J. Am. Chem. Soc. **1986**, *108*, 4729–4735

Helical Twist Sense and Spontaneous Polarization Direction in Ferroelectric Smectic Liquid Crystals. 1

J. W. Goodby,* E. Chin, T. M. Leslie,† J. M. Geary, and J. S. Patel

Contribution from AT&T Bell Laboratories, Murray Hill, New Jersey 07974.

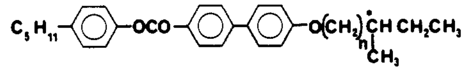
Received November 18, 1985

Abstract: Liquid-crystalline systems of optically active materials, unlike those of pure amorphous liquids or solutions of chiral materials, exhibit regular alternations for the signs of their optical rotations of plane polarized light. In a given homologous series, there is an alternation effect as the asymmetric center is moved incrementally along the terminal carbon skeleton away from the central aromatic core of the molecule. The rotation alternates dextro to levo as the chiral center is moved from one position to the next. Studies on cholesteric phases have related this behavior to the twist sense of the macroscopic helical ordering of the molecules in the phase, to the position of the chiral center within the molecular structure, and to the spatial configuration of the asymmetric center. This present investigation shows that a similar effect also occurs in helical ferroelectric smectic phases, but in this case there are more complex rules relating the above factors to the direction of the spontaneous polarization with respect to the tilt axis of the monoclinic phase, and to the electron distribution about the chiral center itself. General rules that relate these factors are developed which allow for the predictions of various optical and electrical properties to be made directly from the molecular structure of the smectogen in question. The twist sense of the helical ordering of the molecules is shown to have dipolar origins, and it is therefore sensitive to changes in the electron distribution about the asymmetric center. Similarly, the direction of the spontaneous polarization is also dependent on the lateral dipolar nature and orientation of the chiral center with respect to the long axis of the molecule. Thus variations in the original rules occur for smectics depending on the dipole direction at this center. These general rules also apply to the ferroelectric properties of smectic crystal modifications and to the helical properties in cholesterics.

(I) Introduction

(1) Optical Properties of Ferroelectric Liquid-Crystal Phases. Predictions of the sign and calculations of the magnitude of the specific rotation for optically active substances while in solution or liquid form have been demonstrated in detail.[1] Experimental methods, however, generally rely on the optically active compound being dissolved in an achiral medium, or used neat for a liquid, and the specific rotation [α] being measured at known molar concentrations and wavelengths of light.[2] Correlations of results for many materials show that there are no definitive rules for relating the absolute spatial configuration (*R* or *S*) to the sign of the specific optical rotation [α].

In liquid-crystalline systems, unlike those of liquid or solution chemistry, there are guidelines concerning the relationship between the sign of the optical rotation and the spatial configuration of the substance. In the cholesteric phase, for instance, the sign alternates from dextro (*d* or (+)) to levo (*l* or (−)), depending on the absolute configuration (*R* and *S*) and the position of the chiral center of the molecule related to its position in the overall molecular structure. Usually its position is determined by the minimum number of atoms it is removed from the aromatic ring structure of the central core of the compound. For example in the homologous series (I),[3] the asymmetric carbon atom is $n + 2$

(I) 

$C_5H_{11}-C_6H_4-OCO-C_6H_4-C_6H_4-O(CH_2)_n\overset{*}{C}H(CH_3)CH_2CH_3$

atoms from the core. As *n* is increased incrementally the sign of the specific optical rotation of the mesophase alternates from (+) to (−) giving rise to rules for cholesterics first defined by Gray and McDonnell,[3] as shown in Table I (note—there are some exceptions to these rules).

(2) Structures of Liquid-Crystalline Phases of Optically Active Materials. The reason for the odd–even alternation trend in cholesterics lies in the fact that the mesophase possesses a helical orientational ordering of its constituent molecules. This ordering is induced by the chirality of the material. The helix acts as a "guide" for incident plane-polarized light which is parallel to the helical axis. Thus, the rotation of plane-polarized light is dependent on the twist direction of the helix (provided its wavelength is not comparable to the pitch of the helix).[4] The twist direction of the helix alternates in a given homologous series as the chiral center is moved sequentially away from the core, hence the rotation direction of plane-polarized light also alternates in the same manner.

Table I

abs config	*n*	no. of atoms from the core[a]	rotation sign	helix sense
S	even (e)	even (e)	*d* (+)	LH
S	odd (o)	odd (o)	*l* (−)	RH
R	odd (o)	odd (o)	*d* (+)	LH
R	even (e)	even (e)	*l* (−)	RH

[a] The end of the core was originally defined as the C–C bond of the aromatic–aliphatic system.

A number of liquid-crystalline mesophases formed by optically active materials can possess helical distributions of their constituent molecules about a known axis. The structures of these phases, the cholesteric phase, and the ferroelectric smectic modifications C*, I*, and F* are shown in Figure 1.[5,6] In these phases the molecules have no long-range positional ordering, but they have long-range orientational order. There is no net spontaneous polarization in the bulk ferroelectric phases (C*, I*, and F*) because the local spontaneous polarization is averaged to zero by the helical structure of the phase, unless of course this structure is suppressed. For this reason it has been suggested that the term helielectric be used to described their properties.[7]

Another set of mesophases also exist where the molecules have long-range positional and orientational ordering; these modifications have been described as orientationally, disordered crystal, or smectoid phases[8,9] (see Figure 1). In these crystal phases, G*,

---

† Current address: Celanese Research Co., Summit, NJ 07910.

(1) Brewster, J. H. *J. Am. Chem. Soc.* **1959**, *81*, 5475, 5483, 5493.

(2) Orchin, M.; Kaplan, F.; Macomber, R. S.; Wilson, R. M.; Zimmer, H. *The Vocabulary of Organic Chemistry*; Wiley: New York, 1980; p 125.

(3) Gray, G. W.; McDonnell, D. G. *Mol. Cryst. Liq. Cryst. Lett.* **1977**, *34*, 211.

(4) Priestley, E. B. In *Introduction to Liquid Crystals*; Priestly, E. B., Wojtowicz, P. J., Sheng, Ping, Eds.; Plenum: New York, 1974; p 203.

(5) Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals*: *Textures and Structures*; Leonard Hill, Glasgow, 1985.

(6) Gane, P. A. C.; Leadbetter, A. J.; Wrighton, P. G. *Mol. Cryst. Liq. Cryst.* **1984**, *66*, 247.

(7) Brand, H. R.; Cladis, P. E. *J. Phys.* (*Paris*) *Lett.* **1984**, *45*, 1053. Brand, H. R.; Cladis, P. E. *Mol. Cryst. Liq. Cryst.* **1984**, *114*, 207.

(8) Leadbetter, A. J.; Richardson, R. M. In *The Molecular Physics of Liquid Crystals*; Luckhurst, G. R., Gray, G. W. Eds.; Academic Press: London, 1979; Chapter 20.

