ with the ferroelectric torque $\Gamma^{P}\sim PE$. In order to have a good dielectric stabilization, their ratio

$$\varepsilon_a\varepsilon_0E/P$$

must not be small. This means that we cannot permit too high a value for the polarization P of the used material if we want it to be multiplexable.

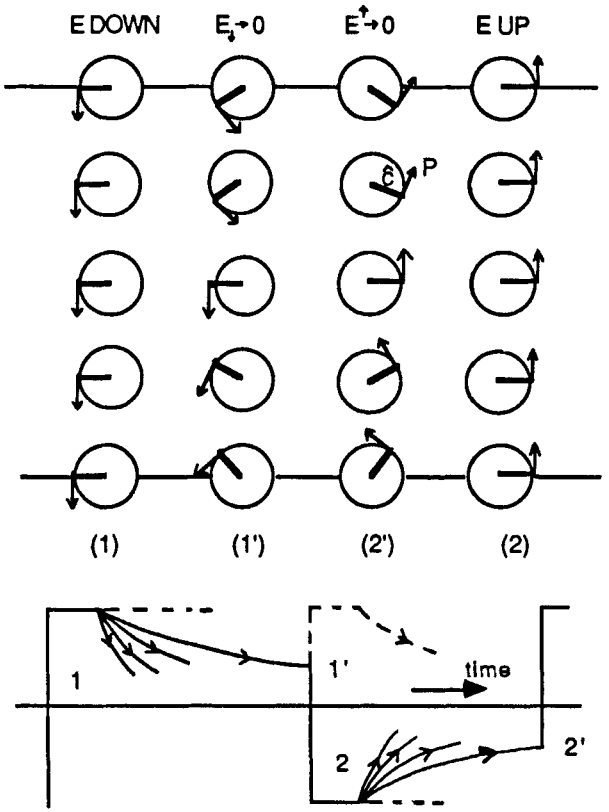


FIGURE 20. Cross section of an SSFLC cell along one layer (in the plane of the paper). States (1) and (2) are the fully polarized states in response to a strong applied field DOWN and UP, respectively, and relax to the corresponding states (1') and (2') without field. This relaxation is sketched in the lower figure as cell transmission as a function of time after applying a latching negative pulse, or again a positive pulse (dotted line). The dashed lines correspond to perfect dynamic memory.

What are desirable material properties?

Until recently there seems to have been an almost automatic trend aiming

at higher and higher values for the spontaneous polarization in FLC materials. There are, however, at least two reasons except addressing requirements that now make this development questionable. First, there is the fact that power dissipation increases with increasing P. Second, it seems probable that the polar surface interaction will be more important at high P, which will favour the undesired splayed state even in relatively thin cells. In addition one may remark that too often in the recent past, a high P value in a new material has been coupled with a fairly proportional increase in γ, so that little or nothing has been gained in terms of switching speed.

In the torque-balancing parameter $\varepsilon_a\varepsilon_0 E/P$, the dielectric anisotropy, of course, plays an important role. For the matter of discussion, let us take a concrete switching pulse, *e.g.* the one (even if academic) in *Fig. 21*. Assume the dynamic threshold to be $500 \cdot 10^{-6}$ Vs, which means that a 25 volt pulse applied under 20 μs leads to latching in a new state. Let us then choose our switching pulse to 20 volts applied during 30 μs ($600 \cdot 10^{-6}$ Vs, thus supercritical) whereas our DC compensating counter pulse will consist of two 30 volt-10 μs pulses separated by a 10 μs zero pulse. Each of these are clearly undercritical ($300 \cdot 10^{-6}$ Vs), but in addition to this they are efficient, due to the quadratic dielectric torque, in stabilizing the surface positions and sharpen the threshold. The duration of the sequence is 2τ if τ is the duration of the switching pulse, 30 μs. If the smallest time unit, 10 μs, is taken as τ, then the whole duration is 6τ. A writing sequence can be made twice the switching time (or even shorter, but then at higher cost). The pulses of 30 μs and 10 μs correspond to a frequency band of 30 to 100 kHz. Thus it is the value of ε_a in this frequency region that is determining the stabilizing or holding effect. To our knowledge no data on ε_a have ever been reported for this frequency region or the neighbouring higher or lower regions. Anyway, the magnitude of ε_a is not likely to be essentially different from 1 (which we used earlier in our numerical estimations),

which confirms that the polarization value cannot be too high.

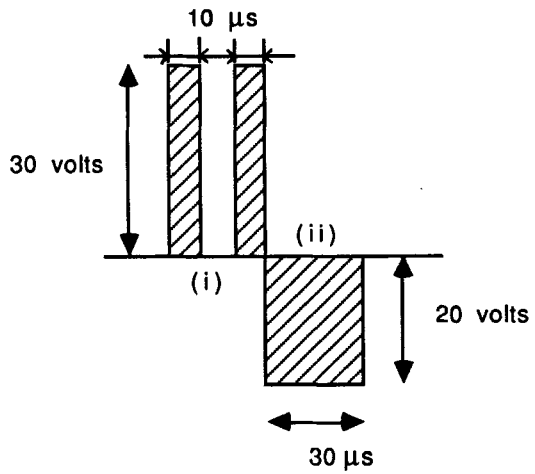


FIGURE 21. DC-compensated pulse train (shaded areas equal, $600 \cdot 10^{-6}$ Vs), with parts fulfilling different tasks: (i) and (ii) are both stabilizing [(i) more effectively than (ii)] whereas (ii) is also switching (threshold $500 \cdot 10^{-6}$ Vs).

Bistability with static memory

As has repeatedly been demostrated, it is quite possible to write information in SSFLC cells in order to store it permanently. There will no doubt be uses for this; however, it is a more delicate technology and less convenient in connection with diplays and screens. One reason for this is that it is hard to get the memory symmetric in a reproducible way. A related more important reason is that the non-symmetry in any case changes with time, with a strong tendency to "burn in" what has been written. It is, in fact, rather hard to activate such a cell with permanent memory once it has been stored on the shelf for the order of weeks.

Few studies have been made on surface memory effects in liquid crystals at all,[52] and the complexity of the phenomena presently makes them less interesting for device physics.

The industrial development

The first multiplexed matrix showing moving pictures was presented in 1986.[53] It was a very modest 16x16 pixel device, but it was genuinly multiplexed with a dielectric stabilization and showed no contrast flicker. It used a 4τ or 5τ sequence (with zero phase) and had a short-term bistability, more than adequate for its purpose. A bar-graph array was developed at the same time and driven according to *Fig. 20* with a decay time of the order of seconds. In this case as in the case of the matrix, the states corresponding to (1') and (2') were the same multidomain grey state. The bar-graph was driven in a duty-rate of 1:1024 with no essential degrading of the contrast corresponding to (1) and (2). A common observation when trying to multiplex a small matrix is that the FLC material is very often *too* rapid to permit efficient multiplexing, which means that non-select pulses get supercritical and causes essentially all elements to flip back and forth. By doping with a non-chiral material it slows down sufficiently to be able to discriminate between select and non-select waves. Thus an FLC material must always be adjusted to the time and amplitude units used by the driving schemes.

