Recent advances in thermotropic liquid crystals

N. V. Madhusudana
Raman Research Institute, C.V. Raman Avenue, Bangalore 560 080, India

Liquid crystals are states of condensed matter whose symmetries lie between those of 3-dimensionally periodic crystals and isotropic liquids. Thermotropic liquid crystalline phases are exhibited by a large number of organic compounds whose molecules have anisotropy of shape. A typical intermolecular energy responsible for the stability of the relevant order in the medium is comparable to the thermal energy, and thus liquid crystals are soft materials. Relatively weak interactions like those between molecular dipoles or chiral centers of appropriate molecules can give rise to new types of liquid crystals. Now more than 35 types are known, and many more are likely to be discovered in the future. The soft nature of the medium, coupled with anisotropic optical and dielectric properties gives rise to many electro-optic effects at relatively low voltages. These are exploited in liquid crystal displays (LCDs), which are the lowest power (~ 1 μW/cm²) consuming flat panel devices and used in all calculators, laptop and palmtop computers, cellphones, etc. Further, phase transitions between different types of liquid crystals, some of which are analogous to those in other materials like magnets or superconductors, offer a rich variety of problems of fundamental significance. As such, the R&D effort on liquid crystals has been growing steadily in the past three decades, resulting in better and cheaper displays as well as discoveries of new types of liquid crystals. The article gives a broad overview of the subject.

THERMOTROPIC liquid crystals¹² which are obtained by heating appropriate organic compounds made of anisotropic molecules are known since 1888. A rod-like shape of molecules is obtained by constructing them with two or more phenyl or cyclohexane rings with relatively rigid central groups and flexible alkyl chains attached to one or both ends, the latter facilitating a reduction in transition temperatures (Figure 1). The simplest liquid crystal is the nematic (N), in which the rods are in a liquid state, but with a spontaneous long-range orientational order (Figure 2). The local alignment direction of the long axes of the rods is denoted by n, an apolar unit vector. Optical, dielectric and other properties of the medium are anisotropic, which also exhibits a very weak curvature elasticity resisting gradients in the alignment of the medium. As such, weak electric poten-

tials (~ 1V) are enough to change the alignment, which can be used to produce large electro-optic effects. Indeed all commercial LCDs use nematic liquid crystals. A large effort to fine tune the elastic and various anisotropic properties to suit particular applications has led to the synthesis of a rich variety of chemicals, and now about 80,000 compounds are known to exhibit liquid crystalline phases. Typically, the nematic used in a display is a complex mixture with ~10 components. The best LCDs have a thin film transistor (TFT) through which each pixel is addressed, to overcome problems caused by the RMS-voltage dependence and the relatively slow (~ 50 msec) response time of the display.

![Figure 1](image1.png)

**Figure 1.** Structural formulae of two typical mesogenic compounds with rod-like molecules. **a**, p-azoxyanisole (crystal 118.2°C nematic 135.5°C isotropic); **b**, 4’-n-octyl-p-cyanobiphenyl (crystal 24°C smectic A, 34°C nematic 42.6°C isotropic) having the strongly polar cyano end group.

![Figure 2](image2.png)

**Figure 2.** Schematic diagram illustrating the orientational order in a nematic liquid crystal made of rod-like molecules. The director n represents the average orientation direction of the molecules.

e-mail: nmadhu@ri.ernet.in

1018

CURRENT SCIENCE, VOL. 80, NO. 8, 25 APRIL 2001
If the molecules are chiral, i.e. have a handedness, the intermolecular interactions produce a helical arrangement of the director $\mathbf{n}$ (Figure 3), and the pitch $P$ is usually of the order of 0.5 $\mu$m, i.e. wavelengths of visible light. The medium then reflects light of an appropriate colour, which shifts towards blue as the temperature is raised, as $P$ shrinks. This effect is exploited in thermography. Such a medium is denoted by the symbol N*, the superscript indicating the chirality of the molecules. It is also known as a cholesteric, as most of the early N* compounds, including cholesteric benzoate in which liquid crystals were discovered by Reinzter in 1888, were based on cholesterol.

Smeectic liquid crystals have a layered arrangement of orientationally ordered rod-like molecules, i.e. they are characterized by a translational periodicity indicated by the wave vector $\mathbf{q}$ of magnitude $2\pi/d$, where $d$ is the layer spacing. The medium is called smectic A (SmA) if $\mathbf{n}$ is parallel to $\mathbf{q}$, and SmC if there is a tilt angle $\theta$ between the two vectors (Figure 4).

