Optical Activity and Ferroelectricity in Liquid Crystals

J. W. GOODBY

Some liquid-crystalline phases of optically active materials are themselves optically active and have dissymmetric structures. The cholesteric phase and smectics C*, I*, and F* have a helical order of their molecules. Plane-polarized light is rotated by the helix, and when the pitch of the helix is comparable to the wavelength of visible light, these phases will reflect irridescent light of a single color. The smectics phases can exhibit ferroelectricity and have been utilized recently in fast-switching light valves. A relation between the microscopic property of molecular configuration and the macroscopic properties of ferroelectricity and the rotation of plane-polarized light is developed.

LIQUID CRYSTALS WERE DISCOVERED IN 1880 (*1*), YET these phases were relatively unknown to the general public until their recent commercialization in low-power, passive display devices. Now the term of LCD (liquid crystal display) has become commonplace. Liquid crystals have also recently received much attention in the scientific community because of their low dimensional ordering. Consequently they have been described as a new (or even sometimes the fourth) state of matter. Certainly they are not liquid, solid, or gas but comprise a number of intermediary states of matter that occur between the isotropic liquid and the organized solid state.

In a normal melting process, the degrees of freedom of the molecules increase in three dimensions: thus molecules that are ordered in the solid state tumble freely in the amorphous liquid. However, in a melting process mediated by liquid-crystalline behavior, there is a stepwise breakdown of order and a concomitant selective increase in the number and variety of degrees of freedom. The steps in the breakdown of order coincide with the formation of thermodynamically stable states, known as mesophases. The most commonly known mesophase is the nematic (N) phase (from Greek *nematos*, threadlike), which is found in most commercial applications of liquid crystals. The optically active version of this phase, known as the cholesteric or chiral nematic (Ch) mesophase, is utilized in encapsulated thermometers and guest-host color displays. Other mesophases also exist in which the molecules pack together in layers; this state, known collectively as the smectic (S) phase (from *smectos*, soaplike), is composed of at least 12 different variants. These structurally different phases have been characterized by miscibility and x-ray diffraction techniques and are classified by code letters A to K inclusive (two new phases have also been recently characterized and given the preliminary code letters O and P) (*2*). An asterisk beside the code letter denotes chirality.

Generally, the molecular structures of materials that exhibit liquid crystal phases have overall shapes that induce this kind of behavior. For example, spherical molecules can form plastic crystals, disklike molecules can form discotic liquid crystals, and rodlike molecules can form nematic, cholesteric, and layered smectic phases. When the phases are composed of molecules with chiral or asymmetric molecular structures, their macroscopic structures sometimes become dissymmetric. For example, chiral disklike molecules can form helical columnar, discotic mesophases, while chiral rodlike molecules can form helical orientationally ordered modifications such as the Blue Phase (I, II, and III), the cholesteric phase, and layered smectic phases (C*, I*, and F*). The cholesteric and smectic phases, because of the relations developed between their macroscopic ordering and their microscopic structures, are the subject of this article. Examples of the molecular structures of materials that exhibit these phases are given in Fig. 1. The overall molecular structures of materials of this type have been described as lathlike (Fig. 1A). When a fluid mesophase—such as the cholesteric phase—is composed of optically active material, its structure becomes helical, whereas in the more ordered smectic state the inclusion of optically active molecules can sometimes result in the introduction of ferroelectricity and other related behaviors. In the following sections the connected phenomenon of form optical activity and the origins of ferroelectricity in these phases, and their relation to molecular structure, will be described.

Structures of Liquid Crystal Mesophases

Three categories can be used to distinguish among the dissymmetric mesophases of optically active liquid crystals. These classifications reflect the progressive stepwise breakdown in order of the system on passing from the solid to the liquid state with increasing temperature. It may be possible for one compound to exhibit all these phases in a melting process as shown in Fig. 2, but this has not yet been observed. These phases occur above the melting point (T_9) but below the clearing point (T_1) and are therefore termed enantiotropic because they are thermodynamically stable. Moreover, the phase transitions are reversible at a definite temperature (T_1 to T_8) and therefore do not undergo large supercooling. Phases that occur below the melting point and are seen on supercooling of the crystal are termed monotropic. [Phases also exist in which the molecules are orthogonal to the layers, for example A, B (hexatic), B (crystal), E, and so forth. Because these phases are not tilted they do not have helical structures, nor do they exhibit form optical activity or ferroelectric properties.]

Orientationally disordered or smectoid crystal phases. Smectic-like phases J*, G*, K*, and H* are the first step toward the liquid from the solid; they are essentially orientationally disordered solids (*3, 4*) that can be loosely described as anisotropic plastic crystals. The prime feature distinguishing these phases from ordinary solids is the molecular dynamics of the phase. Unlike the solid, the molecules in

---

The author is at AT&T Bell Laboratories, Murray Hill, NJ 07974.

these phases undergo rapid reorientational motion about their molecular long axes (*4*) (on a time scale of 10^{11} sec^{-1}). Melting from a solid to these phases involves an increase in the degree of rotational freedom primarily in a single dimension; in this direction, parallel to the tilt axis, they act like plastic crystals. This rapid reorientational motion, whether oscillatory or rotational, is presumed to be cooperative because the intermolecular distances for these phases determined by x-ray diffraction are usually too small for complete rotational freedom (*5*).