The industrial laboratories, at that time exclusively in Japan, had already presented, and continued to present, some very impressive large-screen prototypes, which were, however, not multiplexed in a dynamic mode. This situation has, surprisingly enough, persisted until now. It seems, as would the Japanese companies had set the goal of developing the technology for a static or permanent memory, or applying a separate

holding-voltage rather than to use the inherent dielectric stabilization. In most cases one could therefore easily see the writing sequence scan down the lines: the line being addressed was quite descernible due to the change in cone tilt on addressing, which shows that there is no balance between ferroelectric and dielectric torques.

The British program

At the end of 1986, after 18 month's work, the British Joers/Alvey project released its first prototype, showing that this program probably is the most ambitious collaboration between physics and chemistry, between industrial and academic laboratories in the FLC area. If modest in size, the presented 64x64 element matrix showed a flawless performance in displaying moving pictures at video rate. The British seem to be ahead when analyzing the relevant factors for efficient matrix addressing and developing taylor-made materials.

The first technical step is a black and white video screen with 625 lines. The writing time for each line is 64 μs, which gives 64x625 = 40000 μs = 40 ms frame time, thus corresponding to 25 Hz. Using a simultaneous double-scan technique where every line is first blanked before being written,[54] they succeed in using a two bit writing sequence. This means that the response time of the FLC material used must be 32 μs, and such a mixture was developed by the chemists. Presently STC and Thorn-EMI, belonging to the project, are working on a 7.5" screen and later aiming at a 22.5" TV.

Grey scale and colour TV

To achieve grey scale probably a combination of techniques will be employed. One is "dither", a special form of time-multiplexing. We may remark that SSFLC/soft mode may prove interesting for achieving a grey scale, especially when substances become available for which the induced tilt is of the same order as the spontaneous tilt.

The goal of Thorn-EMI is a full colour SSFLC television. According to their analysis,[55] colour would require a surprisingly low number of additional steps (three for green, two for red, two for blue) which would raise the requirement on response speed from 32 μs to 2 μs. By using double drivers and writing simultaneously + and - minus pulses this may be modified to 4 μs.

MOLECULAR STRUCTURE AND MATERIAL PARAMETERS

As mentioned in the beginning, applications of FLCs involve several physical parameters which, in one way or another, can be related to the molecular structure. Of particular interest, especially for SSFLC applications, is the ferroelectric polarization and the rotational viscosity. In this section we try to evaluate how these parameters, polarization and viscosity, are influenced by changes in molecular structure. We will also discuss the molecular features relevant in the tilting process.

The ferroelectric polarization has been immensely studied during the past few years and the increased amount of available experimental data makes a study of the delecate interplay between the polarization and the molecular structure particularly relevant. On the other hand, although the viscosity is an equally important parameter, studies relating the rotational viscosity to

molecular structure are unfortunately very scarce and the discussion of this parameter is therefore presently more a matter of speculation.

Models for the ferroelectric polarization

Since Meyer and coworkers[2] published their original paper on ferroelectric liquid crystals numerous articles on the subject have appeared in the literature. The dipolar ordering process, caused by, and not causing the transition, and which results in a spontaneous polarization of the liquid crystal, has been an intriguing issue for the last decade. Several authors give a mathematical and statistical description of the process[14,56] but few of the cited papers treat the most interesting and basic question, *i.e.* what are the molecular processes responsible for the dipolar ordering and which molecular features affect the degree of ordering?

The first discussion of this kind was made by Meyer.[6] Beresnev and Blinov,[57] and Lagerwall and Dahl[58] have tried to address this problem by describing the dipolar ordering in a more pictorial way. They base their discussion on the rotational bias, *i.e.* the slowing down of molecular rotation around the director, found in tilted smectic phases.[59] They conclude that an asymmetry in the rotational motion exists and therefore some rotational states are preferred and hence a dipolar ordering occurs. In their model the core part (if itself asymmetric) plays a minor role because of its essentially unbiased rotation (*cf. Fig. 22*). The extent of the ordering is determined by the molecular structure and specifically by the rigid steric coupling between molecular dipoles and the asymmetric center. It is important to note that this is only an assumption, however plausible, and that it has by no means been verified experimentally. There is not, at present, a sufficient body of experimental data to ensure a firm relationship between molecular structure and the magnitude of the polarization.

Escher[60] treats the problem using the same approach and the same arguments as Lagerwall and Dahl, and introduces a steric description that is very illustrative.

Using the same basic argument as in the preceeding papers,[58,60] Walba and coworkers[61] present a more elaborate model for the origin of ferroelectric polarization. Their formulation is however rather different from the ones previously discussed. They state that the spontaneous polarization originates from a novel kind of molecular recognition related to a diastereomeric host-guest complexation. However, the crucial point is again the rotational bias found in tilted smectic structures. If the molecular rotation around **n** proceeds with a barrier to rotation which is determined by the molecular structure, then the important question asked at the beginning of this section can be reformulated: which molecular features affect the depth and shape of the rotational energy well? The question still remains to be answered.

Consistent with their model, in which the core tilts more than the tails (*cf. Fig. 22*), Walba *et al.*[61] assume that molecular dipoles of the core system do not contribute to the ferroelectric polarization. Circumstantial evidence for this is also given by Otterholm *et al.*[62] The reason for the non-contribution of the core is that rotation of the core system, in relation to the tail units, is unbiased, thus confining the rotational asymmetry to the tails (*cf. Fig. 22*).

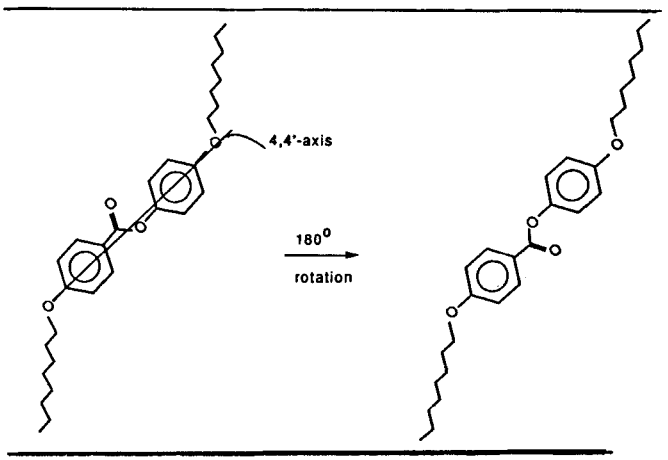


FIGURE 22. 180°rotation around the 4,4'-axis of a phenyl benzoate molecule in a tilted smectic phase. The rotation leaves the system practically unchanged and this motion can therefore be considered unbiased.

