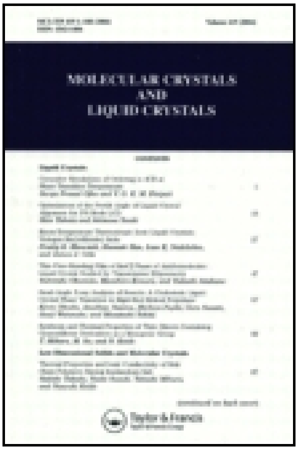

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Direction of the Polarization P on the Bounding Surfaces of Chiral Smectic C Samples

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DIRECTION OF THE POLARIZATION P ON THE BOUNDING SURFACES OF CHIRAL SMECTIC C SAMPLES

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A ferroelectric liquid crystal should have an intrinsic tendency to direct its local polarization vector P towards or away form a bounding surface. This, in principle, leads to an undesired splay inhomogeneity in ferroelectric optic cells. The direction has previously been determined in one case, by Glogarova and Pavel, to be away from the surface. We have found, for two different materials at the same surface, that the tendency is opposite in the two cases. Thereby the possibility exists to achieve an essentially non-polar interaction by mixing, in order to avoid the splay. If the sign of P is known for the material, an optical observation is sufficient for the surface polarity determination. This means that there is even no need for an electric field, which simplifies the method.

Little is known about the polar interaction between a ferroelectric liquid crystal and its confining surfaces, except that it may easily be strong enough to oppose the creation of homogeneously polarized device states. Even in fairly thin cells where surface alignment forces have elastically unwound the helix characteristic of the C* ground state, a kind of splay-twist state tends to persist due to a remaining polar anchoring interaction. This generally gives a complicated threshold behaviour to an electro-optic cell and slows down its dynamics. The achievement of the highest possible switching speeds in ferroelectric liquid crystals thus necessitates the study of surface polarization phenomena, which is the subject of this article.

With a convenient surface treatment a chiral smectic C sample can be brought into the so-called bookshelf geometry with the smectic layers running essentially perpendicular to the confining glass plates. In very thick samples (d >> Z) - typically 20 to 50 μm; however the thickness has to be chosen with regard to the C* pitch Z of the material used - the bulk with its characteristic helix will dominate the structure in the following sense. If we shine a ray of laser light through the cell, a distinct diffraction pattern will disclose an undisturbed helicoidal structure and, with some care, a correct measurement of Z may be made. Visibly, however, e.g in a microscope, the structure may be dominated by the surface, inducing a periodic pattern of defect lines. These lines, often called "fringe lines" have almost universally been misinterpreted as being the helix seen from the side (i.e. the index variations caused by the twisting director) and an even more surprising fact is that the same misinterpretation is so widespread despite the analogous experience from decades of work on cholesterics.

At the other end, for very thin cells, the surfaces dominate in all respects and now give an entirely different appearence : the sample may be smooth and defect-free because the helix is absent (unwound). The chirality can, in this case, only be deferred from the ferroelectric response and the possibility of ferroelectric domains.

In intermediate cases (as well as in thick cells) there will be non-helical regions near the surfaces and a helical region in the middle. These regions will be connected, as was first shown by Brunet and Williams[1] by certain localized patterns of defect lines with regular spacings. The lines (which are ± 2π twist disclinations) have been called "dechiralization lines" but should, more properly, be named "unwinding lines", because the chirality of the material stays the same, regardless of any unwinding phenomenon.

STRUCTURES IN THE FIELD-FREE CASE

In the absence of an applied electric field and with a planar director anchoring-condition the two n directions (1) and (2) in figure 1 are essentially equivalent energetically as long as the interaction between liquid crystal and glass surface can

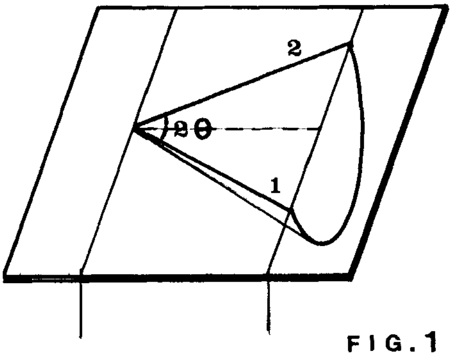


FIG. 1

Fig. 1 The smectic C tilt cone cut by the bounding surface in the case of non-tilted smectic layers. The two directions 1 and 2 are the cone states selected by a degenerate planar anchoring condition.

be considered as non-polar. The local macroscopic polarization **P** is rigidly coupled to the local director n, and for a material of positive sign (P > 0) the **n** direction (1) corresponds to a **P** vector pointing downwards (into the liquid crystal)[8] whereas (2) corresponds to **P** pointing upwards (toward the glass). For a negative material (P < 0) the opposite holds true. When the surface interaction grows increasingly polar, (1) and (2), in any case, become increasingly non-equivalent and, even in treating the simplest electro-optic cell where the liquid crystal is bounded by two identical surfaces (glass, polymer, etc... with identical coating) we will have to consider a number of different cell structures. It will be convenient to distinguish between thin and thick cells.