Order in the phases is similar to that in a solid because the phases are composed of periodic layers in which the long axes of the molecules are tilted with respect to the layer planes (Fig. 3). Consequently, the molecules have long-range positional ordering. All these phases have monoclinic symmetries. Two of the better understood phases, J and G, have an approximately hexagonal close-packed array of molecules in the plane normal to the tilt direction. These two phases differ structurally, however, in the direction of the tilt axis relative to the hexagonal packing matrix, which in the J phase is toward the apex of the hexagon and in the G phase is toward the side (*6*). Generally the phases have an AAA packing arrangement between layers.

When the J*, G*, K*, or H* phase is composed of optically active material, it has ferroelectric properties (*7*) because of its reduced symmetry. Yet the overall phase structure remains the same and does not have a helical ordering, and consequently it does not exhibit form optical activity. However, it contains chiral molecules, has a chiral symmetry (*8*), and hence exhibits ferroelectricity. (*7, 9*). (Conversely, if the phase were indeed helical, the helix would have an extremely large pitch.) Thus a bulk-aligned specimen of these phases would exhibit strong ferroelectric behavior. As with normal ferroelectrics, a multidomain structure usually dominates, which greatly reduces these properties.

Smectic liquid crystal phases. If a liquid crystal mesophase is defined as one in which the molecules do not have long-range positional order, then the phases S_C, S_I, and S_F correspond to the only tilted smectics (*10*). These three phases are divided into two groups. First, the S_I and S_F phases are analogous to the J and G smectic-like crystals except that they have only short-range, in-plane positional ordering of their molecular centers extending over a range of several hundred angstroms. They have long-range bond-orientational ordering, which is a measure of the extent of the registry of the orientation of the pseudohexagonal packing matrix both within and between the layers. The orientation of the packing net is long range in three dimensions; thus S_I and S_F are known as three-dimensionally stacked hexatic phases (*11*). The distinction between these two phases is again one of tilt direction, S_I being tilted toward the apex and S_F toward the side of the hexagonal net (*6, 12*).

Second, the S_C phase is the least ordered of the tilted smectic phases in that it has short-range, in-plane positional ordering of its constituent molecules extending over a range of only 15 Å. However, this phase has long-range orientational ordering of its tilt axis such that the molecules in a single domain are tilted roughly in the same direction. The layered structure is also looser than in the other phases and is essentially a one-dimensional density modulation (*13*).

On melting from the smectic-like crystal phases to the smectic liquid crystal phases, there is a breakdown in positional order. This systematically carries on through S_F or S_I (or both) and into the S_C phase, and the rotational and translational freedom of the molecules correspondingly increase.

When these phases are composed of optically active materials or contain optically active solutes, they too become dissymmetric by virtue of forming a helical ordering of their tilt directions. The tilted long axes of the molecules precess about an axis normal to the planes of the layers; thus, on passing from one layer to the next, the tilt axis is turned through an azimuthal angle in the same direction, causing a spiraling of the tilt direction (*14*). The helix so formed can be right- or left-handed depending on the material, as will be discussed later. The phases, code-lettered C*, I*, and F*, therefore exhibit form optical activity and are also commonly described as ferroelectric.

The cholesteric phase or chiral nematic phase. This phase is the best known of the liquid crystal phases (*1*) of optically active materials. It was termed the cholesteric phase because it was first discovered in derivatives of cholesterol, and the term has now been extended to include many nonsteroid examples. It is the optically active or helical version of the common nematic phase that is used in modern commercial display devices; therefore, the cholesteric phase could be better described as the chiral nematic phase.

In this phase, the molecules have no positional ordering or layered structure. In a given plane the molecules are orientationally ordered and are, on average, parallel to one another. On moving away above or below this plane there is a spiraling of the direction of the orientational order, thus forming a helical structure.

The cholesteric phase can form right- or left-handed helical structures that can selectively reflect light when the pitch of the helix is comparable to that of the wavelength of visible light. Moreover the pitch is temperature- and electrically sensitive (*15*), and consequently this phase has been utilized in surface thermography and in instruments such as encapsulated thermometers and thermochromic