0002-7863/86/1508-4729$01.50/0

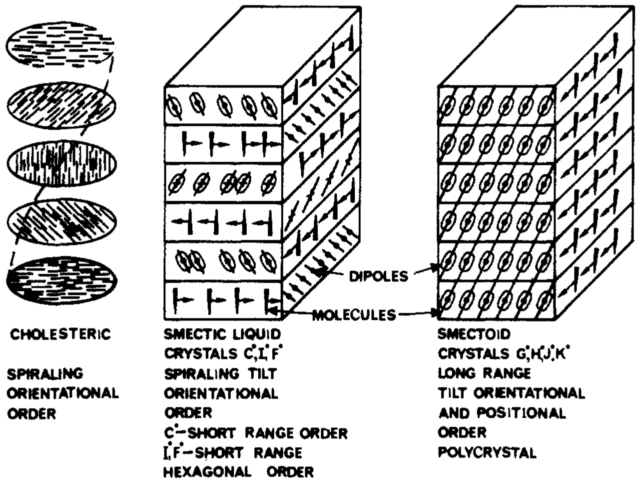


Figure 1. The structures of the cholesteric, ferroelectric smectic liquid crystal, and ferroelectric crystal (smectoid) phases.

H*, J*, and K*, the helical ordering is suppressed by the long-range positional ordering of the molecules. Thus, while the cholesteric and smectic liquid crystal phases C*, I*, and F* exhibit form optical activity due to the helical ordering, the smectoid crystal phases apparently do not. However, these latter phases exhibit similar ferroelectric properties[10] to the other smectic modifications. As with the helical phases, bulk specimens of the crystal phases also have a net zero spontaneous polarization, but this is due to a multidomain structuring which scrambles the spontaneous polarization. An aligned sample of these phases shows that they are improper ferroelectrics.[11]

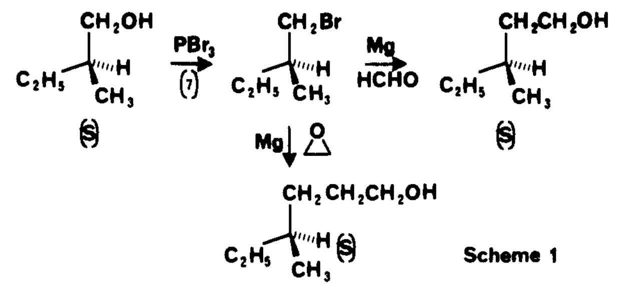
(3) Symmetry in Ferroelectric Smectic Modifications. The smectic modifications C*, I*, F*, J*, G*, K*, and H* formed by optically active materials are ferroelectrics because of their reduced environmental symmetries created by the inclusion of an asymmetric center(s) in the structures of their constituent molecules. The environmental symmetry of an achiral molecule with its long axis tilted with respect to the layer planes of the phase are a center of inversion, a twofold axis of rotation, and a mirror plane. In the chiral system these elements are reduced to a single "polar" C2, twofold axis of rotation normal to the tilt axis of the molecule and parallel to the layer planes.[12] It is along this axis that the spontaneous polarization acts.

Two directions are possible for the spontaneous polarization to act along. These are shown in Figure 2 for an object molecule that is tilted back in a plane normal to the page. If the spontaneous polarization acts along the $(+x)$ direction then it is denoted as being positive, $Ps > 0$, and the symbol used to describe it is Ps(+). If it lies along the $(-x)$ direction then it is negative, $Ps < 0$, and is denoted as Ps(−).[13]

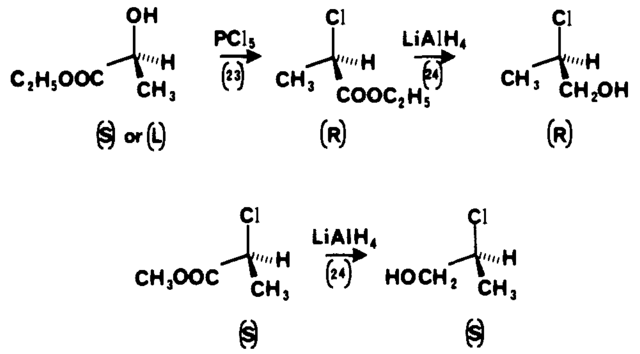
This designation applies to both ferroelectric (helielectric) phases C*, I*, and F*, and the orientaionally disordered solid (smectoid) phases J*, G*, H*, and K*.

The code-lettering system for classifying smectic modifications has been reviewed extensively;[14] however, it should be noted that the ferroelectric smectic liquid crystal phases have chiral molecules and chiral symmetries resulting in dissymmetric helical structures. Alternatively, the crystal phases have chiral molecules and chiral symmetries but possess nonhelical gross structures. As all of the phases have chiral symmetries derived from chiral materials, the asterisk notation is retained to describe them as chiral, ferroelectric phases.[15,16,36]

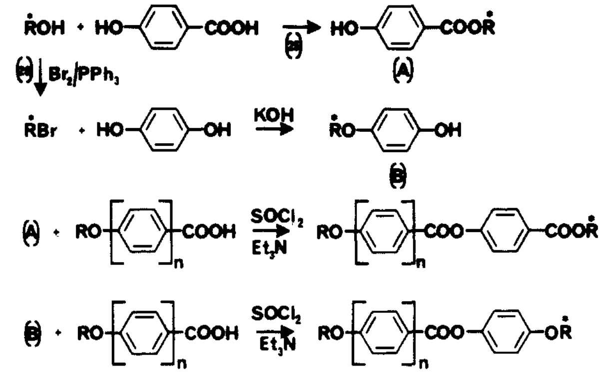
Scheme I



Scheme II



Scheme III



The following sections describe how the optical rotation of the mesophase (*d* or *l*), the helix direction (LH or RH), the absolute spatial configuration of the chiral center (*R* or *S*), and the position (parity) of the chiral center within the molecular structure of the material (e or o) are related to the direction of the spontaneous polarization (Ps(+) or Ps(−)).

(II) Experimental Section

The preparations, purities, properties, and phase transitions of the materials that were investigated in this study have already been reported.[17-25] Optical studies of switching behavior and helical twist sense for these compounds were carried out on a Zeiss Universal polarizing mi-

---

(9) Frank, Sir C. In *Opening Address*, 10th International Liquid Conference; York: England, July, 16, 1984.

(10) Brand, H. R.; Cladis, P. E. *J. Phys. (Paris) Lett.* **1984**, *45*, 217.

(11) See, for example: Lines, M. E.; Glass, A. M. *Principles and Applications of Ferroelectrics and Related Materials*: Oxford, 1977; p 347.

(12) Meyer, R. B. *Mol. Cryst. Liq. Cryst.* **1977**, *40*, 33.

(13) Clark, N. A.; Lagerwall, S. T. *Ferroelectrics* **1984**, *59*, 25.

(14) Goodby, J. W. *Mol. Cryst. Liq. Cryst. Lett.* **1983**, *92*, 171.

(15) Goodby, J. W.; Patel, J. S.; Leslie, T. M. *Ferroelectrics* **1984**, *59*, 121.

(16) Lagerwall, S. T.; Dahl, I. *Mol. Cryst. Liq. Cryst.* **1984**, *114*, 151.