In a thin sample the gain in polar surface energy cannot, in general, match the increase in electric and elastic energy caused by large inhomogeneities in the **n** and **P** fields. For a sufficently thin cell these deformation energies will dominate and force the director to attain the same state throughout the cell. This will then hold, also, for the polarization (div **P** = 0), and we shall call a visible region with such a state (fig. 2a) a "polarized domain". Although depending on material, such domains are fairly typical for a cell thickness of 1 to 3 μm. In somewhat thicker cells the polar surface condition might predominate and instead

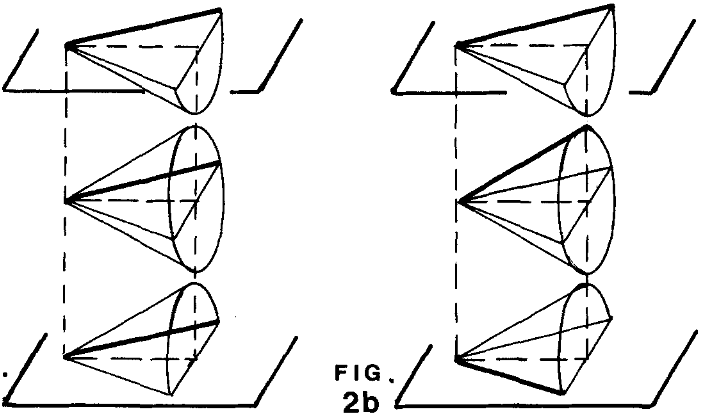


FIG. 2a **FIG. 2b**

Fig.2 Simplified director configuration in a polarized domain (a) and in a splay domain (b).

optimize for the preferred polar anchoring at both surfaces (figure 2b). Now from the lower to the upper glass plate the molecules turn azimutally by π over the smectic tilt cone, corresponding to an angular change of 2 θ in the projection plane. This involves a splay deformation in the P field between the confining plates, (div $\mathbf{P} \neq 0$) and we shall call a visible region with such a state a "splay domain". Such splay states have been identified by Handschy, Clark and Lagerwall[3] and, independently by Glogarova and Pavel[4].

In thick samples the situation is substantially different because of the helicoïdal arrangement that persists in the bulk and the presence of unwinding lines which join untwisted and twisted smectic regions. If the molecules have the same direction on the lower and the upper glass plates (this requires strong directional anchoring), then the unwinding lines will appear symmetrically as doubles lines near the top and bottom according to the pattern of figure 3a ("superimposed lines"). The distance between consecutive superimposed lines is equal to the smectic pitch Z, but the lines themselves must not be mistaken for the helical pitch periodicity. Strong directional anchoring may be obtained by SiO evaporation or by rubbing and is efficient in connection with low-P materials and, particularly, with θ = 45° materials, because the cone directions are maximum apart

(90°) from each other in that case. Both conditions were, in fact, fulfilled in the Brunet and Williams study[1]. For small cone angles the surface conditions will more often be different, giving rise to a pattern of simple lines according to figure 3b, first studied by Glogarova and Pavel[3]. It should be noted that the distance between these "shifted lines" is only half the pitch, or Z/2.

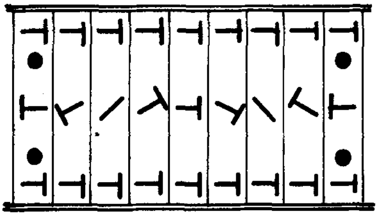


FIG.3a

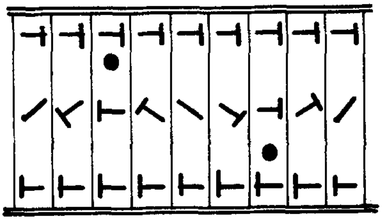


FIG.3b

Fig.3 Regular disclination pattern in superimposed line (a) and shifted line (b) configuration, corresponding to same (a) and different (b) cone state at top and bottom. These are the thick cell structure analogs to figure 2 (a) and (b).

STRUCTURES AND DOMAINS IN THE PRESENCE OF AN APPLIED ELECTRIC FIELD

The important study of structure changes in a chiral smectic C sample, as a function of cell thickness and of applied electric field, was initiated by the Prague group in 1983[2] and followed up in a series of very careful papers[4-7]. In particular the mechanism for the field induced transition from helicoïdal to unwound smectic C* structure was elucidated and the different transition thresholds calculated. The results are most readily described with reference to figure 3b. If a DC electric field is applied across a sample which is sufficiently thick (~ 50 µm) to allow an easy focalization near the upper and lower glass plates, and thereby an observation of the individual unwinding lines, the following sequence of events is observed in the microscope. With a starting configuration as in the figure and with a positive polarity applied to the upper electrode, an increasing field will move the right and lower disclination toward the left one indicating that more and more molecules are turning over into the upper direction. This means that, for the molecules in question (DOBAMBC) the polarization is pointing downwards at the top of the cell, and hence upwards at the bottom. Such observations permitted Glogarova and Pavel[4] to conclude, for the first time, that there was a spontaneous tendency for the polarization to point inwards, into the liquid crystal, at bounding surfaces, at least for the studied material combination together with glass, coated with SnO_2 and washed with acetone. A different material made by doping a non-chiral smectic C with a cholesteric showed the same behaviour. The question then arises whether this is a general feature or not. If yes, the only way to get rid of the splay state is to suppress it by making very thin cells. If no, the surface anchoring may be made non-polar by mixing substances of opposite preferences.