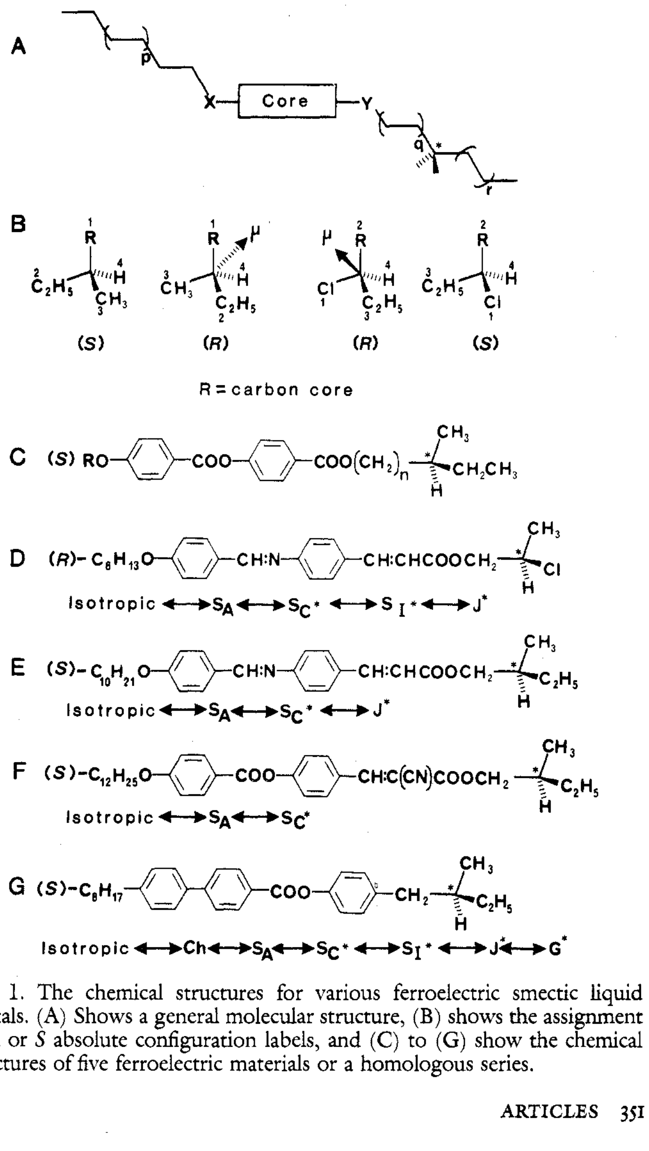


Fig. 1. The chemical structures for various ferroelectric smectic liquid crystals. (A) Shows a general molecular structure, (B) shows the assignment of *R* or *S* absolute configuration labels, and (C) to (G) show the chemical structures of five ferroelectric materials or a homologous series.

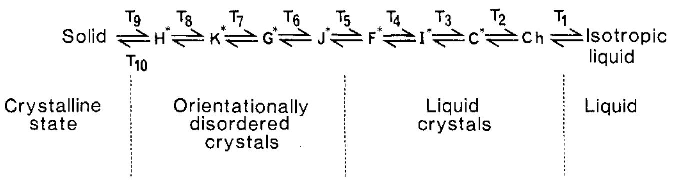


Fig. 2. The thermodynamic phase sequencing of liquid crystal phases that exhibit ferroelectric properties or form optical activity (or both). The asterisk indicates a phase composed of optically active material, which because of its local order has chiral symmetry. $T_9 > T_{10}$; Ch, cholesteric.

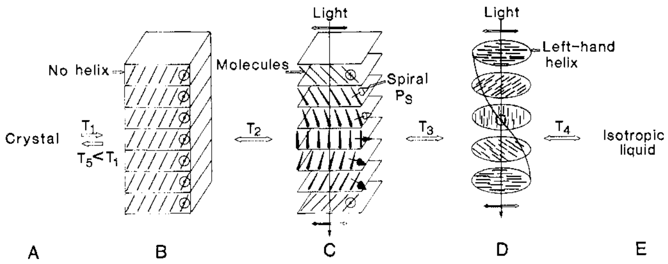


Fig. 3. A melting scheme for an optically active smectogen. First its melts from the crystal (A) to a smectic-like crystal (B, phases G*, H*, J*, and K*) (*7*), then to a smectic liquid crystal (C, phases S_{C*}, S_{I*}, and S_{F*}), to a cholesteric phase (D), and finally to the amorphous liquid (E). The short straight lines indicate the elongated molecules, and the arrows indicate the spontaneous polarization direction in each layer (the arrow symbol indicates the polarization vector relative to the dipole direction as ⊕↔ ⊖).

devices such as battery testers. These helical phases (Ch, S_{C*}, S_{I*}, and S_{F*}) have similar properties of light reflection and rotation of plane-polarized light when the direction of light propagation is parallel to the helical axis of the phase. The following sections will discuss how the macroscopic behavior of the rotation of plane-polarized light and the ferroelectric properties are affected by molecular structure and spatial configuration.

Optical Properties

Optical activity in systems described as being liquid crystalline in nature is restricted to the helical phases that conform to the more rigid definition of a liquid crystal. Thus, the cholesteric and smectic liquid crystal phases S_{C*}, S_{I*}, and S_{F*} exhibit form optical activity because of their helical ordering, while the smectic-like crystal phases apparently do not. Presumably this is because of the three-dimensional, long-range ordering in the structures of the crystal phases (*7*).

The cholesteric S_{C*}, S_{I*}, and S_{F*} phases are inherently optically active because their structures have a helical orientational ordering of the long axes of their constituent molecules. When a beam of plane-polarized light traverses these phases such that its direction of propagation is parallel to the helical axis, the plane of polarization is rotated in the same direction as the helix (*16*). Thus a right-handed helical structure rotates the plane of polarization counterclockwise [levorotatory, (−)], and a left-handed helix will rotate the plane clockwise [dextrorotatory, (+)], when the observer is looking into the oncoming beam. The helix therefore acts as a guide to the plane-polarized light.