The operating voltage of LCDs can be reduced by increasing the dielectric anisotropy of the liquid crystal, which can be achieved by attaching the highly polar cyan or nitro end groups to the molecules. The electrostatic interactions between the molecules are then strong enough to produce new phenomena in such materials. In most such compounds the interaction favours an antiparallel arrangement of nearest neighbours. It is also possible to imagine that antiparallel pairs are formed, due to the frustration effects on the orientation of a third molecule. Further, as the strongest attractive interaction is due to the dispersion forces between the aromatic cores, the pair takes on a configuration in which the alkyl chains are thrown away on opposite sides and hardly interact (Figure 5 a). Indeed the pair is also apolar in character, naturally accounting for the apolar nature of the director $\mathbf{n}$ in the nematics made of the highly polar compounds. Many such compounds with relatively long (with more than 6 carbon atoms) chains exhibit the SmA phase, with a layer spacing $d$ which corresponds to the length of an antiparallel pair, i.e. $d > l$, where $l$ is the molecular length. This is called the partial bilayer smectic structure, and indicated by SmA*.

Curiously, many such compounds reenter the nematic phase as they are cooled from SmA*. Often there is a double reentrance, as the sequence of transitions on cooling is $N \rightarrow$ SmA* $\rightarrow$ N* $\rightarrow$ SmA*, in which the
lower temperature smectic has a monolayer spacing, with \( d = l \). In some very rare cases, a quadruple reentrant occurs, in which an additional pair of \( N_c \) and SmA_{*} is exhibited. A phenomenological Landau theory which takes into account a coupling between two smectic order parameters corresponding to the partial bilayer and monolayer lengths has been developed by Prost to account for all the phenomena\(^2\). It should be noted that the monolayer is not a consequence of the break up of the antiparallel pairs, as this would then be preferred at high temperatures, while the SmA_{*} phase is the low temperature reentrant phase. The permanent dipolar interaction favouring the antiparallel pairing is \( \propto r^3 \), where \( r \) is a typical intermolecular distance, \( = \) the molecular diameter. If we now consider a parallel configuration (Figure 5 b), the dipole of a given molecule induces a dipole in the highly polarizable aromatic core of its neighbour which is oppositely oriented to the permanent dipole of the latter. Thus, the net dipole moment and hence the repulsive interaction is reduced. Further, in this configuration, the chains which are in close proximity have an attractive dispersion interaction. Both these interactions favouring the parallel configuration are \( \propto r^{-n} \), while the dipolar interaction favouring the antiparallel configuration is \( \propto r^3 \). As the temperature is reduced, the density of the medium increases, and the parallel configuration which can exhibit the SmA_{*} phase at relatively low temperatures is favoured, thus making way for the reentrance of the nematic\(^3\). The parallel configuration gives rise to a polar short range order, which has been demonstrated in recent high electric field experiments\(^6\). In compounds with additional dipolar groups in the aromatic core, the longitudinal components of which are opposite in direction to that of the cyano- or nitro- end dipoles, the electrostatic interaction favours a bilayer structure with the layer spacing \( d = 2l \), i.e. twice the molecular length and denoted by SmA_{*}. Many compounds exhibit a SmC_{*} to SmA_{*} transition as they are cooled. As the symmetries of both the smectics are the same, the transition can only be first order in nature, with a jump in the layer spacing \( d \), which can reduce as a function of an external parameter like the composition in a mixture, and beyond a critical point SmA_{*} has a continuous evolution to the SmA_{*} structure without a phase transition, in analogy with the liquid–gas case. Another way of relieving the frustration effects in the highly dipolar compounds with many dipolar groups in the molecules is for the phase of the bilayer to change periodically in the plane of the layers, i.e. the interface between the molecular layers is alternately aromatic and aliphatic in nature (Figure 6). The lateral modulation is necessarily 2-dimensional in nature. The medium has an antiphase character and is denoted by SmA_{*}. In some cases the aromatic and aliphatic regions have different widths and the structure is described as crenellated, and denoted by the symbol SmA_{*}. A few polar compounds also exhibit the tilted versions of these sub-phases. Thus, SmC_{*}, as well as the antiphase and crenellated versions of SmC_{*} are also known\(^3\).