On further increasing the field the lower line moves in under the upper line so that the two become superimposed. At the same time the upper line together with the region of deformed helix have moved downwards, making the picture much less symmetric than that of figure 3a and building up a concentration of elastic deformation towards the bottom. The lines will eventually annihilate by forming closed loops and shrinking, leaving an unsymmectric splay state with no singularities, similar to the one in figure 2b, except that the "neutral state" where P is horizontal (neither up nor down) is not in the middle but near the bottom.

A still further field increase will switch some of the molecules next to the bottom surface : small irregular domains appear, which can be made dark between crossed polarizers. These are polarized domains bounded by new surface disclinations of strength ± π. As Glogarova and Pavel point out it is sometimes (in highly twisted materials) hard to conclude with certainty which of the two line families, the top or the bottom one, is caused to move by the electric field. They therefore base their determination of polarity on whether the polarized domains appear on the top or on the bottom glass slide, which is easier to observe. We will adopt their method as well as using a different entirely optical one, in the following.

EXPERIMENTAL CONDITIONS

Our sample is wedge-shaped, the thickness d going from 2 µm to 36 µm. This means that we have, at the same time, the conditions of a thin and a thick sample.

The optical observations were made in a Leitz Ortolux microscope. The applied electric field varies from zero to about 60 kV/cm or 6 V/µm. The values correspond to an average thickness of 20µm.

Two different materials were used in this study. The first one is the common S-form of DOBAMBC (S- decyloxy-benzylidene-p'-amino-2- methyl-butylcinnamate) mixed with an equal part of its racemic in order to increase the C* pitch to about 10 µm. The observations were made at about 70°C. The sign of the polarization in (S)- DOBAMBC is negative[8], which means that the P vector is antiparallel to the cross product of smectic layer normal **z** and director **n** ($\mathbf{P} = P_0\, \mathbf{z} \times \mathbf{n}$). The second material is the mixture CS-1011 from Chisso Corporation with a room-temperature C* phase and a pitch of 5 µm. Its polarization sign is likewise negative. The sign of P is today an indispensable part of the characterization of a substance and easily and routinely measured by observing the switching motion of the n axis caused by an electric field. It is also found in the investigation method of Glogarova and Pavel.

OPTICAL OBSERVATIONS ON DOBAMBC/ITO

The wedge-shape sample allows for a slighty different observation technique than in reference 4, because splay domains and disclinated domains can be formed simultaneously at different parts of the sample. A splay domain, occurring typically at a thickness of 5 to 7 µm, can be considered as a Mauguin piling for which the twist wavelength (twice the thickness) is large in comparison with the wavelength of light. If, therefore, the direction of vibration of the incoming light is made parallel to the optic axis at the bottom of the cell - by the setting of the polarizer - the transmitted vibration will stay almost rectilinear and will follow adiabatically the twist of the long axis of the molecule across the sample. The upper position of the optic axis will then be found by setting the analyzer to extinction. If the sign of P is known - which is almost always the case - this simple observation is in fact sufficient to determine the surface polarity.

The best extinction is obtained when the observation is made in the area between two shifted lines, because this is an area of uniform splay-twist, and the Mauguin condition is very well fulfilled at the higher thickness. The Mauguin condition is always less well fulfilled in the presence of an electric field because of the concentration of the twist to the top or bottom in that case.

For DOBAMBC in contact with indium tin oxyde coated glass (only washed with acetone) our observations can be described as follows. After choosing an area between shifted lines and after setting polarizer and analyzer to extinction position in the n_1 and n_2 directions, respectively, corresponding to optic axes at bottom and top, we observe that the analyzer makes an angle of 70° clockwise to the polarizer (figure 4). This gives the n_2 direction at the top, confirming the full cone angle to

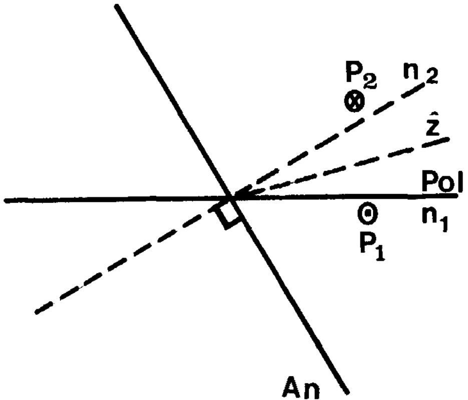


FIG 4

Fig.4 Finding the surface polarity from the sense of director twist in a twist-splay configuration.

be 20°, corresponding to a tilt angle θ of 10° With z lying between $n_1$and n_2, the polarization directions are easily obtained as $-z\mathrm{x}\mathbf{n}_1$ and $-z\mathrm{x}\mathbf{n}_2$ pointing upwards and downwards, respectively, and indicated in the figure (P_1 and P_2). The direction of P is thus towards the bulk of the liquid crystal.