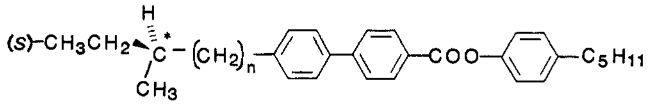
Generally, the degree of the optical rotation for a material in its liquid crystal phase is orders of magnitude greater than for the material in its liquid state or when it is dissolved in a solvent. This is because there is no organization in the liquid (or solution) state, and the plane-polarized light only interacts with randomly oriented individual molecules. Numerous investigations have been performed, most often by polarimetry, on optically active materials in solution or liquid form. The molar optical rotation of a material in a liquid matrix is described by Eq. 1 (*17*).

$$[\alpha]_{\lambda}^{T} = \frac{100\,\alpha}{lc} \qquad (1)$$

where $[\alpha]$ is the specific rotation, α is the measured rotation, c is the concentration (in grams per 100 ml), l is the length of sample in decimeters, T is the temperature, and λ is the wavelength of plane-polarized light. The specific optical rotation $[\alpha]$ of a material can be determined theoretically from Brewster's rules (*18*), which examine local group interactions about the chiral center of the material. Both the sign and magnitude of the optical rotation are determined by these interactions.

In liquid crystal systems, however, the sign and magnitude of the optical rotation are determined by the helical ordering and not by group interactions. Not surprisingly, therefore, there is no relation between the sign of the optical rotation [(+) or (−)] and its magnitude with Brewster's rules. Because no basic rules appeared to describe the relation of optical rotation and helical ordering, results for liquid crystal materials had to be compiled before a consensus of opinion could be reached.

One of the earliest observations made about liquid crystal materials concerned the position of the chiral center within the molecular structure of the material and its relation to optical rotation and spatial configuration. For example, consider the homologous series



As the position of the chiral center is removed incrementally away from the rigid central core of the molecule (from the last phenyl ring), the sign of the optical rotation of the cholesteric phase alternates from, say, (+) to (−) for $n = 1, 2, 3, \ldots$, for the above spatial configuration. Moreover, it was found that, as in solution chemistry, if the chiral center is inverted (say from S to R), then the sign of the optical rotation for the material also changes. A generalized form of these relations (*19*) is shown in Table 1.

R and S are the two absolute spatial configurations of the chiral center (*20*) (Fig. 1E) and are assigned on the basis of the priority of atomic number of the substituents attached to the chiral center. Although the relations given in Table 1 were relatively general for the materials known at the time they were formulated, they have been found to be less accurate for more recently synthesized materials. These relations have also been shown to be operable in the smectic state (*21*), and generally, when a cholesteric phase of known helical twist sense is cooled into a helical smectic phase, the twist direction is maintained. Furthermore, if a material exhibits cholesteric, smectic A (where the molecules are arranged with their long axes normal to the layer planes), and smectic C* phases, the two helical phases will have the same twist sense even though they are separated by a uniaxial phase; this indicates that similar interactions are in effect producing the helical ordering (*21*).

Symmetry and Ferroelectricity

The tilted smectic phases C, I, F, J, G, K, and H of nonoptically active materials have monoclinic environmental symmetries (*22*) and consequently have the following symmetry elements: a center of symmetry, a twofold axis normal to the tilt direction, and a mirror plane perpendicular to the tilt direction. When these phases contain optically active materials, the environmental symmetry elements are reduced to a single polar C_2 axis normal to the tilt direction of the phase and parallel to the layer planes (Fig. 4).

The result of the packing of the dipolar regions of the molecules in these phases requires that a spontaneous polarization, P_s, act along the twofold axis normal to the tilt direction as predicted by Meyer (*22*). Because these phases do not have highly organized structures, the molecules can be reoriented by applying an external field of known polarity. These qualities gave rise to the term ferroelectric for tilted smectic phases. In the helical phases the spontaneous polarization is rotated from one layer to the next about the helical axis (Fig. 3). Hence an individual layer is ferroelectric but the bulk phase is not because the spontaneous polarization is averaged to zero, and consequently the S_{C*}, S_{I*}, and S_{F*} phases have been alternatively described as helielectric (*23*). The smectoid phases that do not have helical ordering usually have multidomain structures in which the direction of the spontaneous polarization is scrambled, and again the bulk unaligned phase is not usually ferroelectric. Where the helix is unwound or multidomains are formed into a single domain, these phases become improper ferroelectrics (*24*). The cholesteric phase does not exhibit these properties because it has a uniaxial local environmental symmetry that is of too high an order to produce ferroelectric properties.

As the spontaneous polarization acts along the normal to the tilt direction of the molecules and parallel to the layer planes, two directions for the spontaneous polarization are possible (*25*) (Fig. 5). If the spontaneous polarization acts along the positive x direction when the molecule is tilted back into the page in the zy plane, it is denoted by $P_s(+)$, but if it acts along the negative x direction it is denoted by $P_s(-)$. Thus a material that exhibits a ferroelectric helical phase can be defined in terms of its optical activity and ferroelectric properties as (+) or (−) and $P_s(+)$ or $P_s(-)$.