(17) Goodby, J. W.; Leslie, T. M. *Mol. Cryst. Liq. Cryst.* **1984**, *110*, 175. Chin, E.; Goodby, J. W.; Patel, J. S.; Geary, J. M.; Leslie, T. M., to be submitted.

(18) Goodby, J. W.; Leslie, T. M. In *Liquid Crystals and Ordered Fluids*; Griffin, A. C., Johnson, J. F., Eds.; Plenum Press: New York, 1984; Vol. 4, p 1.

(19) Keller, P. *Ferroelectrics* **1984**, *58*, 1.

(20) Goodby, J. W. *Ferroelectrics* **1983**, *49*, 275.

(21) Keller, P.; Juge, S.; Liebert, L.; Strzelecki, L. *C. R. Acad. Sci., Ser. C* **1976**, *228*, 639.

(22) Nystrom, R. F. *J. Am. Chem. Soc.* **1958**, *81*, 610.

(23) Lowrance, W. W. *Tetrahedron Lett.* **1971**, *37*, 3453.

(24) See, for example: Schaefer, J. P.; Higgins, J.; Schenoy, P. K. In *Organic Syntheses*; Baungasten, H. E., Ed.; Wiley: New York, 1973; Vol. V, p 142.

(25) Onopchenko, A.; Sabourin, E. T.; Selwitz, C. M. *J. Org. Chem.* **1979**, *44*, 1233.

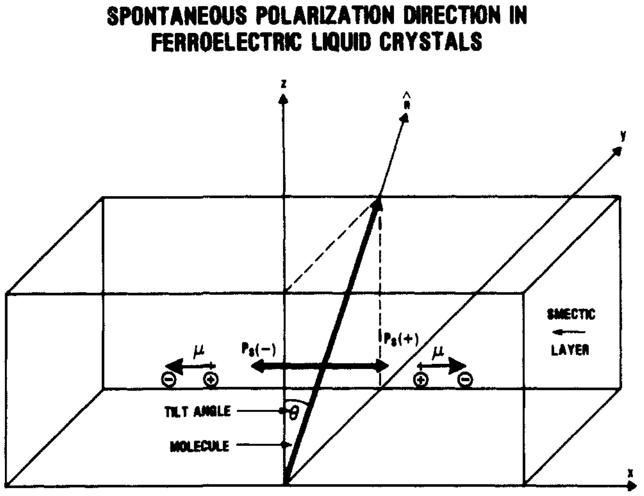
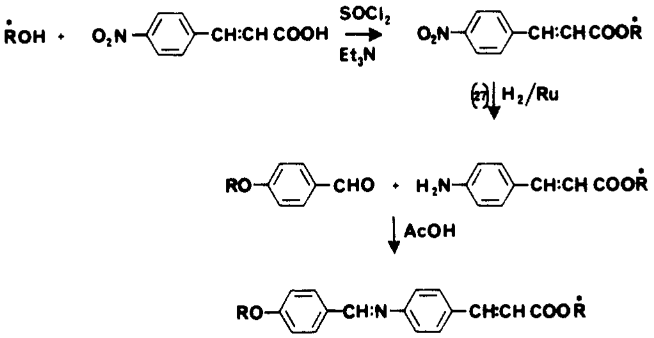


Figure 2. The spatial orientation of the spontaneous polarization in ferroelectric liquid crystals. The arrow indicating the direction of the spontaneous polarization also indicates the local dipole direction (+ → −).

Scheme IV



croscope in conjunction with a Mettler FP-52 microfurnace and FP-5 control unit. Transition temperatures were determined by thermal optical microscopy and by differential scanning calorimetry on a Perkin-Elmer DSC-4-TADS calorimeter. The mesophases exhibited by the materials under investigation were classified from textural and miscibility studies by optical microscopy. The cells used in the electric field experiments were constructed from indium–tin oxide (ITO) conducting glass which had been subjected to a surface treatment described previously.[26]

(1) Synthesis and Classification of Materials. A number of novel ferroelectric smectogens were prepared by trivial methods. Details of their structures, their absolute configurations, and phase transitions have been published elsewhere.[17-20] A representative number of these materials were chosen for further studies by optical and electric field experiments. The transition temperatures for the selected materials are given in Table IIa.

The absolute configurations of the materials selected were predetermined by the reaction pathways by which they were prepared from starting materials with known absolute configurations. For example, Scheme I shows the preparation of (*S*)-3-methylpentan-1-ol (3M5) and (*S*)-4-methylhexan-1-ol (4M6) from commercially available (*S*)-2-methylbutan-1-ol (2M4) (Fluka) by bromination with phosphorus tribromide and chain extension via Grignard coupling reactions. Derivatives of (*S*)-3,7-dimethyloctan-1-ol were prepared by first hydrogenating (*S*)-β-citronellol (Aldrich) in the presence of Adams' catalyst. Again this process does not involve inversion or racemization of the chiral center. Scheme II shows the preparation of both (*R*)- and (*S*)-2-chloropropanol from L-ethyl lactate and (*S*)-chloromethyl propionate, respectively.[21,22] These alcohols are used in esterifications[23] or alkylations[24] (Scheme III) or in esterifications, reductions,[25] and condensation reactions (Scheme IV) to yield the appropriate ester or Schiff's base smectogen. No racemization or inversion of a chiral center can occur in Schemes III and IV, hence the absolute configuration of the starting alcohol is carried through into the final products.

(2) Determination of the Sign of the Optical Rotation of Ferroelectric Smectic Liquid Crystals. The direction of the helix, i.e., right handed or left handed, is directly related to the sign of the optical rotation (*d* or *l*) of the ferroelectric liquid crystal phase because the helix acts as a "guide" to incident plane-polarized light parallel to its axis. A right-hand helix produces a levo rotation and a left-hand helix produces a dextro rotation of plane-polarized light, when the observer is looking into the path of the oncoming beam.

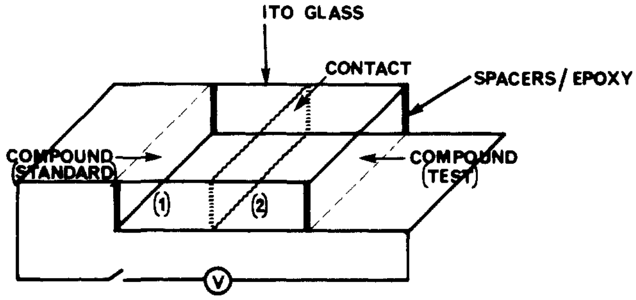


Figure 3. A contact preparation cell.

One of the more useful methods of determining the twist sense is by the contact method[3] with a standard material of known twist sense. Once a standard material has been defined, this method becomes extremely useful because the twist sense, the pitch of the phase at a given temperature, and the direction of the spontaneous polarization of a test material can be determined by similar experimental techniques.

A typical "contact cell" is shown in Figure 3 and consists of two pieces of ITO glass which have been coated with a polymer aligning agent[26] and then joined together at their four corners with an epoxy cement containing 30-μm spacers. The heated cell is half-filled from one of the edges by capillary action with the material that has the higher clearing point (while the material is in its liquid phase). The cell is cooled in order to stop further capillary advancement of the material. The second material is inserted from the opposite side to the first, again by capillary action while in its liquid phase. The two liquids are allowed to make a sharp contact, and then the cell is cooled rapidly to room temperature in order to prevent excessive mixing at the junction of the two materials.