Application of an electic field gives independent confirmation of this (because the sign of P does not have to be known) and fully confirms the results of Glogarova and Pavel : at about 2kV/cm the shifted lines become superimposed and disappear ; at about 6 kV/cm white domains appear against the dark background. If the DC field is applied from top to bottom the domain boundaries can be focalized to the bottom glass slide. On turning the polarizer -not the analyzer- from 70° to a crossed position, these domains turn dark, showing that the director at the lower surface has switched to the majority direction.

When the field is decreased, splay domains reappear and grow through the whole sample ; finally the unwinding lines are recreated. They are first superimposed, and when the field is back to zero they are back again in the shifted position. The successive events in both directions (although in reality not quite reversible, cf the figure caption) are sketched in a kind of shorthand in figure 5, the analyzer-polarizer settings are given in figure 6.

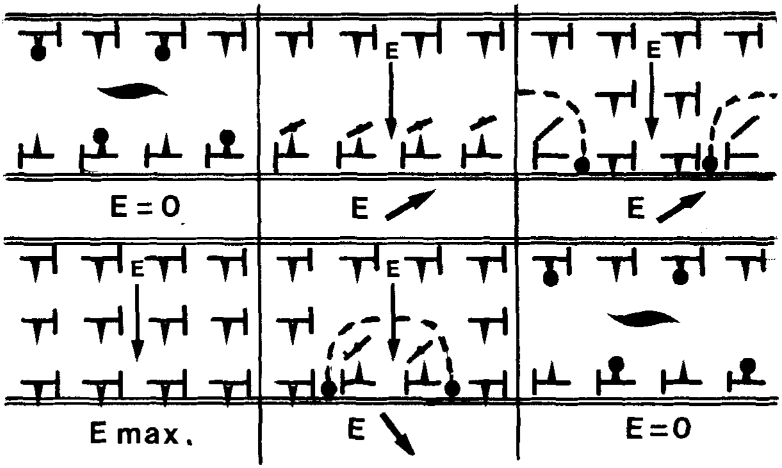


FIG. 5

Fig.5 Symbolic description of events on increasing and decreasing the applied electric field in the case of DOBAMBC/ITO. The splay domains without helix (second frame) appear at about 2kV/cm, the polarized domains (third frame) at about 6kV/cm. The reverse domains (fifth frame) appear after decreasing the field to about 1kV/cm. The horizontal helix is indicated in the first and last frame.

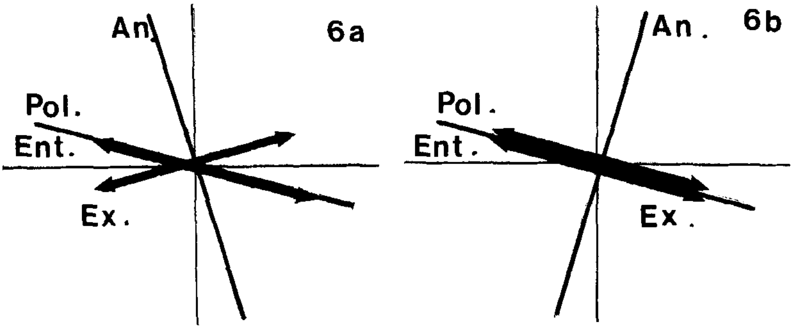


Fig.6 Polarizer-analyzer settings for DOBAMBC/ITO, at zero field (a) and at high field (b).

OBSERVATIONS ON DOBAMBC/SiO

Except that now the ITO conductive layer has been coated with an insulating and aligning sheet of SiO the experimental conditions were the same. The SiO was evaporated onto the glass slide under an angle of 60° to the surface normal, a standard method for facilitating a planar alignment. The observations give a similar but somewhat different result compared with the previous case. In the absence of an electric field the background is set to extinction when the polarizer makes an angle of 80° with the analyzer (instead of 70° in the ITO case). The result for the polarity of the surface is the same, with P pointing into the liquid crystal. The extinction angle ($\pi/2 - 2\theta$) = 80° gives an apparent tilt angle of 5°, half the previous value. This can be interpreted as a tilt of the smectic cone at least at the surface (cf. figure 7) eventually combined with a molecular pretilt, with a layer tilt or with both. Although these structure questions will not here be subject to further discussion, we will assume, in the following, that the molecules have at least a slight pretilt at the surface. Under a growing applied field the observations are qualitatively the same as before : the shifted lines become superimposed and disappear. The extinction is generally less good and the colour is changing progressively. A maximum of darkness can, however, always be obtained by turning

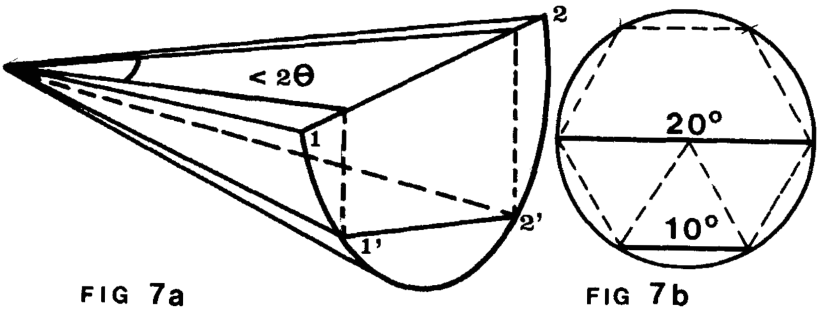


FIG 7a

FIG 7b

Fig.7 The effect of cone tilt on the apparent switching angle (a). In the actual case the states encompass half of the full cone angle (b) which permits the (approximate) illustrative construction of incribing the hexagon to simply arrive at all interesting angles. The half cone angle still gives a high optic contrast, and it is remarkable that a layer tilt of more than 90 per cent of the smectic tilt angle, as in the figure, would preserve good optic contrast as well as still fulfill the requirements of bistability even in the planar anchoring case.