In a subsequent paper, Walba and coworkers[63] show how the sign of the polarization can be predicted using the proposed model. The model must however be used with caution since the sign prediction relies on the assumption that in the "zig-zag" formed molecules[64] (*Fig. 23*) the tail units are less tilted than the core. This will not always be the case. The first counter example for which the opposite is true has been given by Goodby and Chin.[65]

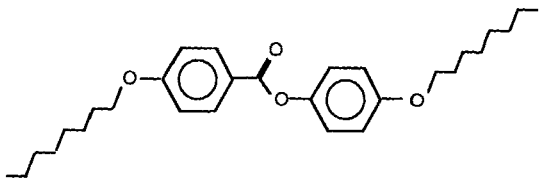


FIGURE 23. "Zig-Zag" conformation of a liquid crystalline molecule with the alkyl chains in their fully extended form.

Goodby *et al.*[66] have also discussed the origin of ferroelectric polarization in terms of molecular structure. They consider the molecular dipole at the asymmetric center to be responsible for the polarization and are in this way able to explain the alternation of the sign of P as the asymmetric center is sequentially moved away from the core.

Molecular structure and spontaneous polarization

The first generation of ferroelectric liquid crystals (FLCs) were in almost all cases derived from (*S*)-2-methylbutanol (*cf. Fig. 24*) which renders the surrounding of the asymmetric center quite non-polar. The polarization data for some of these compounds are collected in *Table 2* and we can infer that P seldom exceeds 5 nC/cm^2. Moreover, as the main dipoles are confined to the core, the relative position of the asymmetric center and the core becomes quite significant. A study of compounds **1** reveals that the polarization inducing power of the stereo-center rapidly fades as n increases which indicates the importance of the stereo-polar coupling.[62]

TABLE 2. Polarization values for some FLCs derived from 2-methylbutanol. For molecular structures, see Fig. 24.

Compound	P (nC/cm^2)	Ref.
I	3.5	67
II	2*	68
DOBAMBC	(-) 3	69
III	(-) 3	70
MBRA 8 (1, n=1)	(-) 3	71
IV	5.1	72,73,74
V	4.5	72
VI	6	72,73,75
VII	3.5	72

* The sign of P changes at ca 30 °C

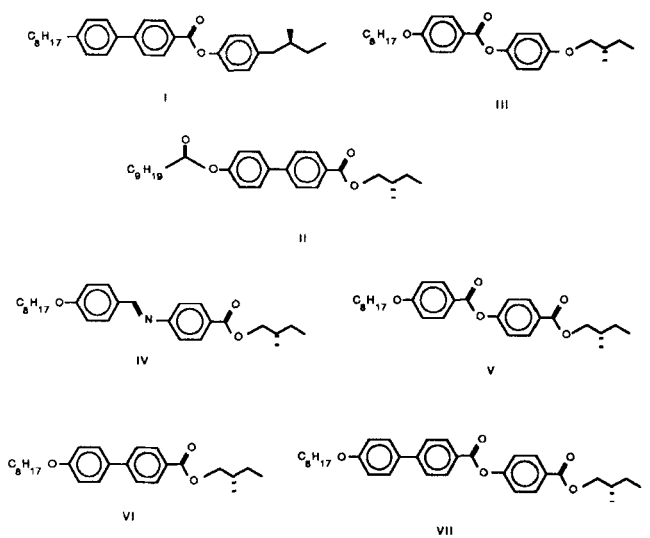
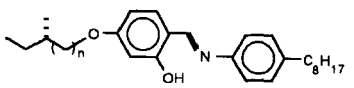
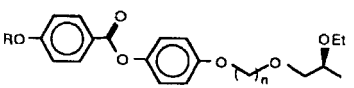


FIGURE 24. Molecular structures I-VII of TABLE 2.

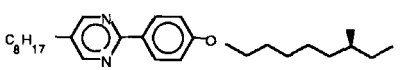
Although there seems to be an upper limit for P in the cases in which 2-methylbutanol is used as chiral group - this is probably true for most other chiral hydrocarbon groups as well - compounds of the discussed type might nevertheless qualify as components in high-performance multi-component mixtures due to their sometimes low viscosity, favourable C*-range or favourable surface interaction. Compound **2**, for example, shows quite fast switching in spite of a very modest P-value, 0.5 nC/cm^2, a behaviour which can be attributed to low viscosity and very good alignability. This example emphasizes that, as far as the response times are concerned, other parameters than P are important for the performance of a FLC and the development of new fast materials must not always be focussed on the ferroelectric polarization.



1



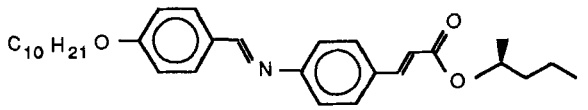
3



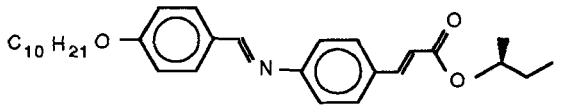
2

On the other hand, if polar groups are attached to the stereogenic center, as in **3**, its position becomes fairly insignificant.[76] The P-values are still modest, 4 nC/cm^2 or less (but almost independent of the value of n), attributed to high intrinsic rotation of the stereo-polar unit, a motion which can be restricted by small changes in the molecular architecture. If, for example, secondary alcohols are used as chiral starting materials (instead of primary alcohols as 2-methylbutanol) a significant increase in the polarization is obtained. Yoshino *et al.*[77] showed that if 2-butanol or 2-pentanol are used as chiral sources the polarization increased considerably.

The values for **4** and **5**, P equal to 42 and 18 nC/cm^2, respectively, should in a first approximation be compared with the value for DOBAMBC which is 3 nC/cm^2 (*cf. Table 2*).



4



5

This substantial enhancement, about one order of magnitude, of the ferroelectric polarization might be interpreted in terms of changes in the barrier to rotation of the C-O bond, see *Fig. 25*. There is a strikingly high *syn* barrier (ca 20 kJ/mol), and a severe steric repulsion between methyl and carbonyl is suggested to account for this (*cf. Fig. 26*).[78] In the molecules discussed above (**4** and **5**) there are two *syn* barriers (as compared to only one in DOBAMBC) resulting in a significant asymmetry of the rotational motion.