If the smectogen has chiral molecules, the helix of SmC_{*} has a helical arrangement about the layer normal, i.e. about \( \mathbf{q} \), as in the cholesteric phase. Further, in each smectic layer as the plane containing \( \mathbf{n} \) and \( \mathbf{q} \) lacks mirror symmetry, the direction along \( \mathbf{n} \times \mathbf{q} \), which is orthogonal to that plane, has the characteristic of a polar vector\(^7\). It exhibits an electric polarization \( \mathbf{p} \), which also has a helical arrangement and the medium is helielectric in nature, though it is usually called ferroelectric in the literature. If a SmC_{*} sample is taken in a very thin (~2 \( \mu \)m) cell, the helix is unwind due to surface interactions and the structure is then a true ferroelectric which exhibits a fast (~10 \( \mu \)s) and bistable electro-optic switching\(^8\), depending on the sign of the external electric field which has a linear coupling with \( \mathbf{p} \). Though much effort has been expended in the past two decades to exploit this effect in LCDs, large scale commercialization has not materialized, because of the complex surface interaction of the polarized medium and the rather slow healing of any misalignment caused by mechanical vibrations of the cell.

The effort, however, resulted in the discovery of several new liquid crystals. Some materials were found to have a trilevel switching at low temperatures, which can be understood if successive layers have opposite tilt orientations, and hence an antiferroelectric (SmC_{*}*) character\(^2\). Later studies showed that the materials exhibit a variety of different liquid crystals. A typical sequence on cooling\(^9\) is: SmA–SmC_{*}–SmC_{*}^{*}–SmC_{*}^{*}_r–SmC_{*}^{*}_{r2}–SmC_{*}^{*}_{r3}–SmC_{*}. The full sequence
can be understood on the basis of a chiral axial next-nearest neighbour $xy$ (ANNXY) model in which the charge densities created by splay fluctuations of the layer polarization lead to a frustrating antiferroelectric NNN interaction. Both SmC*$_{a}$ and SmC*$_{b}$ have ferroelectric characteristics, and an effective polarization less than that of the full value in the ferroelectric, which is now called SmC*$_{d}$. The structures predicted by this model (Figure 7) can explain the observations of the influence on them of an external DC electric field and are supported by the recent anomalous X-ray scattering experiments. The antiferroelectric liquid crystal may also be used to make LCDs, but the really technologically important electro-optic effect is shown by some materials taken in very thin cells: they exhibit thresholdless (also called V-shaped) switching which requires TFT-backing for exploitation. It has a short switching time, and a very large viewing angle and may be exploited commercially in the near future.

Smectic liquid crystals are 1-dimensional crystals, and the compression elastic constant measured along the crystalline direction is rather large (~$10^{7}$ cgs units) compared to the weak curvature elastic constants of the director field (~$10^{5}$ cgs units). A twist deformation of $\mathbf{n}$, involving $\nabla \times \mathbf{n}$ necessarily changes the layer spacing in the SmA liquid crystal and is disallowed, just as a magnetic field ($\nabla \times \mathbf{A}$, where $\mathbf{A}$ is the vector potential) is expelled from a superconductor. However as in the latter case, in a type II material, a ‘mixed’ phase can be stabilized if the molecular chirality is strong enough. It is called a twist grain boundary $A$ (TGB$_{A}$) liquid crystal, in which TGBs made of linear arrays of screw dislocations produce a relative twist (~$10^5$) between smectic A-like blocks which are ~ 200 Å thick. The TGB helical axis is orthogonal to $\mathbf{n}$, i.e. $\mathbf{q}$ (Figure 8). In the TGB$_{C}$, smectic C-like blocks twist across TGBs, with the helical axis being orthogonal to both $\mathbf{n}$ and $\mathbf{n} \times \mathbf{q}$ (Figure 9). In the undulated twist grain boundary $C^*$ (UTGB) liquid crystal, the blocks are smectic.
Indeed TGB liquid crystals corresponding to even the antiferroelectric structure have been discovered\textsuperscript{11}, though the twist angle between the relatively thin (\textasciitilde 30 \text{ Å}) blocks is rather large, either 90\textdegree in a few different tetragonal (T\textsubscript{1}–T\textsubscript{3H}) structures or 120\textdegree in a hexagonal (H) one. The TGB liquid crystals are examples of states in which defects are generated by the incompatibility of the tendency to twist because of strong chirality of the molecules with the layering order. The earliest examples of such defect structures are found in the blue phases which occur in a narrow temperature range (\textasciitilde 2\textdegree) between the cholesteric and isotropic phases of several highly chiral compounds\textsuperscript{2}. The director \( \mathbf{n} \) has a tendency to twist about two mutually orthogonal directions in a plane perpendicular to itself, which would produce a double twisted cylindrical structure. These in turn can organize themselves in different 3-dimensional structures which would inevitably result in disclinations lines, about which the orientation of director \( \mathbf{n} \) changes discontinuously. As the temperature is raised, some materials exhibit three different blue phases. In BP\textsubscript{1} the disclinations have a simple cubic structure, while in BP\textsubscript{2} they have a body-centered cubic structure. BP\textsubscript{3} has a liquid-like arrangement of the double twist cylinders. As the temperature is lowered by even a couple of degrees the cost of the disclinations becomes larger than the chiral energy gained in the double twisting in the cylinders and the medium adopts the cholesteric structure with a helical arrangement along a single axis.