The overlapping edges of the ITO glass supports are cleaned of all material so that they can be used as electrical contacts for electric field studies. The cell is then heated until the materials are both in their liquid forms, and then it is cooled at a controlled rate (10 °C/min) in a Mettler microscope oven to form an aligned specimen. The alignment continues from one material through the contact region into the second substance. The two materials are then cooled down until they are in their ferroelectric liquid-crystal phases.

At this point, provided the pitch of the helix is considerably less than the cell thickness, disclinations described as pitch bands are observed in transmission plane-polarized light microscopy. If these bands continue through the contact region from one substance to the other then the materials have the same twist sense, i.e., the test compound has the same helical handedness as the standard, and if they disappear at the junction the pitch has increased towards infinity, thus the twists of the two helicies are compensating for each other, i.e., the twist sense of the test compound is opposite to that of the standard.

This method is similar to that used for cholesterics and determines twist sense by direct comparison of two materials. The pitch of the helicies of the phases of the standard and test compounds can be determined directly by measuring the distance between the pitch bands observed. Moreover, the variation of the pitch with temperature can be determined in the same manner with the cell placed in a Mettler oven.

Table IIa,b lists results for some of the materials studied. It can be seen from this table that small pitch lengths were found for a number of materials that possess a spacer group between the chiral terminal chain and the core (e.g., COO). This suggests that the spacer group acts as though it belongs to the core structure.

(3) Determination of the Direction of the Spontaneous Polarization. The direction of the spontaneous polarization related to the direction of the tilt axis can be determined directly from electric field studies with the contact cell preparation. The unswitched cell is heated into the smectic A phase in the microscope oven. The sample is rotated until the aligned focal-conic or planar homogeneous domains are aligned with a reference direction, e.g., the cross-hairs of the eyepiece. Extinction is then obtained along the reference direction by rotation of the polarizer and analyzer. The material is then cooled down into its ferroelectric phase, and a weak form of extinction is maintained in the same direction as the A phase because of the formation of the helical ordering in this direction. The sample is then subjected to a DC voltage (67.5 V) of known polarity

---

(26) Patel, J. S.; Leslie, T. M.; Goodby, J. W. *Ferroelectrics* **1984**, *59*, 137.

(27) Patel, J. S.; Goodby, J. W., to be submitted.

(28) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

Table II

(a)

compound[d]	transition temperatures (°C)
(*S*)-C_8H_{17}OPhCOOPhCOO2M4	Iso-A, 58; A-C*, 32; mp 33
(*S*)-$C_{10}H_{21}$OPhCOOPhCOO2M4	Iso-A, 59.5; A-C*, 35; mp 52
(*S*)-$C_{12}H_{25}$OPhCOOPhCOO2M4	Iso-A, 60; A-C*, 35.5; mp 55
(*S*)-$C_{14}H_{29}$OPhCOOPhCOO2M4	Iso-A, 60; A-C*, 35; mp 40
(*S*)-C_8H_{17}OPhCOOPhCOO3M7M8	Iso-A, 51; A-C*, 30.2; mp 40.5
(*S*)-C_9H_{19}OPhCOOPhCOO3M7M8	Iso-A, 50; A-C*, 40.3; mp 41.5
(*S*)-$C_{10}H_{21}$OPhCOOPhCOO3M7M8	Iso-A, 51.3; A-C*, 46; mp 40.5
(*S*)-$C_{11}H_{23}$OPhCOOPhCOO3M7M8	Iso-A, 50.4; A-C*, 47.4; mp 43
(*S*)-$C_{12}H_{25}$OPhCOOPhCOO3M7M8	Iso-A, 51.8; A-C*, 49; mp 37.5
(*S*)-$C_{13}H_{27}$OPhCOOPhCOO3M7M8	Iso-A, 49.8; A-C*, 48.6; mp 42.8
(*S*)-$C_{14}H_{29}$OPhCOOPhCOO3M7M8	Iso-A, 51.0; A-C*, 50; mp 41.5
(*S*)-$C_{16}H_{33}$OPhCOOPhCOO3M7M8	Iso-C*, 49.7; mp 48.3
(*S*)-$C_{10}H_{21}$OPhCOOPhO3M7M8	Iso-A, 60.4; A-C*, 49; mp 48
(*S*)-$C_{10}H_{21}$OPhOOCPhO3M7M8	Iso-Ch, 46.5; Ch-C*, 40.9; mp 39.5
(*S*)-C_8H_{17}OPhPhCOO1M3	Iso-A, 53; A-C*, 30; mp 64.5
(*S*)-C_8H_{17}OPhPhCOO2M4	Iso-A, 66; A-C*, 44; mp 49
(*S*)-C_8H_{17}OPhPhCOO3M5	Iso-A, 72; A-C*, 58; mp 59
(*S*)-$C_{12}H_{25}$OPhPhCOO3M7M8E	Iso-A, 53; A-C*, 47; mp 50
(*S*)-C_8H_{17}OPhCOOPhCOO2M4	Iso-Ch, 171; Ch-A, 168; A-C*, 100; mp 86
(*S*)-$C_{10}H_{21}$OPhCH:NPhCH:CHCOO2M4	Iso-A, 118; A-C*, 94; C*-I*, 60.5; mp 76
(*S*)-C_4H_9OPhCH:NPhCH:CHCOO2Cl3	Iso-A, 135; A-C*, 72; C*-I*, 63; I*-J*, 55; mp 98
(*S*)-C_6H_{13}OPhCH:NPhCH:CHCOO2Cl3	Iso-A, 134; A-C*, 81; C*-I*, 73; I*-J*, 63; mp 65
(*R*)-C_6H_{13}OPhCH:NPhCH:CHCOO2Cl3	Iso-A, 134; A-C*, 81; C*-I*, 73; I*-J*, 63; mp 65
(*S*)-C_6H_{13}OPhOOCPhOOCPhO4M6	Iso-Ch, 175.3; Ch-C*, 115; mp 78.5
(*R*)-C_8H_{17}OPhPhCOO1M3	Iso-A, 53; A-C*, 30; mp 64.5
(*S*)-$C_{12}H_{25}$OPhCOOPhCH:CHCOO2M4	Iso-A, 93; A-C*, 53; mp 53