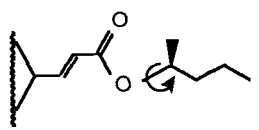
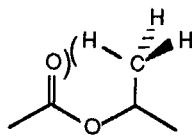


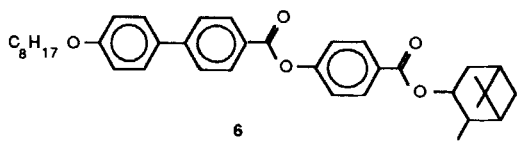
FIGURE 25. Rotation around the C-O bond in carboxylic esters.



syn

FIGURE 26. Repulsion between the hydrogen of the methyl group and the carbonyl oxygen in the syn conformation of a carboxylic acid.

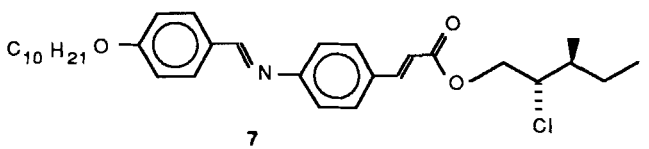
Secondary alcohols, such as cyclic terpenols, have been successfully utilized by Bone *et al.*[79] who obtained P-values of ca 60 nC/cm^2 for compounds like **6**. These authors also report several extrapolated values of similar compounds which are all of the same order as for **6**. They interpret these results in terms of restricted rotation of the stereo-polar unit, which is in accord with the above discussion of the non-cyclic secondary alcohol derivatives (**4** and **5**).



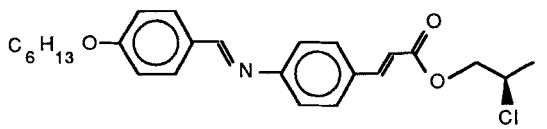
6

Furtheremore, restricted rotation of the stereo-polar unit can conceivably explain the high P-value (50 nC/cm^2) of DOBAC-3-MPC, shown as structure **7** below.[80] The molecular structure of **7** resembles that of HOBACPC (**8**) with the exception that the polar carbon chain is elongated, keeping the position of the chlorine relative to the core constant, and that it has a vicinal methyl group introducing a second asymmetric carbon. The P-value of **7** is about three times higher than that of HOBACPC (15 nC/cm^2)[81] and the following question may be raised: is this increase due to restricted rotation of the stereo-polar unit alone, or does the introduction of a second asymmetric carbon play an important role? Considering the

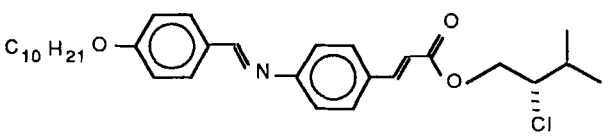
homologous compound DOBAC-3-MBC (**9**), for which P is about 17 nC/cm^2, one may conclude that the second stereo-center is important and the consecutive question will then be: what is the significance of the absolute configuration of the two asymmetric carbons, and further: can independent manipulation of two asymmetric centra be a valuable tool in the development of new materials?



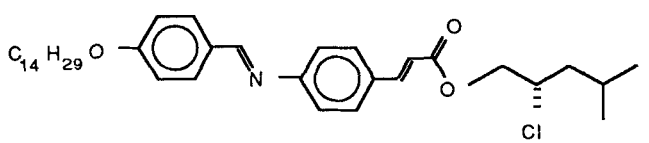
7



8



9

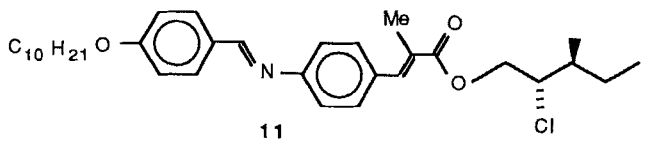


10

However, the compound **10** (TDOBAC-4-MPC), similar to **7** and **9** but without a vicinal methyl group, does not really fit into this reasoning. The unexpectedly high P-value of 34 nC/cm^2 suggests that other factors than restricted rotations of the stereo-polar unit, such as intermolecular interactions, are influential as well.

If we continue to look upon the compounds of Sakurai *et al.*[80] we find

some interesting facts concerning substitution in the core system. If an α-methyl group (the α,β-unsaturated carbonyl moeity may be regarded to be included in the core) is introduced the polarization drops dramatically. DOBAC-3-MPCM, structure **11** below, has a polarization value of only 6.3 nC/cm^2 which should be compared with the corresponding value for the unsubstituted analog, **7**, which is 50 nC/cm^2. This almost 10-fold decrease may be interpreted as being due to conformational changes, induced by the α-methyl group, which affect the dipolar ordering process but unfavourable interactions with the monoclinic environment, *i.e.* with neighbouring molecules, may also be considered to contribute to the lowering of the polarization.

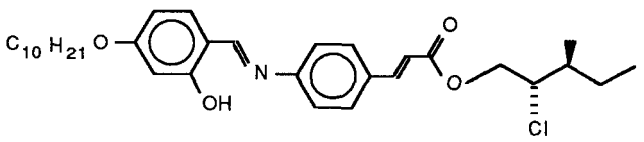


11

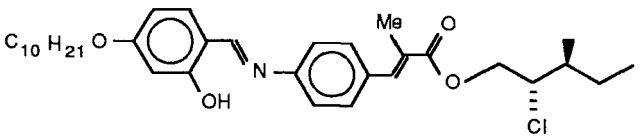
On the other hand, the introduction of an *o*-hydroxy group into the benzylidene ring of the above discussed Schiff bases slightly increase the polarization. HDOBAC-3-MPC (**12**) and HDOBAC-3-MPCM (**13**) both have slightly higher P-values, 62 and 8.7 nC/cm^2, respectively, than their corresponding unsubstituted analogs (**7** and **11**). The OH-group increases the molecular dipole moment, especially its lateral component[62] but as already pointed out, the dipoles of the core seem to be insignificant as far as the ferroelectric polarization is concerned. Instead, increased intermolecular interactions[62] might in this case cause the slight increase in the polarization.

Finally, Sakurai *et al.*[80] give one example in which the chlorine of **12** is replaced by a bromine resulting in a decrease in P, 39 as compared to 62 nC/cm^2. The slightly lower dipole moment of the C-Br bond (1.38 D as compared to 1.46 D for the C-Cl bond) may account for the lowering of P but the different size and polarizability of the bromine may also cause

changes in the conformational distribution and intermolecular interactions disfavouring the dipolar order.