The layered smectic liquid crystals can be drawn across holes (\textasciitilde 5 \text{ mm} in diameter) in glass or other substrates to form stable free standing films whose
thickness can be controlled to be anywhere between two to a few hundred layers. Such essentially monodomain smectic films with very low mosaicity have been used to study the structure within the layers using both X-ray and electron diffraction techniques. Very thin films with just a few layers are 2-dimensional in nature and the dislocation unbinding theory of the melting of 2-D crystals with quasi-long range translational order becomes applicable. The melt then exhibits a quasi-long range bond orientational order (BOO) in which the fictitious bonds between the centers of the molecules in the layers exhibit a six-fold symmetric correlation in a monodomain sample. This hexatic phase is obviously a two-dimensional liquid crystal and goes over to a true isotropic structure with only a short range BOO by the unbinding of disclinations. In thick films with several hundred layers the sample can be considered to be three-dimensional in nature and the hexatic phase exhibits a truly long range BOO. If the molecules are orthogonal to the layers, it is called hexatic smectic B (SmB). If the molecules are tilted, three different structures become possible. If the tilt is along intermolecular bonds, it is called hexatic smectic I (SmI), if it is along the direction between the given molecule and the mid-point of the bond between two of its closest neighbours, it is hexatic smectic F (SmF). If the tilt orientation is between these two, it is hexatic smectic L (SmL), in which the layer has no mirror planes and is hence chiral in nature, even though the molecules can be non-chiral (Figure 11). Chiral compounds also exhibit hexatic phases and many examples of compounds exhibiting SmL* and SmF* are known. Further, many antiferroelectrics also exhibit at low temperatures the antiferroelectric version of the hexatic I, i.e. the SmL*_a phase.

Shape anisotropy of a different kind is realized in molecules which are disc shaped. Compounds with such molecules also exhibit the nematic phase in which the director is defined as the average orientation direction of the symmetry axes of the disc, i.e. their short axes, and denoted by N_d. Further, the discs can stack on each other to form columns in which the molecules have liquid-like correlations. The columns themselves can be arranged to form different 2-dimensional lattices. A hexagonal lattice is denoted by D_h, a rectangular one by D_r and a tilted one by D_t (Figure 12). If the molecules are chiral the tilted columnar liquid crystal exhibits a ferroelectric polarization as well. The columnar liquid crystals which have a 2-dimensional crystalline and 1-dimensional liquid nature are the most highly ordered ones at the molecular level.

In all the compounds which have been synthesized up to now, the molecules do not deviate strongly from cylindrical symmetry whether they are rod like or disc like. However a new type of geometrical shape which is characterized by such a deviation has been shown to lead to the formation of liquid crystals in the past couple of years. The molecules have a strongly bent core, with a bend angle of about 120°. They are also described as bow shaped, or more popularly, as banana-shaped molecules. In the simplest liquid crystalline structure, the molecules are packed in smectic layers such that the 'arrow' directions are parallel and lie in the layer plane. This obviously produces a transverse polarization of the layers, even though the molecules are achiral. Careful observations on free standing films have shown that the molecules are not upright, but tilt about the arrow direction. This has the consequence that the layers have no mirror planes (Figure 13), i.e. they become chiral, even though the constituent molecules are achiral. The chiral sense depends on that of the tilt with reference to the polarization p. The molecules in successive layers are oriented such that they have an antiferroelectric arrangement. If the chiral sense of successive layers is the same, a helical structure results. Both left-handed and right-handed helices occur with equal probability, as the molecules themselves are achiral. An arrangement in which successive layers have opposite chirality, i.e. are racemic, has a slightly lower energy than the homochiral one. The layer polarization can be switched by moderate electric fields. This is a new type of structure, not seen in other liquid