(b)

compound[a]	abs config	helix	chiral post.	twist sense	ind. effect	ps dir.	pitch,[c] μm
C_8H_{17}OPhCOOPhCOO2M4	*S*	LH	e	*d*	+I	Ps(−)	1.2
$C_{10}H_{21}$OPhCOOPhCOO2M4	*S*	LH	e	*d*	+I	Ps(−)	1.2
$C_{12}H_{25}$OPhCOOPhCOO2M4	*S*	LH	e	*d*	+I	Ps(−)	
$C_{14}H_{29}$OPhCOOPhCOO2M4	*S*	LH	e	*d*	+I	Ps(−)	1.9
C_8H_{17}OPhCOOPhCOO3M7M8	*S*	RH	o	*l*	+I	Ps(+)	
C_9H_{19}OPhCOOPhCOO3M7M8	*S*	RH	o	*l*	+I	Ps(+)	3.0
$C_{10}H_{21}$OPhCOOPhCOO3M7M8	*S*	RH	o	*l*	+I	Ps(+)	2.6
$C_{11}H_{23}$OPhCOOPhCOO3M7M8	*S*	RH	o	*l*	+I	Ps(+)	2.3
$C_{12}H_{25}$OPhCOOPhCOO3M7M8	*S*	RH	o	*l*	+I	Ps(+)	2.2
$C_{13}H_{27}$OPhCOOPhCOO3M7M8	*S*	RH	o	*l*	+I	Ps(+)	3.9
$C_{14}H_{29}$OPhCOOPhCOO3M7M8	*S*	RH	o	*l*	+I	Ps(+)	2.8
$C_{16}H_{33}$OPhCOOPhCOO3M7M8	*S*	RH	o	*l*	+I	Ps(+)	7.6
$C_{10}H_{21}$OPhCOOPhO3M7M8	*S*	LH	e	*d*	+1	Ps(−)	1.3
$C_{10}H_{21}$OPhOOCPhO3M7M8[b]	*S*	LH	e	*d*	+I	Ps(−)	
C_8H_{17}OPhPhCOO1M3	*S*	RH	o	*l*	+I	Ps(+)	
C_8H_{17}OPhPhCOO2M4	*S*	LH	e	*d*	+I	Ps(−)	1.9
$C_{10}H_{21}$OPhPhCOO2M4	*S*	LH	e	*d*	+I	Ps(−)	1.8
C_8H_{17}OPhPhCOO3M5	*S*	RH	o	*l*	+I	Ps(+)	
$C_{12}H_{25}$OPhPhCOO3M7M8E	*S*	RH	o	*l*	+I	Ps(+)	
C_8H_{17}OPhCOOPhCOOPhCOO2M4[a]	*S*	LH	e	*d*	+I	Ps(−)	
$C_{10}H_{21}$OPhCH:NPhCH:CHCOO2M4[a]	*S*	LH	e	*d*	+I	Ps(−)	
C_4H_9OPhCH:NPhCH:CHCOO2Cl3[a]	*S*	RH	e	*l*	−I	Ps(+)	3.0
C_6H_{13}OPhCH:NPhCH:CHCOO2Cl3[a]	*S*	RH	e	*l*	−I	Ps(+)	
C_6H_{13}OPhCH:NPhCH:CHCOO2Cl3[a]	*R*	LH	e	*d*	−I	Ps(−)	
C_6H_{13}OPhOOCPhOOCPhO4M6[b]	*S*	RH	o	*l*	+I	Ps(+)	
C_8H_{17}OPhPhCOO1M3	*R*	LH	o	*d*	+I	Ps(−)	
$C_{12}H_{25}$OPhCOOPhCH:CHCOO2M4	*S*	LH	e	*d*	+I	Ps(−)	

[a] These materials exhibit other ferroelectric smectic phases notably I*, J*, and G* as well as the C* phase. [b] All of the materials exhibit a smectic A–smectic C* phase sequence except for these which exhibit a cholesteric–smectic C* sequence. In this second sequence the spontaneous polarization direction is determined by a surface alignment method which is reported elsewhere.[27] [c] Pitches were measured at a reduced temperature ($T - T_{A-C}$) of −5 °C. [d] Where Iso is the isotropic liquid, Ch is the cholesteric phase, and A, C*, I*, J* are smectic modifications. [e] Where 1M3 is 1-methylpropyl, 2M4 is 2-methylbutyl, 3M5 is 3-methylpentyl, 4M6 is 4-methylhexyl, 3M7M8 is 3,7-dimethyloctyl, 2Cl3 is 2-chloropropyl, 3M7M8E is 3,7-dimethyloct-6-enyl, and Ph is a 1,4-substituted phenyl ring.

(normally the top plate is positively charged). The helix unwinds and the material becomes poled in a uniform direction with its spontaneous polarization being coupled to the applied field. The extinction direction is now at an angle relative to the reference axis. The sample is then rotated through the minimum angle required to return it to extinction along the reference direction. The sense of the rotation of the sample defines the direction that the molecules are tilted with respect to the layer normal, and thus the direction of the spontaneous polarization, as shown in Figure 4. This figure shows the spatial relationship between Ps(−) and Ps(+) with respect to the tilt axis of the molecules. Figure 4a shows a material with a negative spontaneous polarization Ps(−), and Figure 4b shows a material with a positive spontaneous polarization Ps(+).

The angle the sample is rotated through in order to bring it back to extinction with respect to the reference axis is equivalent to the optical tilt angle (α) of the phase (provided the molecules lie parallel to the plane of the cell glass). This is usually the case when large electric fields are applied. The variation of the optical tilt angle (α) with temperature can be measured directly from these studies.

(III) Results

Spontaneous Polarization Direction Measurements. Table IIb lists a number of compounds that were synthesized with known

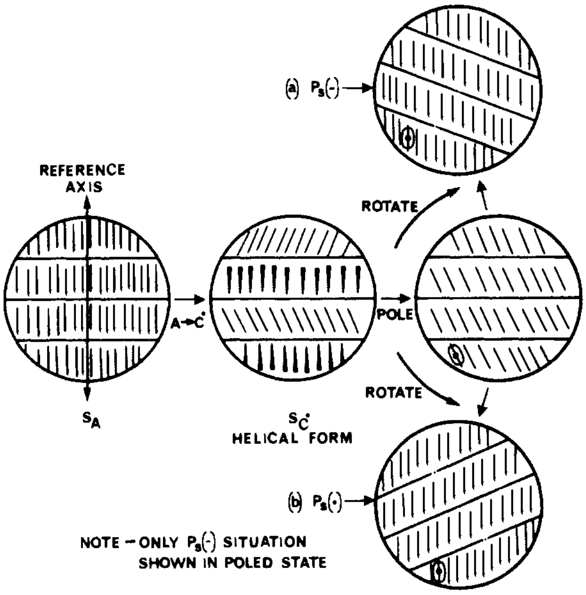
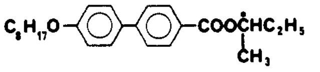


Figure 4. Electric field switching studies in a contact preparation cell, note only one of the poled states is shown.

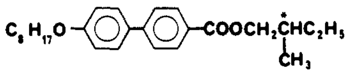
absolute spatial configurations and were subjected to electric field studies. Their absolute configurations, the positions of the chiral centers relative to the cores, the inductive effect of the lateral substituents at the chiral center, the rotations of plane-polarized light, and the observed spontaneous polarization directions are given.