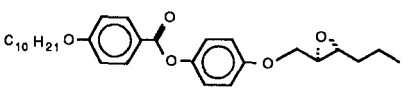


12

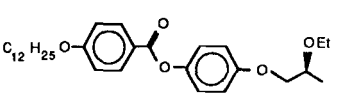


13

Walba and coworkers[63] showed in a recent paper the importance of a conformationally rigid stereo-polar unit. In the studied compound, **14**, the stereo-dipole is incorporated in a three-membered ring, an epoxy-unit, and the conformational flexibility is thus diminished. The polarization of compound **14**, ca 30 nC/cm^2, is about 2-3 times higher[82] than that of similar open chain ethers like **15**.[61]



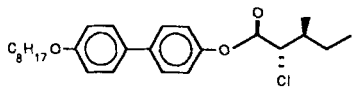
14



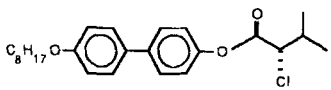
15

A ferroelectric polarization exceeding 200 nC/cm^2 is reported for liquid crystalline materials derived from amino acids[83] and these values are the highest reported so far for liquid crystals. In these compounds, exemplified as structure **16** below, the chiral unit consists of a vicinally branched α-chloro carbonyl group - derived from *i*-leucine - comprising two contiguous asymmetric carbons. Again we may ask about the significance of the second asymmetric center. The homologous compound **17**, also shows quite a high polarization[84] which indicates a moderate importance of

the second stereo-center in this case (*cf.* the previously discussed example, compounds **7** and **9**).



16



17

In any case, the α-chloro carbonyl grouping promotes a high ferroelectric polarization and this unit has been successfully used by other workers as well.[85,86,87] Crystallographic data of α-chloro carbonyl compounds are scarce but the available information[88] suggests a reinforcement of the two contiguous dipoles (see *Fig. 28*) which seems to be particularly favourable in the above discussed examples.

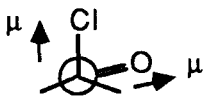


FIGURE 28. Reinforcement of the the two contiguous dipoles of the α-chlorocarbonyl moiety. Viewed along the bond connecting the carbonyl carbon and the chlorine substituted one.

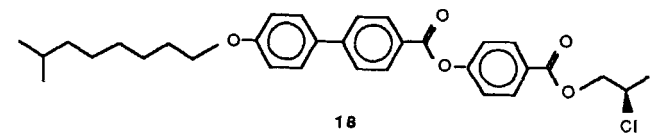
The polarization values for the compounds mentioned in this chapter are displayed in *Table 3* below.

TABLE 2. Polarization values for the discussed compounds including the commercial mixtures CS-1011 (Chisso) and ZLI-3488 (Merck)

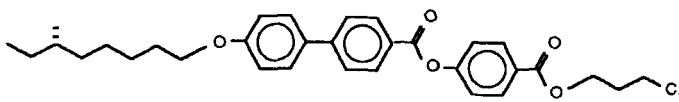
Compound	P (nC/cm^2)	Ref.
3	(+) 4	76
4	42	77
5	18	77
6	(-) 60	79
7	50	80
8	(-) 15	81
9	17	80
10	34	80
11	6.3	80
12	62	80
13	8.7	80
14	(+) 30	82
15	(+) 10	82
16	220	83b
17	170	84
CS-1011	(-) 15	
ZLI-3488	(+) 9.7	

In an investigation aimed at clarifying the significance of the stereo-polar coupling two specially designed molecules, **18** and **19**, were considered.[89] The studied compounds are similar in their polar character but quite different as far as the stereo-polar coupling is concerned. Measurement of the polarization could not be realized, due to difficulties in sample preparation, but optical rise time measurements of a non-ferroelectric C-mixture doped with 20% of **18** and **19**, respectively, yielded some interesting results. The mixture doped with **18** switched about 10 times faster than the corresponding **19**-mixture, and if the

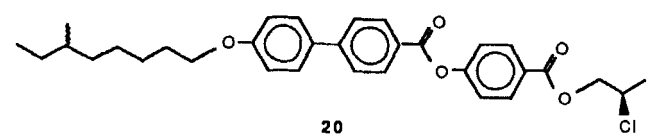
viscosity is considered equal in the two mixtures, this result indicates that a strong stereo-polar coupling is advantageous when a high polarization is desired. If the considerably smaller tilt angle of the **19**-mixture is taken into account, the difference in switching speed is further accentuated. In addition, the same result is found for the compounds **20** and **21** which again emphasize the importance of a strong stereo-polar coupling.



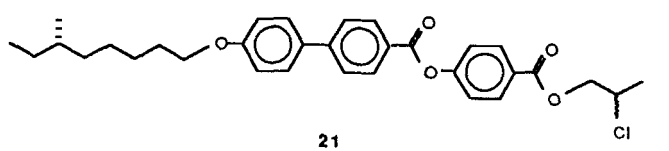
18



19



20



21

We may then try to summarize this section by pointing out the most salient molecular attributes - besides the strenght of the molecular dipoles - which may influence the dipolar order and promote a high polarization.

- polar and chiral side chains

- a rigid steric coupling between stereo-center and molecular dipoles

- a slow intrinsic rotation of the dipoles attached to the asymmetric center, an effect which can be obtained by, for example, vicinal branching

- increased intermolecular attraction, obtained by, for example, favourable core substitution

Molecular structure and rotational viscosity

Although being an important parameter, the rotational viscosity γ has so far been poorly investigated. From first principles very little can be said about its relation to structure. One might conjecture[90] that γ should scale as $L^{0.5}$ if L is the lenght of the molecule. Empirically there is some evidence from nematics that γ for different mixtures compare as the inverted values of the respective glass temperatures, $\gamma \sim 1/T_{glass}$.[91] However, as we have seen above, there are not only different flow viscosities, but also more than one rotational (twist) viscosity in tilted smectics. This complicates both measurements and interpretation. Moreover, until recently measurement methods have been indirect. Some estimated values have been reported, most of which are obtained from optical rise time measurements.[76,92] None of the cited works are aimed at a systematic study of the viscosity with reference to the molecular structure and it is therefore difficult to draw any reliable conclusions except that the viscosity seems to be fairly constant within a homologous series.[76]

Recently, however, Geelhaar *et al.*[85] presented a study aimed at gaining some understanding of the relation between molecular structure and

rotational viscosity. All of the studied compounds are of the α-chloro carbonyl type, similar to the previously discussed compounds **16** and **17**. The viscosity of a non-ferroelectric base mixture doped with 10% of the studied chiral compounds was determined from the measurement of the polarization reversal current with a triangular wave voltage. In this manner they were able to draw some tentative conclusions regarding the influence of structure on the viscosity.

The result is that changing the length of the normal alkyl chain of a homologous series does not considerably affect the viscosity neither does the change of a benzene ring for a pyrimidine ring. A small increase was found when an *iso*-propyl group, contiguous to the asymmetric center, was replaced by an *iso*-butyl group but the most striking effect was obtained when both tail units were substituted by polar groups or when one of the benzene rings contained a lateral chlorine. In these latter cases a significant increase in γ was found which indicates that polar groups increase the viscosity.

To end this section, we can conclude that too little is known to establish any relation between the rotational viscostiy and the molecular structure. Consequently, the body of experimental data relating to viscosity must be considerably increased.