Applications

One of the first utilizations of optically active liquid crystal mesophases came from their property of selectively reflecting visible light. When the pitch of the helix of the phase is comparable to the wavelength of visible light, it will reflect light of a single color. The pitch of the phase is also temperature-dependent, so that the combination of these properties can be used in the form of temperature sensors. In a gel formulation they have been used in the early detection of some cancers that show up as hot spots in the body. For these applications it is desirable to obtain the phase in the required temperature range with the necessary pitch to reflect visible light. Thus it is important to control the pitch and helical handedness by mixing materials together to produce the appropriate properties for the application.

Cholesteric mesophases have also been used in display technology as biasing additives for the common twisted nematic LCD to prevent reverse twist domains (*26*) from forming, in phase-change electrooptic displays, and as the host medium in colored guest-host displays. Thus the helical twist direction and the pitch of the helix are important factors in cell design and construction.

Applications of the smectic modifications arise from their ferroelectric properties; for example, recent studies have shown that the smetic C* phase can be utilized in a fast-switching light-valve device that has memory (*27*). This kind of application requires some control on the pitch of the helix such that it is comparable to, or larger than, the cell thickness. This allows the helix of the phase to be unwound in a homogeneously aligned cell by surface boundary conditions. The pitch of the helix can be controlled in a manner similar to that for cholesterics by blending together materials whose helices have different pitches or opposite twist directions. It is also desirable to control the magnitude of the spontaneous polarization in such applications because this has direct implications for the switching process of the device.

Table 1. Generalized (*19*) form of the relations between optical rotation and position of the chiral center relative to the core in cholesteric liquid crystal materials. The position of the chiral center is given by the odd (o) or even (e) number of atoms by which it is removed from the core.

Absolute configuration	Position of chiral center	Sign of optical rotation*
S	o	(−)
S	e	(+)
R	o	(+)
R	e	(−)

*(−) Levorotatory; (+) dextrorotatory.

It is also important to understand the relation between the microscopic properties of molecular structure and spatial configuration and the macroscopic properties of helical twist sense and spontaneous polarization direction. By knowing these relations, it may be possible to predict the absolute configuration of a material that has a single chiral center; the absolute configuration is a quality that cannot usually be determined by polarimetry for a previously uncharacterized substance.

Microscopic and Macroscopic Studies

Optical activity, spontaneous polarization, and parity. Investigations of the properties of optically active liquid crystal materials are often best performed on smectic mesophases because they offer opportu-

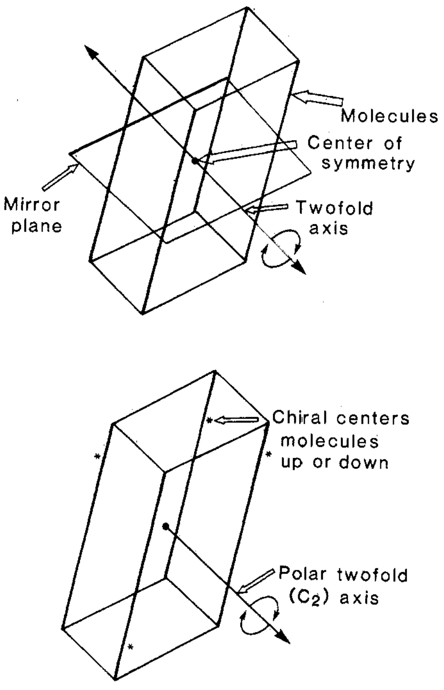


Fig. 4. Symmetry argument by Meyer (*22*) for ferroelectricity in tilted smectic liquid crystals. Monoclinic environmental symmetry is exhibited in smectic C (top), and reduced symmetry is exhibited in smectic C* (bottom).

Table 2. Effect of induction (I) and spontaneous polarization (P_s) on the extended rules for ferroelectric smectic liquid crystals. In these homologous series, $P_s(+)$ is equivalent to $(-)$ and $P_s(-)$ is equivalent to $(+)$.

Absolute configuration	Position of chiral center	Sign of optical rotation	Sign of inducive effect	Direction of spontaneous polarization
		Methyl-branched system $(+I)$		
S	o	$(-)$	$+I$	$P_s(+)$
S	e	$(+)$	$+I$	$P_s(-)$
R	o	$(+)$	$+I$	$P_s(-)$
R	e	$(-)$	$+I$	$P_s(+)$
		Chloro-branched system $(-I)$		
S	o	$(+)$	$-I$	$P_s(-)$
S	e	$(-)$	$-I$	$P_s(+)$
R	o	$(-)$	$-I$	$P_s(+)$
R	e	$(+)$	$-I$	$P_s(-)$

nities to study both optical activity, which is related to molecular configuration, and spontaneous polarization, which is related to the dipolar properties of the molecular structure. Therefore most of the examinations described were performed on ferroelectric smectic C* phases.