(IV) Discussion

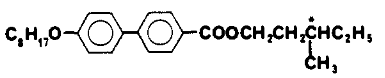
(1) Alternations in Homologous Series. From Table IIb it can be seen that ferroelectric substances incorporating a lateral methyl substituent at the chiral center follow the rules given by Gray and McDonnell[3] for the helical twist sense of the cholesteric phase. As the chiral center is moved incrementally away from the core there is an alternation of the twist direction. Accompanying this effect there is also an alternation of the spontaneous polarization direction. For example, in the materials II, III, and IV, the twist sense and spontaneous polarization alternate for a given spatial configuration(s). Thus it appears for a methyl substituent at the chiral center that the spontaneous polarization and the helical twist sense are coupled. Moreover, these rules are not effected, in this series a least, by extending the carbon chain on the external side of the chiral center, hence the ester V also fits the above sequencing pattern. The first tentative conclusion that can be drawn from these studies is that for these particular homologous series a positive sign for the specific rotation is associated with a negative sign for the spontaneous polarization and vice versa, e.g.,

(II)

$\mathrm{C_8H_{17}O{-}C_6H_4{-}C_6H_4{-}COO\underset{\displaystyle CH_3}{\overset{*}{C}}HC_2H_5}$

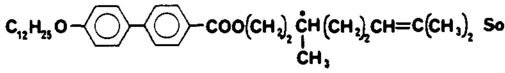
Sol $P_s(+)$

(III)

$\mathrm{C_8H_{17}O{-}C_6H_4{-}C_6H_4{-}COOCH_2\underset{\displaystyle CH_3}{\overset{*}{C}}HC_2H_5}$

Sed $P_s(-)$

(IV)

$\mathrm{C_8H_{17}O{-}C_6H_4{-}C_6H_4{-}COOCH_2CH_2\underset{\displaystyle CH_3}{\overset{*}{C}}HC_2H_5}$

Sol $P_s(+)$

(V)

$\mathrm{C_{12}H_{25}O{-}C_6H_4{-}C_6H_4{-}COO(CH_2)_2\underset{\displaystyle CH_3}{\overset{*}{C}}H(CH_2)_2CH{=}C(CH_3)_2}$

Sol $P_s(+)$

$$\mathrm{Ps}(+) \equiv l(-) \equiv \mathrm{RH\ helix}$$

$$\mathrm{Ps}(-) \equiv d(+) \equiv \mathrm{LH\ helix}$$

where right- and left-hand helicies are as defined by Cahn et al.[28] In assuming that the molecules prefer an all-trans conformation, previous indications[17] have shown that the conformation change caused by moving the chiral center away from the core by one atom involves an alternation in the steric bulk of the lateral substituent (methyl in this case) relative to the long axis of the molecule (see Figure 5). However, the direction of the dipole associated with the chiral center also alternates in the same way as the steric bulk of the substituents, thus, it is impossible to distinguish for a given type of chiral center or homologous series which effect is responsible for the twist direction and the spontaneous polarization (see Figure 5).

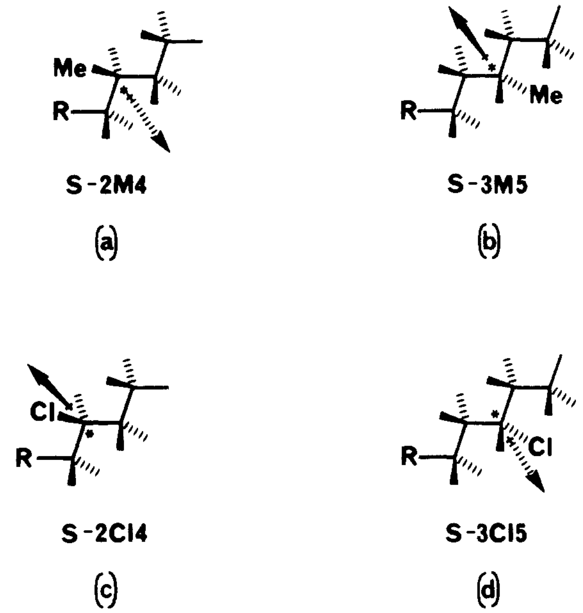
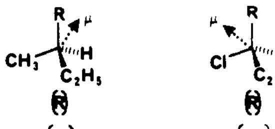


Figure 5. Conformational structure of the most extended molecular forms of methyl- and chloro-substituted smectogens.

(2) Dipolar vs. Steric Forces in Helix Formation. These effects (dipolar or steric) are the possible driving forces in the formation of a helix in the ferroelectric smectic mesophases. Under these circumstances a distinction between the two cannot be drawn because they are coupled together. However, other substituents at the asymmetric center can be obtained in which the bulk and the dipole are either on the same side or directed toward opposite sides of the long axis of the molecule. For example, in the two structures VI and VII, VI has a methyl branch which has a positive electron-donating or inductive effect (+*I*) relative to hydrogen along the σ-bond framework. This is directed to the opposite side of the long axis to the steric bulk in an all-trans conformation. Thus, for VI the steric bulk is on one side of the molecular axis while the net electron density associated with the σ bonds around the chiral center resides on the opposite side of the long axis (see Figure 5a,b). In case VII when the methyl substituent is replaced by a chlorine atom, which has a negative inductive effect (−*I*) relative to hydrogen, the electron density about the chiral center and the steric bulk now lie on the same side of the molecular long axis (see Figure 5c, d).

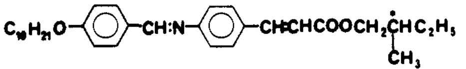


(VI) (VII)

Comparison between the twist senses and the spontaneous polarization directions for the methyl and chloro equivalently substituted materials can be used to distinguish between the two driving forces for helix formation. If the same twist senses are obtained for these two substituents, then the helix formation is steric driven; if they are opposite, then it is dipolar driven.

Studies by Clark and Lagerwall[13] on the two materials VIII and IX show that they have the same spontaneous polarization direction (Ps(−)); however, they failed to report the absolute configuration of these materials, but presumably they were obtained from their original source, Keller,[21] and therefore DO-

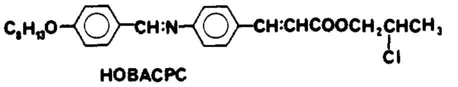
(VIII)



Sed Ps(-)

DOBAMBC

(IX)



Red Ps(-)

HOBACPC

BAMBC[29] is *S* and HOBACPC is *R*. Both of these samples were shown to be dextrorotatory (*d*(+)), so DOBAMBC (VIII) is classified as a *Sed* Ps(−) material and HOBACPC (IX) as a *Red* Ps(−) compound.

The issue has been confused further by a report[30] that when mixed these two materials produced a mixture with infinite pitch and sizable polarization, but yet they had opposite polarization directions. We succeeded, however, in preparing a sample of HOBACPC with a defined *S* absolute configuration and obtaining an original sample of *R*-HOBACPC (Keller).[31] Contact studies and electric field experiments showed that the two samples were of opposite twist senses and spontaneous polarization directions in their ferroelectric smectic C* and I* phases and that they had opposite spontaneous polarization directions in their ferroelectric crystal J* phases. Thus *S*-HOBACPC was found to be an *el* Ps(+) material and *R*-HOBACPC has an *ed* Ps(−) classification, and furthermore *S*-DOBAMBC is an *ed* Ps(−) compound, as shown in Table IIb. It should be noted that these cinnamate esters can undergo trans to cis isomerization, but this does not affect the spatial configuration related to the molecular long axis in an overall trans structuring (even when incorporating a lone cis double bond). The isomerization to a cis structure would, however, effect the transition temperatures of the material drastically.