Molecular structure and tilt

The origin of tilt has long been a matter of discussion. Several models for the tilt mechanism have been proposed, usually based on dipolar forces[93] or steric interactions.[94] Priest[95] and, most recently, Goossens[36] have proposed other models, none of which relate to molecular structure. These will therefore not be discussed in this context.

The models of McMillan[93a] (dipolar) and Wulf[94] (steric) both rely on a

freezing out of molecular rotations as the liquid crystal enters the tilted phase. NMR and neutron diffraction data, which show that there is no freezing out of molecular rotations in the C phase, put these models in serious doubt. Moreover, any model based mainly on steric interactions may be disregarded because no tilted structures are found in liquid crystals built of weakly polar molecules. The general opinion consequently converges on a model based on polar interactions.

In this respect, the models of Cabib and Benguigui[93b] and of van der Meer and Vertogen[93c] are the most elaborate. Both allow a free molecular rotation and they fit fairly well with experimental data. The nature of the polar interactions is however quite different in the two proposed models. Cabib's and Benguigui's model is based on interactions between longitudinal dipoles of neighbouring molecules whereas the van der Meer-Vertogen model relies on transverse dipole-induced dipole interactions.

It is difficult to distinguish the models experimentally since all polar molecules neccessarily have both transverse and longitudinal dipoles. Furthermore, it is an intricate task to pin down the effect of either transverse or longitudinal dipoles since they are usually cross-conjugated through the aromatic π-system. Nevertheless, bearing in mind that compounds featuring benzene rings with electron-withdrawing and/or -donating substituents, such as carbonyl- or alkoxy-groups, quite often exhibit C phases, the role of longitudinal dipole moments seems rather important (*cf. Fig. 29*). Furtheremore, chain branching is generally believed to aid tilting and this has recently, most effectively, been shown by Coates.[96]

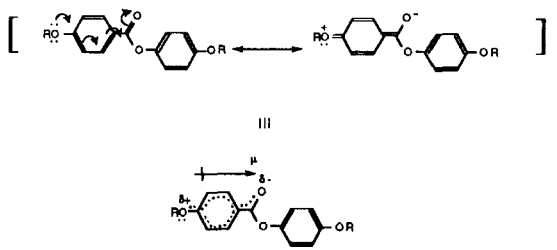


FIGURE 29. π-electron delocalization resulting in a strong longitudinal dipole moment.

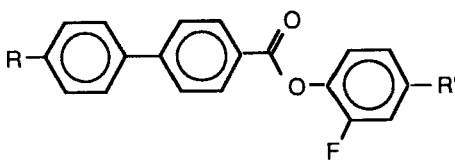
We may then try to summarize our current understanding concerning the molecular features important for the tilt process.

- A large polarizable core system; at least two conjugated or cross-conjugated aromatic rings
- Electron-donating and/or electron-withdrawing groups directly attached to the aromatic π-system, ensuring a strong longitudinal dipole
- Sufficiently long alkyl/alkoxy chains of comparable lengths[97] giving a fairly symmetrical gross molecular shape
- Branched alkyl chains

Phase stability

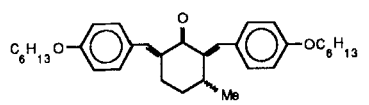
Due to its combination of simplicity and speed the smectic C* phase has so far been the prime candidate for FLC applications. The more highly ordered chiral smectic phases, especially the F* and I* phases, are also interesting and they may well be suited for applications, especially when bistability is more important than speed.

Of prime interest for devices is the temperature range of the FLC material. A broad range around ambient temperature is only found in a few cases for a pure compound, for example in the previously discussed MORA-series[62] and in some laterally fluorine-substituted compounds (**22**).[98] The higher order phases are effectively suppressed in these compounds and thus only the C phase appears. Some aspects of hydrogen bonding have been discussed to account for the high preponderance for the C phase of compounds **1** but the role of fluorine in compounds **22** has not been evaluated. Even if the MORA-compounds show a remarkably high stability of the C* phase occurring around room temperature, they are not convenient for use in electro-optical applications. This is due to the peculiar behaviour of these compounds: the surface interactions seem quite polar and the molecules are probably also subjected to electrochemical reactions when high electrical fields are applied. On the other hand, fluorine substitution may be a powerful tool in producing materials exhibiting broad C ranges.

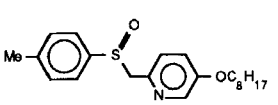


22

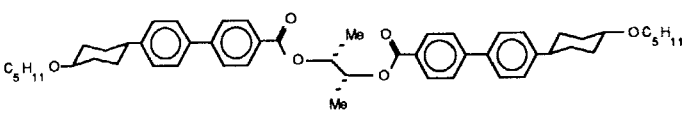
Previously we concluded that stereo-polar side chains are important in the search for compounds with high polarization and we have reasons to believe that dipoles in the core are not as important in the dipolar order process. However, we draw these conclusions from cases in which the cores are polar but non-chiral and we still lack the piece concerning stereo-polar cores. There are very few studies made in this context and no ferroelectric liquid crystal with a stereo-polar core has been reported. Pavel *et al.*[99] have studied the polarization inducing power of the chiral cyclohexanone derivative, **23**, (with a monotropic N* phase) which was found to induce a polarization of about 1 nC/cm^2 in bis-decyloxyazoxy-benzene (20% dopant). Other attempts are being made to evaluate the significance of stereo-polar cores but, so far, they have been unsuccessful.[89] The chiral but non-liquid crystalline sulfoxide **24** has been tentatively examined but definite results are still pending. The compound **25**, derived from (*R,R*)-2,3-butanediol,[100] might also be subject to investigations in this context.



23



24



25

Conclusions and outlook

The synthetic chemistry and the physical chemistry of ferroelectric liquid crystals are progressing rapidly. The development has taken place during a

very short time only, but three major companies, Chisso, BDH and Merck (in starting order) have now made major efforts and contributed considerably to (the still little) what we know today. Hoechst, Roche and other companies are following. That we are nevertheless near the starting point in some respects can be judged from the simple fact that even today quite a share of the industrial R&D is taking place using single compounds - something that would be inimaginable in nematic device engineering.

Acknowledgments. The authors would like to acknowledge the support from the National Swedish Board for Technical Development and from the Swedish National Research Council.