polarizer and analyzer. When the field has being raised to about 50 kV/cm the maximum of darkness is obtained with an integral shift of 15° anticlockwise for the polarizer (Pol→Pol') and a shift of 5° for the analyzer in the same direction (An→An') as depicted in figure 8a. At this point the analyzer and polarizer are thus back to a crossed position indicating a homogeneously polarized state. The interpretation of this result is given in figure 8b and strengthens the assumption of cone tilt. A further element of support is given

FIG 8

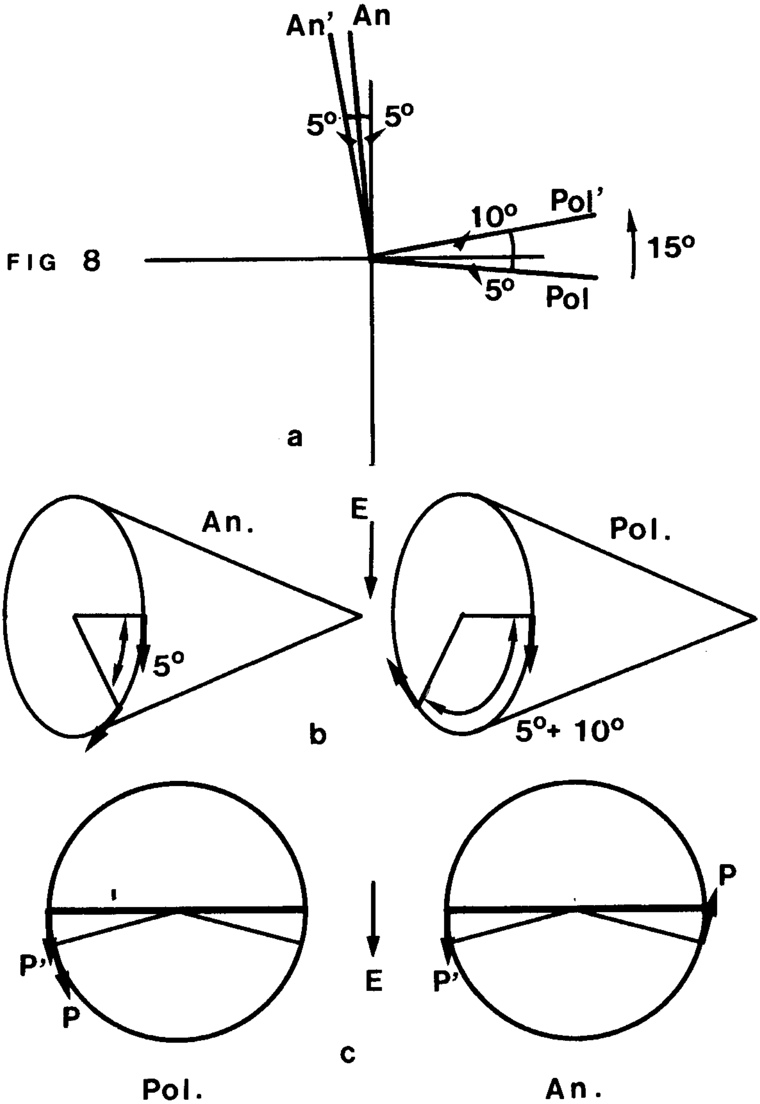


Fig.8 The extinction settings at low (An, Pol) and high (An', Pol') fields, in the case of DOBAMBC (a), together with the interpretation (b) as for the movements of the director on the smectic cone. The corresponding movements in the case of CS-1011 are found in (c).

by the irreversibility of the whole sequence which is illustrated in the shorthand of figure 9. In fact, during the first growth of the field up to 50 kV/cm no polarized domains appear. Only on diminishing the field again, the reverse domains appear (at the bottom with field down) at about 1 kV/cm. The reason for this different behaviour is that, with pretilt, the structure can continuously transform from P UP to P DOWN without any defect line involved. (This transformation