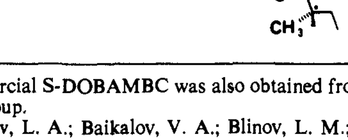
Clearly when the direction of the flow or distribution of electrons about the asymmetric center is inverted, without significant change to the steric shape of the system, the twist sense of the helix and the direction of the spontaneous polarization are also changed. Gray and McDonnell's rules[3] applied to smectics are inverted in chloro systems, indicating that the formation of the helix is probably dipolar driven. However, this is not a simple dipolar coupling interaction which would possibly lead to an alignment of dipoles and no helix formation but rather a complex one which must involve many other factors, such as steric shape, to some degree.

(3) General Rules. General rules for the systems studied which govern the twist sense and the spontaneous polarization direction for a compound of known absolute configuration are given in Table III for smectic liquid-crystal modifications C*, I*, and F*.

(4) Crystal or Smectoid Phases. Orientationally disordered solid phases J*, G*, H*, and K* possess similar properties to smectic liquid crystals C*, I*, and F*, except that they do not possess a helical structure.[10] This ordering is suppressed by the long-range positional ordering of the constituent molecules of the phase. However, these phases still have optically active molecules and therefore possess chiral symmetries. Thus these phases have the same relationships between the spontaneous polarization direction and molecular structure as described earlier for the C*, I*, and F* phases. General rules that cover these phases, for the materials studied in Table IIa,b which exhibited smectoid crystals, are given in Table IV.

(5) Layer Structuring in Smectic C*. One of the more intriguing aspects of these investigations becomes apparent when the layering structures of the tilted smectic phases are examined. Consider the material X,

(X)



Sed Ps(-)

which has the following phase sequence:[18]

$$\mathrm{Iso} \underset{58}{\rightleftarrows} \mathrm{S_A} \underset{32}{\rightleftarrows} \mathrm{S_c}^* \qquad \underset{33}{\mathrm{mp}}$$

In the smectic C* phase this material exhibits a negative spontaneous polarization. One way to understand this observation is to consider the orientation and disposition of the individual molecules in their layered structure. If the molecules are assumed to be rotating rapidly about their long axis[32] then the spontaneous polarization would be reduced to a zero value because of the isotropic motion of the lateral dipoles about this axis. However, if we consider all of the conformers that this material can exhibit, the most thermodynamically stable ones will include those in which the core and the first few terminal alkyl carbon atoms are in their all-trans conformations.[33] The molecule will then have a zigzag shape about its central region. This type of conformation demonstrates the symmetry arguments for ferroelectricity better than assuming that the molecules are roughly cylindrical in shape, i.e., rotation about a polar C2 twofold *axis* by 180° effectively reproduces the zigzag structure in a similar orientation, while cylindrical structures can be rotated along different axes and still produce a cylindrical molecule in a similar orientation.

Molecules with zigzag structures can be packed together basically in two different formats to give a tilted layered structure; these are shown in Figure 6. In Figure 6a the cores are less tilted than the overall molecular structures, while in Figure 6b the reverse is the case. If material X is now examined in its all-trans conformation it becomes apparent that when it is in the layer structure defined in Figure 6b then its tilt and dipole orientations conform to the definition of a negative spontaneous polarization, as shown in Figure 7. In the orientation shown in Figure 6a, the lateral dipole component associated with the dipole at the chiral center will be pointing in the opposite direction, and consequently this molecular orientation would produce a positive spontaneous polarization.

It can be seen from Figure 7 that, in this orientation, the core of the molecule is more tilted than the overall molecular structure. As the optic axis is associated with the delocalized electrons and dipolar nature of the core, this means that in this orientation the optic tilt angle will be greater than that for the whole structure (tilt angle by X-ray). This model has already been suggested as a possibility for describing the achiral C phase[34] and the ferroelectric C* phase.[35]

The consequences of such a model would necessitate changes to present views of the molecular dynamics in these phases. Certainly the molecules in this model are not undergoing free rotation as a whole about their long axes. Also the fact that plane-polarized light passing through the contact cell is not elliptically polarized would indicate that the cores do not possess biaxiality. Therefore it is possible that the cores are rotating rapidly about their long axes but that this motion is not coordinated with that of the aliphatic terminal chains. The terminal chains may in fact be moving through many conformational changes as well as total rotations of the whole chain. However, it is likely, because of the flexibility of the aliphatic chains, that conformational changes are the more dominant features of the motions of these portions of the molecule. Thus, the terminal chains may

---

(29) Commercial S-DOBAMBC was also obtained from CPAC Organic Specialities Group.

(30) Beresnev, L. A.; Baikalov, V. A.; Blinov, L. M.; Pozhidaev, E. P.; Purvantskas, G. V. *JETP Lett.* **1981**, *33*, 536.

(31) R. Pindak for the gift of R-HOBACPC given to him by P. Keller.

(32) Leadbetter, A. J.; Mazid, M. A.; Richardson, R. M. In *Liquid Crystals*, Chandrasekhar, S., Ed.; Heydon: London, 1980; p 65.

(33) Samulski, E. T.; Dong, R. Y. *J. Chem. Phys.* **1982**, *77*, 5090.

(34) Bartolino, R.; Doucet, J.; Durand, G. *Ann. Phys.* **1978**, *3*, 389.

(35) Martinôt-Lagarde, Ph.; Duke, R.; Durand, G. *Mol. Cryst. Liq. Cryst.* **1981**, *75*, 249.

(36) The asterisk nomenclature was originally used to describe an asymmetric carbon atom and was later used incorrectly to describe the dissymmetric helical structure of the smectic C phase. Here it is used to show that the phase is comprised of optically active material that is ordered such that the local environment has chiral symmetry. Recently Brand and Cladis[7] have proposed that phases which they describe as being helielectric should retain the asterisk nomenclature, while orientationally disordered phases should adopt a circumflex notation, e.g., C*, I*, and F* are helielectric, Ĵ, Ĝ, Ĥ, and K̂ are ferroelectric. The cholesteric phase is not ferroelectric because it has a local uniaxial order unlike the smectic phases which are biaxial.