The types of material studied by Gray and McDonnell (*19*) were mostly derivatives of *S*-(−)-2-methylbutan-1-ol, and complete agreement was found with their rules for cholesterics (Table 1). Also as they suggested, the same helical twist sense [(+) or (−)] for a cholesteric mesophase was found in helical smectic phases formed on cooling. Thus for a system of the form shown in Fig. 1C in its smectic C* phase, for the absolute *S* configuration, and for removal of the chiral center from the core by an even number of atoms ($n + 1$ for $n = 1, 3, 5, \ldots$), a (+) rotation of the plane of plane-polarized light was found (*21*). The core, as defined in this case (*19*), terminates at the last phenyl ring, but more generally the atom count (for odd or even) should begin at the last axial bond of the most extended rigid structure that constitutes the core (*28*). In the case of the system shown in Fig. 1C, this is at the oxygen-carbon bond of the ester-terminal alkyl chain structure. The odd or even number count is denoted as the parity (*29*). When the chiral center is removed from the core by an odd number of atoms ($n + 1$ for $n = 2, 4, 6, \ldots$), the rotation becomes (−). Thus there is an alternation effect between the optical rotation [(+) or (−)] and incremental changes in n. As the homologous series ascends, the helical twist flips from left to right to left. Also there is an inversion in the sign of the optical rotation [(+) or (−)] if n is kept constant and the spatial configuration (*R* or *S*) is changed.

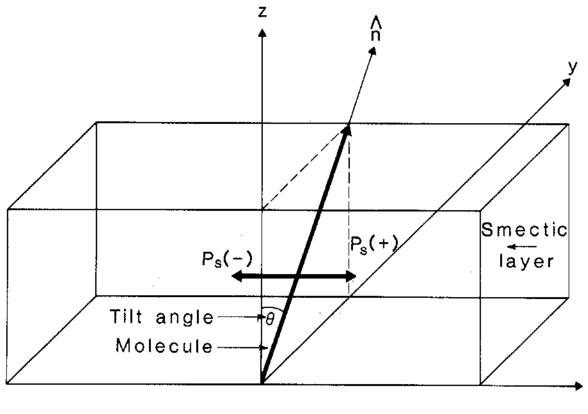


Fig. 5. The spontaneous polarization direction $P_s(+)$ or $P_s(-)$ in smectic liquid crystals.

The spontaneous polarization direction [$P_s(+)$, $P_s(-)$] was also found to alternate in a manner similar to that for the optical rotation (*21*). In the particular homologous series described, with even parity ($n + 1$ for $n = 1, 3, 5$), *S* absolute configuration, and (+) rotation, a negative spontaneous polarization [$P_s(-)$] was found; the reverse was the case for the odd members. From these initial studies it seems that the optical rotation and the spontaneous polarization are closely linked. Thus the rules for cholesterics were extended for smectics to include the spontaneous polarization direction (Table 2) (*21, 30*).

Steric and dipolar effects. The alternation of the spontaneous polarization and the optical rotation for incremental changes in parity suggests that both properties have similar causes. This cause resides at the chiral center of the molecule because, for example, the stronger its dipolar nature (*31*) or the more restricted the rotation of this center, the higher the spontaneous polarization; also the closer the chiral center is to the core, the tighter the helix (*32*). Conversely, the larger the dipole moment at the chiral center, the more effect it has on the spontaneous polarization. However, the helical pitch length is effected more by position than by dipolar environment (*15, 19*), so that although the two properties are closely related they are not strictly linked together.

As the parity is changed from even to odd, the molecular conformation in its all-*trans* conformation changes such that the position of the chiral center alternates back and forth along the terminal carbon chain (Fig. 6). Thus the lateral or off-axis substituent effect of the chiral center, whether it be dipolar or steric, also alternates with change in parity. This alternation of spatial configuraton in the extended all-*trans* conformation is probably the source of the alternations in the spontaneous polarization and optical rotation. This is based on the assumption that the all-*trans* or zig-zag conformation is the dominant conformation of the molecular species, even though the molecules are in a dynamic liquid-crystalline state (*33*). Yet as the value of n (or the parity) is increased, it is possible that changes in the terminal chain conformation can occur; this may produce inversions in the rules.

A distinction between the driving forces (steric or dipolar) for the optical and ferroelectric properties cannot be made on the basis of these results. However, the dipolar nature of the chiral center can be altered such that the steric bulk remains effectively in the same position as the dipole direction is reversed. This can be seen by comparing methyl- and chloro-branched systems (Fig. 1B) (*21*). The methyl group has a weak positive ($+I$) and the chloro group a strong negative ($-I$) inductive effect relative to hydrogen (Table 2). By comparing derivatives of these two systems in which the same absolute spatial configuration is maintained, an inversion of the rules for cholesterics (Table 1) can be obtained. Moreover, there is an inversion of the spontaneous polarization direction predicted earlier. For example, Fig. 1, D and E, shows the structures of two materials, (*R*)-HOBACPC and (*S*)-DOBAMBC (*34*). Although these materials do not quite fit the desired structures, for comparison they are fairly close (in HOBACPC the terminal chiral carbon chain is only three atoms long, whereas in DOBAMBC it is four atoms long). The absolute configuration is inverted (*R* to *S*) from one system to the other, but the optical rotation and spontaneous polarization remain the same (*21, 25*).