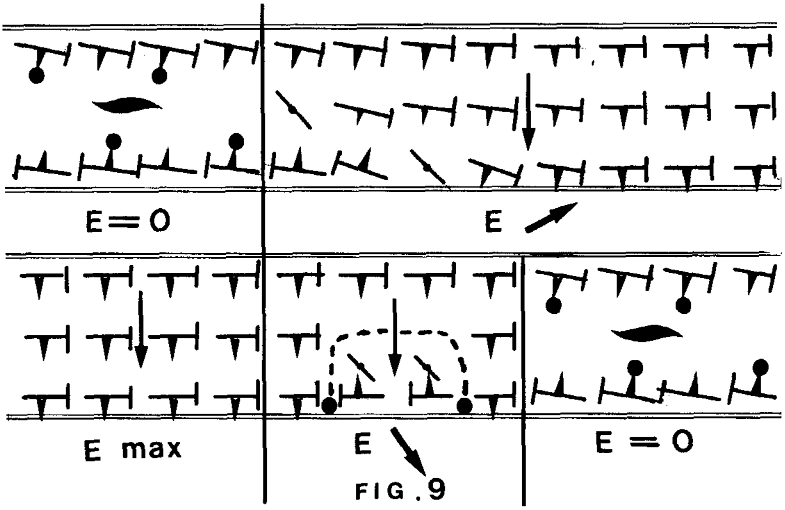


FIG. 9

Fig. 9 Symbolic description of events on increasing and decreasing the applied electric field in the case of DOBAMBC/SiO. The large second frame symbolizes the continuous color contrast change in the first increase from zero to 50 kV/cm, with no domains appearing : instead of molecules switching at the bottom, a continuous rotation over the cone takes place to the final homogeneous state. The situation in the third frame essentially stays until the field has been reduced to under 1 kV/cm. The molecular tilt reappears only at E = 0 in time is found in space in the defect-free region in the bulk between two shifted lines). After the application of the (still modest) field of 5 V/µm, the structure becomes planar (no pretilt) which can be seen in the fact that the measured angle between the bounding molecules attains its normal 2 θ value. When the field has finally been taken off the pretilt reappears. On the other hand, when recycling the whole process several times the planar stucture has a pronounced tendency to stay with the effect that polarized domains can now be observed even in the case of increasing electric field.

OBSERVATION ON CS-1011/SiO

In absence of an electric field the extinction position is now obtained with the analyzer setting 60° anticlockwise relative to the polarizer. This gives an apparent tilt angle of 15° instead of the true value of $\theta = 22°$. The anticlockwise direction (cf. figure 10) means that the polarization vector P is pointing upwards at the top slide and downwards at the bottom slide. The Chisso ferroelectric mixture CS-1011 thus prefers the opposite surface polarity than DOBAMBC in contact with the same surface.

The behaviour in an electric field (cf. figure 11) is fairly analogous to the previous case, with two differences. When

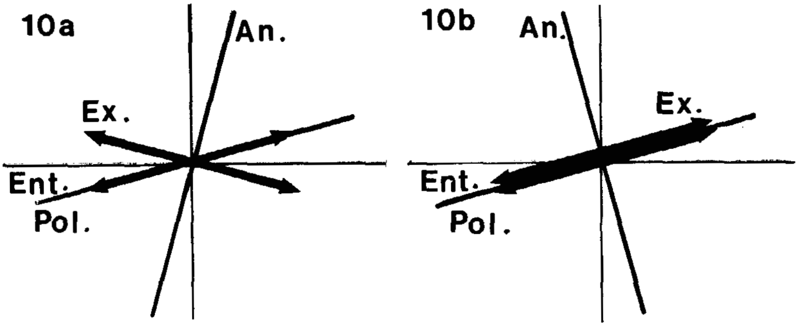


Fig. 10 Polarizer-analyzer settings for Chisso CS-1011/SiO, at zero field (a) and at high field (b).