Table III

dipolar inductive effect at chiral center	abs config	position of chiral center	rotation of plane-polarized light	helix twist sense	spontaneous polarization direction
+I	*S*	e	*d*	LH	Ps(−)
+I	*R*	o	*d*	LH	Ps(−)
+I	*R*	e	*l*	RH	Ps(+)
+I	*S*	o	*l*	RH	Ps(+)
−I	*S*	e	*l*	RH	Ps(+)
−I	*R*	o	*l*	RH	Ps(+)
−I	*R*	e	*d*	LH	Ps(−)
−I	*S*	o	*d*	LH	Ps(−)

Table IV

dipolar inductive effect at chiral center	abs config	position of chiral center	spontaneous polarization direction
+I	*S*	e	Ps(−)
+I	*S*	o	Ps(+)
+I	*R*	e	Ps(+)
+I	*R*	o	Ps(−)
−I	*S*	e	Ps(+)
−I	*S*	o	Ps(−)
−I	*R*	e	Ps(−)
−I	*R*	o	Ps(+)

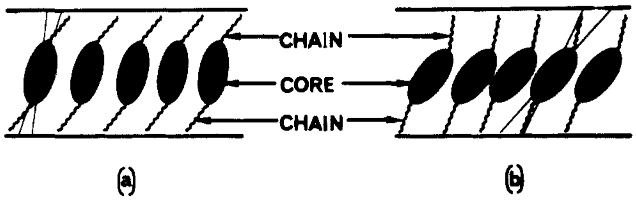


Figure 6. The zigzag packing orientations of smectic C.

exhibit a Boltzmann distribution of conformers, and as Samulski and Dong[33] have shown, those atoms closest to the core will have predominantly trans conformations. This would provide a plausible explanation for the existence of a lateral dipole associated with the chiral center that couples to the other dipoles in the system and to an external field to produce a spontaneous polarization. This is supported to some degree by the fact that the spontaneous polarization is usually proportionately less than 5% of the actual molecular dipole, i.e., other conformations reduce the full strength of the dipole from being observed. Moreover, the magnitude of the spontaneous polarization is markedly effected by the position of the chiral center in the terminal alkyl chain. The closer the asymmetric center is to the core the larger is the spontaneous polarization. This is probably due to the higher proportion of trans bonds and restricted rotation of the chiral center due to steric hindrance.

(V) Conclusion

In this study we have shown that there are simple relationships between the molecular structure of a smectogen in a given absolute configuration, the helical twist sense, and the direction of the spontaneous polarization in its ferroelectric smectic liquid-crystalline phases (C*, I*, and F*). Moreover, these relationships appear to be maintained between the absolute configuration and the direction of the spontaneous polarization in the ferroelectric smectic crystal phases (G*, H*, J*, and K*). Furthermore, it is expected that these relationships will operate between the twist sense and the molecular configuration in cholesteric phases. Thus, a general set of rules for specific rotation have been generated for all forms of liquid-crystal modifications constituted of optically active materials. The guidelines that govern the direction of the spontaneous polarization are, however, subject to changes in the conformation and orientation of the molecules in their layers.

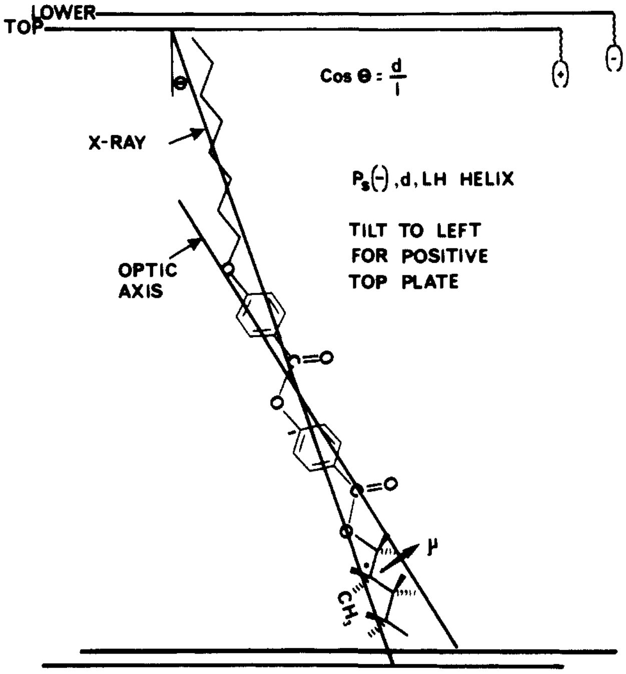


Figure 7. The orientation of a "switched" molecule of known twist sense for a positive top plate.

The conformational models used to explain some of these relationships are relatively simple and naive. It should be remembered that the molecules are themselves undergoing rapid reorientational motion about their long axes and that parts of the molecule are also rotating independently of each other. Thus, the models used are based only on the lowest energy forms of the molecules, but these only exist for short periods of time because of the high rate of the molecular motion, i.e., the model is a time-dependent one. This is reflected by the fact that the observed spontaneous polarization of a material is often two orders of magnitude lower than that which would have been expected from frozen or locked-in dipole moments.

For a full understanding of these preliminary results it is important that further examples of ferroelectric smectogens be prepared and tested to see if they comply with the basic rules and that studies on the molecular dynamics in these phases be examined in order to understand these relationships and the magnitude of the spontaneous polarization.

Finally it should be noted that the absolute configuration of a material can be determined from these studies. Therefore, liquid crystals provide a method of determining *R* and *S* for a given substrate.

Acknowledgment. The authors are very grateful for useful discussions with Professor S. T. Lagerwall and Dr. A. R. Kmetz.

Registry No. II, 102853-05-4; III, 90955-61-6; IV, 102853-06-5; V, 102853-07-6; VIII, 60951-46-4; IX, 82189-68-2; X, 90937-62-5; (*S*)-$C_{10}H_{21}OPhCOOPhCOO2M4$, 90937-64-7; (*S*)-$C_{12}H_{25}OPhCOOPhCOO2M4$, 90937-65-8; (*S*)-$C_{14}H_{29}OPhCOOPhCOO2M4$, 90937-66-9; (*S*)-$C_8H_{17}OPhCOOPhCOO3M7M8$, 102852-95-9; (*S*)-$C_9H_{19}OPhCOOPhCOO3M7M8$, 102852-96-0; (*S*)-$C_{10}H_{21}OPhCOOPhCOO3M7M8$, 102852-97-1; (*S*)-$C_{11}H_{23}OPhCOOPhCOO3M7M8$, 102852-98-2; (*S*)-$C_{12}H_{25}OPhCOOPhCOO3M7M8$, 102852-99-3; (*S*)-$C_{13}H_{27}OPhCOOPhCOO3M7M8$, 102853-00-9; (*S*)-$C_{14}H_{29}OPhCOOPhCOO3M7M8$, 102853-01-0; (*S*)-$C_{16}H_{33}OPhCOOPhCOO3M7M8$, 102853-02-1; (*S*)-$C_{10}H_{21}OPhCOOPhO3M7M8$, 102853-03-2; (*S*)-$C_{10}H_{21}OPhOOCPhO3M7M8$, 102853-04-3; (*S*)-$C_4H_9OPhCH{=}NPhCH{=}CHCOO2Cl3$, 82169-93-5; (*R*)-$C_6H_{13}OPhCH{=}NPhCH{=}CHCOO2Cl3$, 67036-26-4; (*S*)-$C_6H_{13}OPhOOCPhOOCPhO4M6$, 90937-89-6; (*R*)-$C_8H_{17}OPhPhCOO1M3$, 102853-08-7; (*S*)-$C_{12}H_{25}OPhCOOPhCH{=}CHCOO2M4$, 102853-09-8.