REFERENCES

1. J. Valasek, *Phys. Rev.* **17** 475 (1921)
2. R.B. Meyer, L. Liébert, L. Strzelecki, and P. Keller, *J. Physique (Lett.)* **36** L-69 (1975)
3. J. Doucet, P. Keller, A.M. Levelut, and P. Porquet, *J. Physique* **39** 548 (1978); J. Billard, A. Dahlgren, K. Flatischler, S.T. Lagerwall, and B. Otterholm, *J. Physique* **46** 1241 (1985)
4. W. Helfrich and C.S. Oh, *Mol. Cryst. Liq. Cryst.* **14** 289 (1971); J.A. Castellano, C.S. Oh, and M.T. McCaffrey, *Mol. Cryst. Liq. Cryst.* **27** 417 (1973)
5. J. Grindlay, *An Introduction to the Phenomenological Theory of Ferroelectricity,* (Pergamon Press, Oxford, 1970).
6. R.B. Meyer, *Mol. Cryst. Liq. Cryst.* **40** 33 (1977)
7. L.A. Beresnev, V.A. Baikalov, L.M. Blinov, E.P. Pozhidaev, and G.V. Purvanetskas, *JETP Lett.* **33** 536 (1981)
8. H.R. Brand,P.E. Cladis,and P.L. Finn, *Phys. Rev.A* **31** 361 (1985)
9. N.A. Clark and S.T. Lagerwall, *Appl. Phys. Lett.* **36** 899 (1980)
10. A. Stieb, cited in Ref. 60
11. N.A. Clark and S.T. Lagerwall, *Ferroelectrics* **59** 25 (1984)
12. R. Blinc and B. Zeks, *Phys. Rev.* A **18** 740 (1978)
13. B. Zeks, *Mol. Cryst. Liq. Cryst.* **114** 259 (1984)

14. L.G. Benguigui, *Ferroelectrics* **58** 269 (1984)
15. W. Kuczynski, S.T. Lagerwall, and B. Stebler, submitted to *Phys. Rev. Lett.*
16. N.A. Clark and S.T. Lagerwall, in *Recent Developments in Condensed Matter Physics,* vol. 4, p. 309 (Plenum Publishing Corporation, 1981, Eds. J T. Devreese, L.F. Lemmens, V.E. van Doren, and J. van Royen)
17. S. Meiboom and R.C. Hewitt, *Phys. Rev. Lett.* **34** 1146 (1975)
18. E.P. Pozhidayev, L.M. Blinov, L.A. Beresnev, and V.V. Belyayev, *Mol. Cryst. Liq. Cryst.* **124** 359 (1985)
19. Earlier results were reported in Ref. 18. The measurements referred to now (Blinov, Beresnev, Baikalov, Pozhidayev) were reported in the oral presentation by Prof. Blinov at this conference. We are grateful to him for the permission to use these remarkable graphs in our discussion
20. S. Garoff and R.B. Meyer, *Phys. Rev. Lett.* **38** 848 (1977)
21. G. Andersson, I. Dahl, P. Keller, W. Kuczynski, S.T. Lagerwall, K. Skarp, and B. Stebler, *Appl. Phys. Lett.* in press
22. T. Geelhaar, private communication
23. I. Dahl, S.T. Lagerwall, and K. Skarp, *Phys. Rev. A* in press
24. Xue Jiu-Zhi, M.A. Handschy, and N.A. Clark, *Ferroelectrics* **73** 305 (1987)
25. G. Durand, *e.g.* oral presentation at this conference
26. C. Rosenblatt, R.B. Meyer, R. Pindak, and N.A. Clark, *Phys. Rev. A* **21** 8140 (1980)
27. A.C. Diogo and A.F. Martins, *Liquid Crystals of One and Two Dimensional Order,* (Eds. W. Helfrich and G. Heppke, Springer Verlag, Berlin, 1980), p. 108.
28. M.A. Handschy and N A. Clark, *Ferroelectrics* **59** 69 (1984)
29. M. Odamura, S. Nonaka, K. Kondo, M. Isogai, and K. Anjyo, *Proceedings of the SID Meeting in San Diego,* 1985, p. 228
30. P.G. Amaya, M.A. Handschy, and N.A. Clark, *Optical Engineering* **23** 261 (1984)
31. L.M. Blinov and L.A. Beresnev, *Sov. Phys. Usp.* **27** 92 (1985)
32. C. Escher, T. Geelhaar, and E. Böhm, private communication
33. W. Kuczynski, *Ber. Bunsenges. Phys.Chem.* **85** 234 (1981)
34. J.E. Maclennan, M.A. Handschy, and N.A. Clark, *Phys. Rev. A* **34** 3554 (1986)
35. C.C. Huang and S. Dumrongrattana, *Phys. Rev. A* **34** 5020 (1986)
36. W.J.A. Goossens, *Liquid Crystals* **1** 521 (1986)

37. B. Zeks, A. Levstik, and R. Blinc, *J. Physique* **40** C3-409 (1979)
38. N. Éber, L. Bata, and A. Jakli, *Mol. Cryst. Liq. Cryst.* **142** 15 (1987)
39. S.T. Lagerwall, J. Wahl, and N.A. Clark, *Proc. IEEE Intl. Display Res. Conf. (San Diego)*, 213 (1985)
40. K. Yoshino amd collaborators, see for example their contribution to the Berkeley conference 1986, *Mol. Cryst. Liq. Cryst.* **144** (1987)
41. Manufactured by Displaytech Inc., PO Box 7246, Boulder, Colorado 80306, USA
42. B. Schäuble, private communication
43. Displaytech Inc., Boulder, *cf.* Ref. 41
44. See for instance T.D. Margerum, L.J. Miller, *J. Colloid and Interface Science* **58** 559 (1977) and G.R. Knight in S.H. Lee (ed.) *Optical Information Processing (Topics in Applied Physics)*, (Springer, Berlin, 1981), vol. 48, p. 111
45. T.E. Bell, *Special Report on Optical Computing, IEEE Spectrum*, August 1986
46. R.P Bocker, H.J. Caulfield, and K. Bromley, *Applied Optics*, **22** 804 (1983)
47. A.A. Sawchuk, in Ref. 45
48. M. Brunet, G. Andersson, and S.T. Lagerwall, this conference
49. K. Iwasa, private communication
50. T.P. Rieker, N.A. Clark, G.S. Smith, D.S. Parmar, E.B. Sirota, and C.R. Safinya, *Phys. Rev. A*, in press
51. N.A. Clark and T.P. Rieker, *Phys Rev. Lett.*, in press
52. N.A. Clark, *Phys. Rev. Lett.* **55** 292 (1985)
53. J. Wahl, T. Matuszcyk, and S.T. Lagerwall, *Mol. Cryst. Liq. Cryst.* **146** 143 (1987)
54. W.A. Crossland, private communication
55. C.M. Waters, B.J. Green, P.H. Surguy, D.J. Gibbons, and J.H. Smith, paper presented at this conference
56. A. Michelson, L. Bengiugui, and D. Cabib, *Phys. Rev. A* **16** 394 (1977); M.A. Osipov, *Ferroelectrics* **58** 305 (1984); L.A. Beresnev, E.P. Pozhidayev, and L.M. Blinov, *Ferroelectrics* **59** 1 (1984); M. Nakagawa, *Mol. Cryst. Liq. Cryst.* **130** 349 (1985)
57. L.A. Beresnev and L.M. Blinov, *Ferroelectrics* **33** 129 (1981)
58. S.T. Lagerwall and I. Dahl, *Mol. Cryst. Liq. Cryst.* **114** 151 (1984)
59. J. Seliger, R. Osredkar, V. Zagar, and R. Blinc, *Phys. Rev. Lett.* **38** 411 (1977)
60. C. Escher, *Kontakte (Merck)* (2) 3 (1986)