Thus it appears that the optical rotation and the spontaneous polarization are sensitive to changes in the dipole direction at the chiral center, not to steric forces, and that the helical handedness is controlled by the spatial orientation of this dipole. It is therefore probable that the initial rules for optical rotation in cholesterics (Table 1) are only half the possible rules because they were based on derivatives of *S*-(−)-2-methylbutan-1-ol, which has a positive inductive ($+I$) effect of the methyl group at the chiral center. When the optical center has a negative inductive ($-I$) effect (as in the chloro-

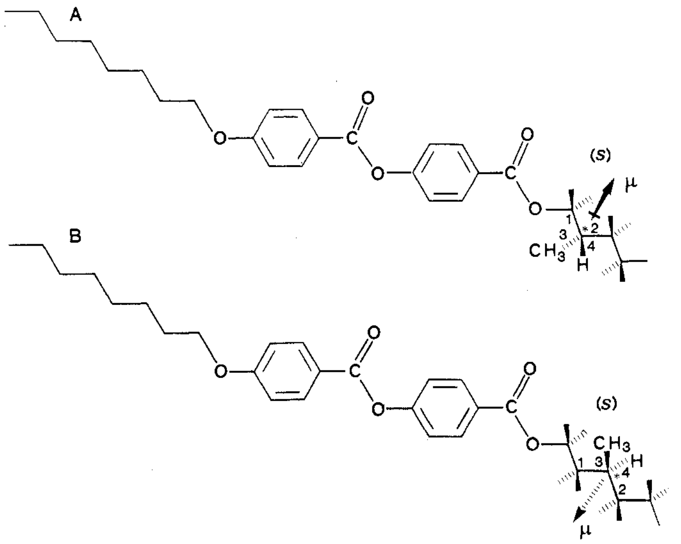


Fig. 6. All-*trans* conformational structure for liquid crystal materials showing the spatial configuration and dipole direction at the chiral center. The spatial dipolar orientation and steric bulk alternate with changing value of the parity. (A) Even, *S* absolute configuration, dextrorotatory, positive inductive effect, $P_s(-)$. (B) Odd, *S* absolute configuration, levorotatory, positive inductive effect, $P_s(+)$.

branched system), then the rules become inverted so that there are two forms (Table 2). These general rules for twist sense appear to encompass most of the materials investigated so far, in which the zig-zag-shaped molecules are packed in their layers in such a way that the terminal chains are closer to the normal to the layer planes than to the cores (*35*). Furthermore, in this situation it also seems that the optical rotation and the spontaneous polarization direction have opposite signs. However, there are some exceptions to these guidelines, and not enough materials have yet been examined to gain a more definite picture of the situation.

Exceptions. Until recently there seemed to be a direct one-to-one correlation between the spontaneous polarization direction and the sign of the optical rotation; that is, $P_s(-)$ is equivalent to $(+)$ and $P_s(+)$ is equivalent to $(-)$. However, recent studies have shown that this is not always the case. For example, derivatives of α-cyanocinnamic acid (*36, 37*) (Fig. 1F) exhibit the same sign of polarization and rotation. The well-known liquid crystal *S*-4-(2-methylbutyl)phenyl 4-*n*-octylbiphenyl-4′-carboxylate (8SI) (*38, 39*) (Fig. 1G) also falls into this category. Both these materials are therefore classified as follows: *S* absolute configuration, an even number of atoms by which the chiral center is removed from the core, (+) optical rotation, positive inductive effect, and positive spontaneous polarization. The optical rotation follows the predicted course, but the spontaneous polarization alters. Although these observations are the subject of continued investigations, it is believed that these compounds have a different layered structure in which the core is closer to the normal of the layer planes than are the terminal chains. This would cause an inversion of the spontaneous polarization but not necessarily of the optical rotation (*40*).

Investigations of the parity and its relation to molecular spatial arrangements, the effects of changing the priority in absolute configurations, and the resulting layered structures that are formed in the smectic phase continue. However, the rules given in Tables 1 and 2 for optical activity appear to apply in the helical, cholesteric phases and smectics C*, I*, and F*, whereas the rules relating microscopic structure to spontaneous polarization generally apply in the helical and nonhelical smectic modifications (C*, I*, F*, J*, G*, K*, and H*). These initial rules are important because (i) they allow the absolute spatial configuration of a material of unknown configuration to be determined, (ii) they provide guidelines for the blending of cholesterics to obtain pitch lengths for the helix of the phase that are useful in surface thermography techniques, and (iii) they allow the blending of ferroelectric smectics to provide mixtures with controlled helical pitch and spontaneous polarization for a range of devices and applications.