Figure 11. Schematic representation of the different types of hexatic phases with tilted molecules, indicated by arrow heads (a) SmI, (b) SmF and (c) SmL.
crystals. It is now called the B₂ liquid crystal. Theoretical studies show that several smectic structures with different mutual orientations of the polarization and tilt, which can be such that \( p \) has a longitudinal component, are possible, and remain to be discovered\(^\text{22} \). Experimentally, four other types of ‘banana (B)’ liquid crystals have been discovered. In the B₁ phase there is a two-dimensional periodicity, i.e., a columnar structure which is not switchable by an electric field. The B₂ phase is moderately switchable. The B₁ and B₂ phases are identified only in a couple of compounds. The B₁ forms beautiful twisted thread-like structures as it separates from the isotropic phase\(^\text{29} \). Monodomain samples of these liquid crystals have proved to be difficult to get, and their detailed structures are not established.

An interesting aspect of recent studies is that in a homologous series the longest ones exhibit the B₂ phase, intermediate ones the B₁ phase and the short ones the B₆ phase\(^\text{27} \). In a recent study on a binary mixture of a banana compound which shows the B₂ phase and one with rod-like molecules which shows the SmA₂ phase, the mixtures were found to show the B₁ and B₆ phases as the concentration of the rods was increased. More interestingly, mixtures with a relatively low concentration of the bananas (~5 to 12%) showed a biaxial SmA₂b phase\(^\text{28} \), in which the bow-shaped molecules are arranged with their arrows along the layer normal, i.e., rotated by 90° with respect to their orientation in the B-liquid crystals (Figure 14). A biaxial smectic phase has to be described by three mutually orthogonal apolar director fields and was known earlier only in a polymeric liquid crystal\(^\text{39} \), which also exhibits a biaxial nematic (N₆) phase. In low molecular weight liquid crystals, the N₆ phase appears to have been unambiguously seen only recently\(^\text{40} \).

Though around 35 different types of liquid crystals have been identified up to now, the LCD industry almost exclusively uses nematics, as mentioned earlier. The most useful electrooptic effects are those which occur in...
twisted nematic (TN) devices, in the simplest of which the director rotates by 90° from the top to the bottom plate. An electric field applied between the plates reorients the director out of the plane parallel to the plates beyond a threshold voltage. The optical anisotropy is then exploited to convert this reorientation to a contrast between the energized and nonenergized parts of the display. The optical anisotropy also produces an undesirable effect: light beams propagating in directions in which they are essentially along the director feel a different anisotropy compared to those which are in an orthogonal direction. This produces the well-known ‘angle of viewing’ problem seen in typical LCDs. Compensation films which can to some extent overcome this problem, as well as the problem arising because of dispersion of birefringence in the supertwisted nematic (STN, with a twist angle of 180°) have been developed. The best solution to the angle of viewing problem is the in-plane switching mode in which the electric field is applied between electrodes separated by ~50μm on the same plate, so that the director reorientation occurs only in a plane parallel to the glass plates. Commercial displays using this technique (called super-TFT) have become available recently. Most TFTs use amorphous silicon in which the mobility is relatively low. There have been serious attempts to grow polysilicon transistors on display glass plates. The increased mobility allows the addressing circuitry also to be incorporated at the periphery of the display itself, thus bringing down the complexity and cost of the display module. In relatively simpler and cheaper devices (as in cell phone displays, for example), it is useful to directly address a matrix display without the aid of TFTs. In relatively fast responding devices, it is far better to use a multitine rather than a line-by-line addressing technique to get a uniform appearance of the display, and to lower the supply voltage.

In this article, we have given a brief summary of the many new types of liquid crystals which have been discovered in thermotropics made of relatively low molecular weight compounds, and the status of the LCDs exploiting nematics. We have not discussed liquid crystals made of other types of materials. Lyotropic liquid crystals are made of self-assembled anisotropic objects which are formed when amphiphilic molecules (like soap molecules) are dissolved in a solvent like water. Such liquid crystals are obviously important in the soap industry. Some biological systems also exhibit lyotropic mesomorphism. Polymeric liquid crystals find applications in the manufacture of high strength fibres.


ACKNOWLEDGEMENTS. I thank Drs R. Pratibha, P. A. Pramod and Mr S. Seshachala for the figures.