61. D.M. Walba, S.C. Slater, W.N. Thurmes, N.A. Clark, M.A. Handschy, and F. Supon, *J. Am. Chem. Soc.* **108** 5210 (1986)
62. B. Otterholm. M. Nilsson, S.T. Lagerwall, and K. Skarp, submitted to *Liquid Crystals*
63. D.M. Walba, R.T Vohra, N.A. Clark, M.A. Handschy, J. Xue, D.S. Parmar, S.T. Lagerwall, and K. Skarp, *J. Am. Chem. Soc.* **108** 7424 (1986)
64. R. Bartolino, J. Doucet, and G. Durand, *Ann. Phys. (Paris)* **3** 389 (1978)
65. J.W. Goodby and E. Chin, *J. Am. Chem. Soc.* **108** 4736 (1986)
66. J.W. Goodby, E. Chin, T.M. Leslie, J.M. Geary, and J.S. Patel, *J. Am. Chem. Soc.* **108** 4729 (1986)
67. M.F. Bone, D. Coates, and A.B. Davey, *Mol. Cryst. Liq. Cryst. (Lett.)* **102** 331 (1984)
68. N. Mikami, R. Higuchi, T. Sakuari, M. Ozaki, and K. Yoshino, *Jpn. J. Appl. Phys.* **25** L833 (1986)
69. Chalmers Liquid Crystal Group, unpublished
70. K. Skarp and G. Andersson, *Ferroelectrics (Lett.)* **6** 67 (1986)
71. K. Skarp, I. Dahl, S.T. Lagerwall, and B. Stebler, *Mol. Cryst. Liq. Cryst.* **114** 283 (1984)
72. S. Hattori, K. Kondo, T. Kitamura, Y. Hanawa, A. Mukoh, and T. Nakata, *Eur. Pat.* **163 229 A2** (1985)
73. K. Kondo, S. Era, M. Isogai, and A. Mukoh, *Jpn. J. Appl. Phys.* **24** 1389 (1985)
74. T. Kitamura, A. Mukoh, M. Isogai, T. Inukai, K. Furukawa, and T. Terashima, *Mol. Cryst. Liq. Cryst.* **136** 167 (1986)
75. M. Isogai, S. Hattori, K. Iwasaki, K. Kitamura, T. Inukai, K. Furukawa, S. Saito, and K. Terashima, *Eur. Pat.* **110 299 A2** (1984)
76. B. Otterholm, C. Alstermark, K. Flatischler, A. Dahlgren, S.T. Lagerwall, and K. Skarp, *Mol. Cryst. Liq. Cryst.* **146** 189 (1987)
77. K. Yoshino, M. Ozaki, T. Sakurai, K. Sakamoto, and M. Honma, *Jpn. J. Appl. Phys.* **23** L175 (1984)
78. J. Dale, *"Stereochemistry and Conformational Analysis"*, p. 85 (Universitetsförlaget, Oslo, 1978)
79. M.F. Bone, D. Coates, G.W. Gray, D. Lacey, K.J. Toyne, and D.J. Young, *Mol. Cryst. Liq. Cryst. (Lett.)* **3** 189 (1986)
80. T. Sakurai, N. Mikami, M. Ozaki, and K. Yoshino, *J. Chem. Phys.* **85** 585 (1986)
81. J. Wahl and S.C. Jain, *Ferroelectrics* **59** 161 (1984)

82. G. Andersson, I. Dahl, S.T. Lagerwall, and K. Skarp, *Mol. Cryst. Liq. Cryst.* **144** 105 (1987)
83. a. K. Yoshino, S. Kishio, M. Ozaki, T. Sakurai, N. Mikami, R. Higuchi, and M. Honma, *Jpn. J. Appl. Phys.* **25** L416 (1986); b. T. Sakurai, N. Mikami, R. Huguchi, M. Honma, M. Ozaki, and K. Yoshino, *J. Chem. Soc. Chem. Commun.* 978 (1986)
84. K. Yoshino, M. Ozaki, S. Kishio, T. Sakurai, N. Mikami, R. Higuchi, and M. Honma, *Mol. Cryst. Liq. Cryst.* **144** 87 (1987)
85. T. Geelhaar, C. Escher, and E. Böhm, 17. *Freiburger Arbeitstagung Flüssigkristalle,* 1987
86. K. Mohr, S. Köhler, K. Worm, G. Pelzl, S. Diele, H. Zaschke, D. Demus, G. Andersson, I. Dahl, W. Kuczynski, S.T. Lagerwall, K. Skarp, and B. Stebler, *Mol. Cryst. Liq. Cryst.* **146** 151 (1987)
87. Ch. Bahr and G. Heppke, *Mol. Cryst. Liq. Cryst. (Lett.)* **4** 31 (1986)
88. L. Kryger, S.E. Rasmussen, and J. Danielsen, *Acta Chem. Scand.* **26** 2339 (1972); T.J. King, M.R. Harnden, and N.D. Wright, J. *Chem. Research (S)* 6 (1978)
89. B. Otterholm, *Dissertation,* Chalmers University of Technology, Göteborg, 1987
90. A.F. Martins, private communication
91. M.A. Osman, private communication
92. K. Flatischler, K. Skarp, S.T. Lagerwall, and B. Stebler, *Mol. Cryst. Liq. Cryst.* **131** 21 (1985)
93. a. W.L. McMillan, *Phys. Rev. A* **8** 1921 (1973); b. D. Cabib and L. Benguigui, *J. Physique* **38** 419 (1977); c. B.W. van der Meer and G. Vertogen, *J. Physique (Coll.)* **40** C3-222 (1979)
94. A. Wulf, *Phys. Rev. A.* **11** 365 (1975)
95. R.G. Priest, *J. Chem. Phys.* **65** 408 (1976)
96. D. Coates, *Liquid Crystals* **2** 63 (1987)
97. See for example J.W. Goodby and G.W. Gray, *J. Physique (Coll.)* **37** C3-17 (1976); see also Fig. 3 of Ref. 61
98. G.W. Gray, private communication
99. J. Pavel, M. Glogarova, D. Demus, A. Mädicke, and G. Pelzl, *Crystal Res. & Technol.* **18** 915 (1983)
100. R. Diehl, G. Heppke, and F. Oestreicher, *10th International Liquid Crystal Conference,* 15-21 July, 1984 York, U.K.