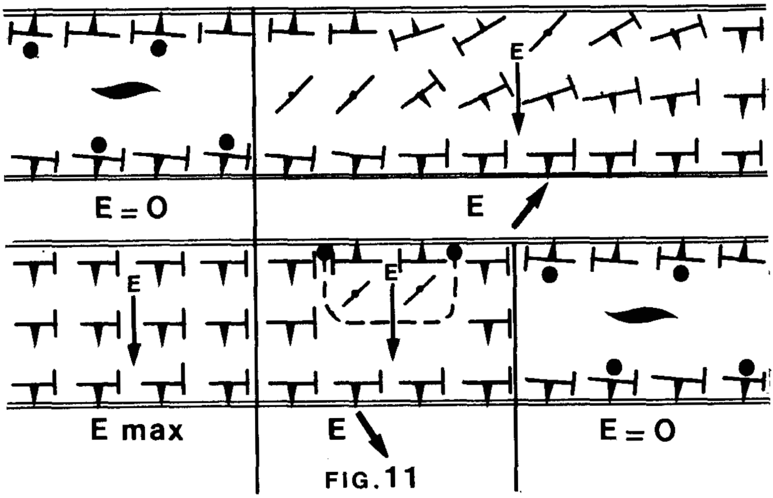


FIG. 11

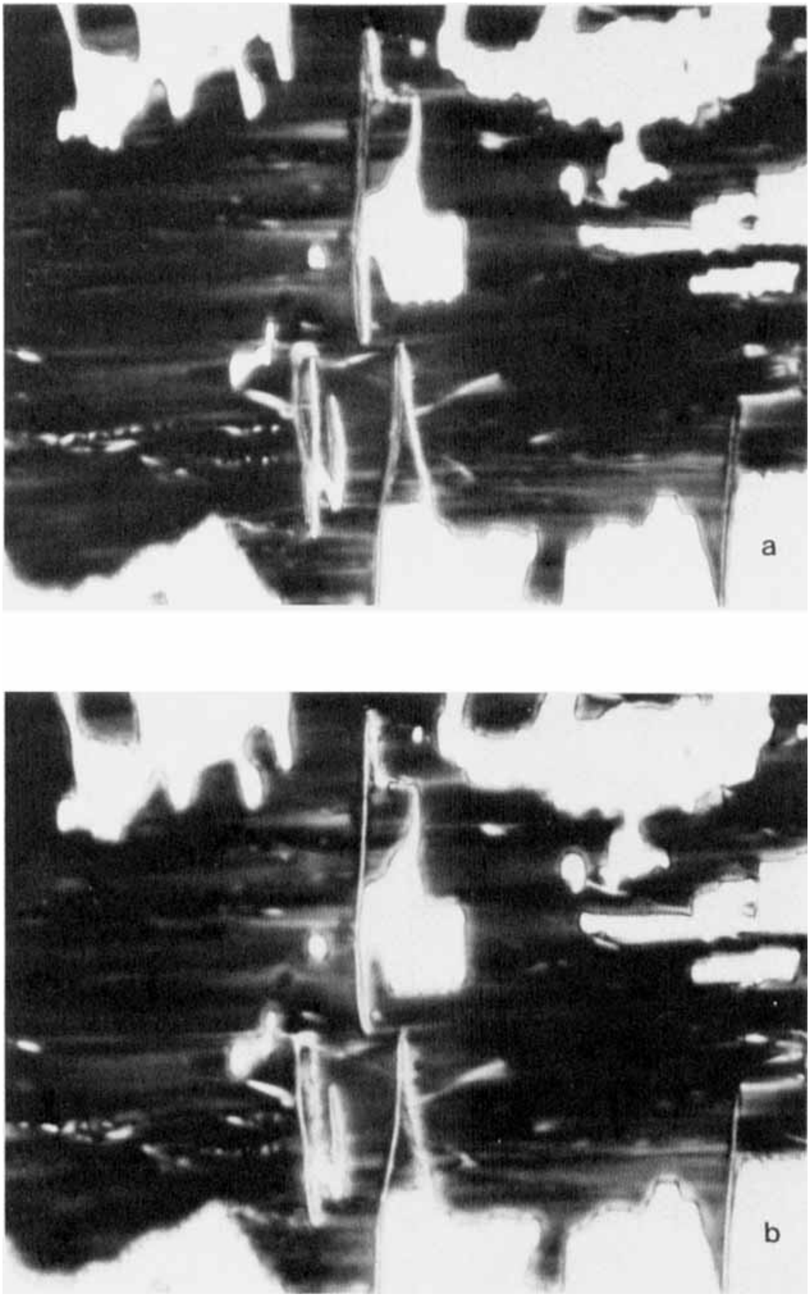
Fig. 11 Symbolic description of events anologous to figure 9, this time concerning Chisso CS-1011/SiO. The main difference is that the formation of reverse domains is observed to take place at the upper surface, not at the lower one.

the field is increased to 50kV/cm the maximum of darkness is obtained when the angle between the polarizers goes from 60° to 90°, but in this case mainly by turning the analyzer (30°). We interpret this with a fairly small cone tilt according to figure 8c. When the field is decreased, still directed from top to bottom, reverse domains appear, but now at the top, in contrast to the DOBAMBC case, confirming the polarity designation together with the negative sign of P. Typical micrographs of the reverse domains (white) are shown in figure 12 together with a sketch of the three-dimensional structure across the sample from the top to the bottom glass plate.

CONCLUSIONS

We have found two ferroelectric liquid crystal materials which have opposite preferences for their surface polarity in contact with the same surface. Hence there is the possibility of neutralizing the polar interaction, or at least diminishing its strengths, by choosing appropriate materials of opposite polar preference as mixing ingredients in compositions for electro-optic use. Such "neutral" compositions should greatly reduce the tendency of forming splay domains in SSFLC cells. The findings are symbolically summarized in figure 13.

If the sign of P is known for the material in question, which


a
b

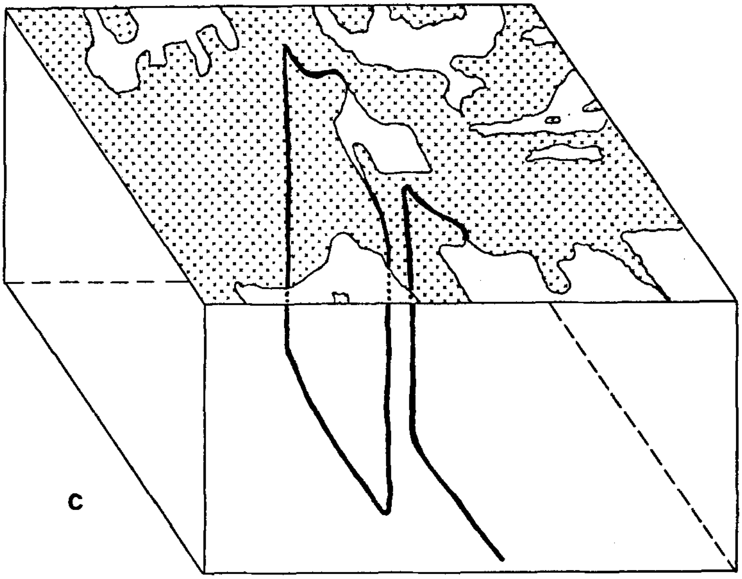


FIG 12

Fig.12 Observations of reverse domains (white) appearing at the top glass plate in the case of Chisso CS-1011. In the first micrograph (a) the microscope is focussed on the top plate making the boundary domains sharp. Focussing on the bottom plate (b) instead sharpens the bottom disclinations.