REFERENCES AND NOTES

1. F. Reinitzer, *Monatsh. Chem.* **9**, 421 (1888); O. Lehmann, *Z. Phys. Chem.(Leipzig)* **4**, 462 (1889).
2. J. W. Goodby, *Mol. Cryst. Liq. Cryst. Lett.* **92**, 171 (1983); H. R. Brand, P. E. Cladis, P. L. Finn, *Phys. Rev. A* **31**, 361 (1985). A. M. Levelut *et al.*, *J. Phys. (Paris)* **49**, 623 (1983).
3. G. P. Johari and J. W. Goodby, *J. Chem. Phys.* **77**, 5165 (1982).
4. A. J. Leadbetter, M. A. Mazid, R. M. Richardson, *Liquid Crystals*, S. Chandrasekhar, Ed. (Heyden, London, 1980), p. 65.
5. See, for example, A.-M. Levelut and M. Lambert, *C. Acad. Sci. Ser. B* **272**, 1018 (1971). The results are for the crystal B phase, which is the orthogonal variant of G and J.
6. P. A. C. Gane, A. J. Leadbetter, P. G. Wrighton, *Mol. Cryst. Liq. Cryst.* **66**, 247 (1984); G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals, Textures and Structures* (Hill, London, 1984).
7. H. R. Brand and P. E. Cladis, *J. Phys. (Paris) Lett.* **45**, 1053 (1984); *Mol. Cryst. Liq. Cryst.* **114**, 207 (1984).
8. S. T. Lagerwall and I. Dahl, *Mol. Cryst. Liq. Cryst.* **114**, 151 (1984).
9. J. W. Goodby, J. S. Patel, T. M. Leslie, *Ferroelectrics* **59**, 121 (1984).
10. Sir C. Frank, paper presented at the Tenth International Liquid Crystal Conference, York, England, 16 July 1984.
11. J. J. Benattar, F. Moussa, M. Lambert, *J. Chim. Phys.* **80**, 99 (1983); J. Budai *et al.*, *J. Phys. (Paris) Lett.* **45**, 1053 (1984).
12. A. J. Leadbetter *et al.*, *J. Phys. (Paris)* **40**, 27 (1979).
13. See, for example, J. Als-Nielsen *et al.*, *Phys. Rev. B* **22**, 312 (1980).
14. J. Doucet *et al.*, *J. Phys. (Paris)* **39**, 548 (1978).
15. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.* **37**, 189 (1976).
16. E. B. Priestley, *Introduction to Liquid Crystals*, E. B. Priestley, P. J. Wojtowicz, P. Sheng, Eds. (Plenum, New York, 1974), p. 203.
17. M. Orchin, F. Kaplan, R. S. Macomber, R. M. Wilson, H. Zimmer, *The Vocabulary of Organic Chemistry* (Wiley, New York, 1980), p. 125.
18. J. H. Brewster, *J. Am. Chem. Soc.* **81**, 5475 (1959); *ibid.*, p. 5483; *ibid.*, p. 5493.
19. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst. Lett.* **34**, 211 (1977).
20. E. L. Eliel, *Stereochemistry of Carbon Compounds* (McGraw-Hill, New York, 1962), p. 92.
21. J. W. Goodby and T. M. Leslie, *Mol. Cryst. Liq. Cryst.* **110**, 175 (1984).
22. R. B. Meyer, *ibid.* **40**, 33 (1977).
23. H. R. Brand, P. E. Cladis, P. L. Finn, *Phys. Rev. A.* **31**, 361 (1985).
24. See, for example, M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Oxford Univ. Press, Oxford, 1977), p. 347.
25. R. B. Meyer *et al.*, *J. Phys. (Paris) Lett.* **36**, L69 (1975); N. A. Clark and S. T. Lagerwall, *Ferroelectrics* **59**, 25 (1984).
26. Licristal, Liquid Crystals, EM Chemicals, data sheets EM154-81, p. 11, and EM11281.
27. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).
28. J. W. Goodby, unpublished results.
29. B. S. Schneider, personal communication.
30. J. W. Goodby, paper presented in the Tenth International Liquid Crystal Conference, York, England, 19 July 1984.
31. K. Yoshino *et al.*, *Jpn. J. Appl. Phys.* **23**, L175 (1984).
32. Ph. Martinôt-Lagarde, R. Duke, G. Durand, *Mol. Cryst. Liq. Cryst.* **75**, 249 (1981).
33. E. T. Samulski and R. Y. Dong, *J. Chem. Phys.* **77**, 5090 (1982).
34. P. Keller *et al.*, *C. R. Acad. Sci. Ser. C* **282**, 639 (1976).
35. R. Bartolino, J. Doucet, G. Durand, *Ann. Phys.* **3**, 389 (1978).
36. Ph. Martinôt-Lagarde, *J. Phys. (Paris) Colloq.* **C3**, 27 (1976); *ibid.*, p. 129.
37. J. W. Goodby and T. M. Leslie, *Liquid Crystals and Ordered Fluids*, A. C. Griffin and J. F. Johnson, Eds. (Plenum, New York, 1984), vol. 4, p. 1.
38. J. W. Goodby and G. W. Gray, *Mol. Cryst. Liq. Cryst. Lett.* **41**, 145 (1978).
39. *S*-4-(2-methylbutyl)phenyl 4-*n*-octylbiphenyl-4′-carboxylate (8SI) is now sold as CE8 by BDH Chemicals, Poole, England.
40. J. W. Goodby, unpublished results.
41. I thank J. S. Patel, J. M. Geary, T. M. Leslie, and E. Chin for their contributions to this work and S. T. Lagerwall, A. R. Kmetz, and P. E. Cladis for their helpful discussions. I dedicate this article to my late father.