The structure is sketched in (c). The dark areas (polarized domains) have P directed everywhere away from the observer whereas P has switched towards the observer at the top in areas that are white (splay domains). The pictures have been taken at decreasing field, at about 1 kV/cm. The tickness of the section shown is about 10μm. See Color Plate I.

is normally the case, the surface polarity determination can be made already by an optical observation, without access to an electric field. This simplifies routine determinations, for instance for any given material in combination with a series of different surfaces.

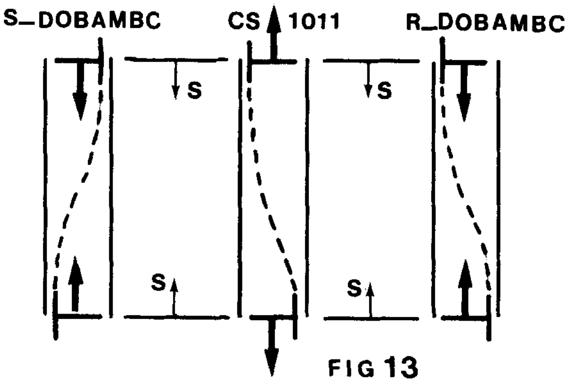


FIG 13

Fig. 13 Shorthand of the result of the study S-DOBAMBC and CS-1011. Both have P< 0 but opposite surface-polarity in contact with ITO/SiO. For a comparison the analogous situation in the case of R-DOBAMBC (the optic antipode) is shown. This substance has P > 0, thus a different steric connection between P and n, but has the same polar interaction with the surface as S-DOBAMBC. If we introduce the surface normal s to the bounding surface, then S-DOBAMBC has P and s parallel and CS-1011 has them antiparallel for this surface.

The polar surface interaction is a further element making the composition of ferroelectric cocktails much more complicated than in the nematic case. Because the sign of P (positive or negative) determines the steric connection with n, and because the vector **P** can be either parallel or antiparall to the surface normal **s**, or, more generally (because P may have an oblique direction), the scalar product **P**.**s** is either positive or negative, four principal **n**-**P**-**s** relations have to be distinguished, as shown in figure 14. These have to be

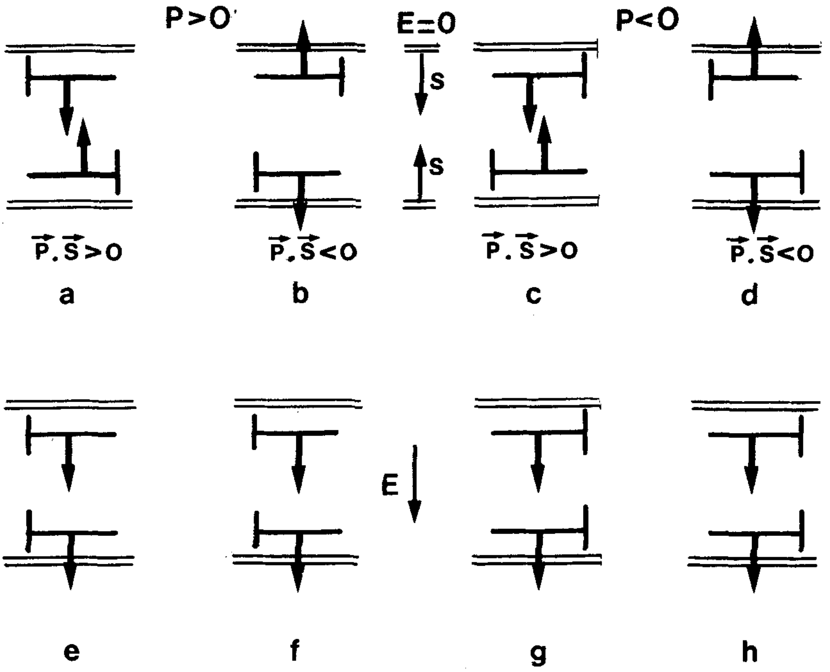


FIG 14

Fig. 14 Representation of all qualitative possibilities of n-P-s connections. For a positive substance (P > 0), P can be parallel or antiparallel to s as shown in (a) and (b). On application of a strong electric field the molecules flip on the lower surface in the first case, on the upper surface in the second case, cf. figures (e) and (f). The corresponding situations for a negative substance is shown in (c), (d) and (g), (h).

accounted for when preparing mixtures, which ideally should have a cancellation of the helix, of the splay, but not of the polarization. Of all the factors that are relevant, (±) q (cholesteric wave vector), (±) k (smectic C* wave vector) and (±) P are simple at least in the sense that they are material parameters - even if not generally additive - whereas the factor **P.s** describes an interaction between two materials, the interaction between a liquid crystal and a solid surface.

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