Liquid crystals have been known for about one hundred years. Friedrich Reintzer is given credit for their discovery. However, papers written in the mid-1850s describe systems that match the properties we now ascribe to liquid crystals. Studies of the properties and structures of liquid crystals began in the 1950s after the publication of the review by G. H. Brown and W. G. Shaw in Chem. Rev., 57, 1049 (1957).

Conventionally, scientists think of matter existing in one of three well-defined states of aggregation, namely solids, liquids, and gases. In the gaseous state the particles are free to roam through the entire volume of their container with almost no constraints. The liquid state does not exhibit long range molecular order; however, the molecules are relatively uninhibited in rotation around the long axis of the molecule. In the solid state, the intermolecular distances are about the size of the molecules. The dominant feature of the crystalline state is the strong bonding between molecules giving this state of matter an orderly arrangement. Liquid crystals are another state of matter, structurally falling between the solid and the liquid states.

Reintzer found the compound cholesteryl benzoate (thermotropic liquid crystal) changed phases on heating. At room temperature the benzoate is a white crystalline solid. On heating to 145° the crystal structure collapses to form a turbid liquid (liquid crystal). On further heating the turbid structure collapses at 179° to a liquid. On cooling the process reverses itself.

Reintzer's second and most interesting observation was that the turbid liquid changed color as the temperature changed, going from red to blue with an increase in temperature and reversing the color pattern as the system was cooled. Not all liquid crystalline compounds show color changes with change in temperature.

Presently liquid crystals can be divided into two categories, thermotropic and lyotropic, according to the principal means of destroying the order in the parent solid state. Probably the most widely studied category is the thermotropic. Thermotropic liquid crystals are prepared by heating a substance or substances.

Lyotropic liquid crystals can be formed when certain compounds are treated with a controlled amount of water or other polar solvent. The properties of this birefringent fluid resemble those of the birefringent fluid formed by heating certain solids. Liquid crystals exhibit properties that are not found in either liquids or solids. Some specific properties of thermotropic liquid crystals include (1) formation of “monocrystals” (molecular order in one dimension) with application of ordinary magnetic and/or electric fields; (2) optical activity of cholesteric liquid crystals of a magnitude without parallel in other states of matter; (3) sensitivity of the cholesteric structure to a temperature change which results in color changes.

Molecular Shape and Liquid Crystallinity

As an aid in selecting compounds that may exhibit liquid crystallinity, some general statements can be made about the geometry of molecules that form liquid crystals. Some guidelines for selection of organic thermotropic liquid crystalline compounds may be summarized as follows: (1) The majority of liquid crystalline compounds have aromatic nuclei which are polarizable, planar, and rigid; (2) the central group (x) in the molecule usually contains a multiple bond along the long axis of the molecule or a system of conjugated double bonds, or involves a dimerization of carboxyl groups; (3) the central group (x) connecting two benzene rings should constitute a flat or rod-like core of the molecule; (4) the length of the molecule should be greater than its diameter (assuming a cylindrical geometry); (5) a strong polar group near the center of the molecule and along the molecular axis generally enhances liquid crystallinity; and, (6) weak polar groups at the extremities of the molecule enhance liquid crystallinity.

The most common molecular shape is the cylindrical one. A typical molecular structure may be illustrated as follows:

```
     (terminal group) A—O——X——O——B (terminal group)

     Central group
```

A and B are terminal units such as methyl (CH₃), ethyl (C₂H₅), methoxy (OCH₃), ethoxy (OC₂H₅), halogens etc. The central group or linkage can be, for example,

```
     —N=C—C——C——C=N—
```

A typical compound would be p-methoxybenzylidene-p-n-butyrylaniline (MBBA). The molecule is about 20 Å long and 7 Å in diameter.

A second molecular shape is the cholesteric. Cholesteric liquid crystals (often called cholesteric-nematic or chiral-nematic) require the existence of a center of chirality within the molecule. A chiral molecule cannot be superimposed on its mirror image. The cholesteric esters are the most common cholesteric structures and have a molecular shape which accounts for their unique optical properties. In the table is shown the skeletal structure for cholesteryl nonanoate.

A third molecular shape is disc-like. Probably the first
Thermotropic Liquid Crystalline Compounds Typically Have Aromatic Nuclei

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>Liquid crystalline range, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CLASSICAL NEMATIC LIQUID CRYSTALS</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_2\text{O} ) ( \text{C}=\text{N} ) ( \text{C}_6\text{H}_5 ) ( \text{n} )</td>
<td>4-Methoxybenzylidene-4'-n-butylaniline (MBBA)</td>
<td>21-47</td>
</tr>
<tr>
<td>( \text{CH}_2\text{O} ) ( \text{N}=\text{N} ) ( \text{C}_6\text{H}_5 ) ( \text{n} )</td>
<td>4-Methoxy-4'-n-butylazoxybenzene</td>
<td>19-76 (mixture of isomers)</td>
</tr>
<tr>
<td>( \text{CH}_2\text{O} ) ( \text{N}=\text{N} ) ( \text{O}\text{CH}_3 )</td>
<td>( p )-Azoxyanisole (PAA)</td>
<td>117-137</td>
</tr>
<tr>
<td>( n\cdot\text{C}_6\text{H}_5 ) ( \text{C} ) ( \text{CN} )</td>
<td>4-n-Hexyl-4'-cyanobiphenyl</td>
<td>14-25</td>
</tr>
<tr>
<td><strong>SPONTANEOUSLY TWISTED NEMATIC LIQUID CRYSTALS (CHOLESTERICS)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cholesteryl nonanoate</td>
<td>145-179</td>
</tr>
<tr>
<td>( \text{CH}_3\text{(CH}_2\text{)}_3 \text{COO} ) ( \text{H} )</td>
<td>((-)-2-Methylbutyl 4-methoxybenzylidene-4'-aminocinnamate</td>
<td>76-125</td>
</tr>
</tbody>
</table>

| **SMECTIC LIQUID CRYSTALS** | | |
| Smectic A: | | |
| \( \text{C}_6\text{H}_5\text{OH} \) \( \text{C} \) \( \text{N}=\text{N} \) \( \text{C}\text{H}=\text{O} \) \( \text{COOC}_6\text{H}_5 \) | Ethyl-\( p\)-(\( p'\)-phenylbenzalminio)-benzoate | 121-131 |
| Smectic B: | | |
| \( \text{C}_6\text{H}_5\text{OH} \) \( \text{C} \) \( \text{N}=\text{N} \) \( \text{CH}=\text{OH} \) \( \text{COOC}_6\text{H}_5 \) | Ethyl-\( p\)-ethoxybenzal-\( p'\)-amino cinnamate | 77-116 |
| Smectic C: | | |
| \( n\cdot\text{C}_6\text{H}_5\text{O} \) \( \text{COOH} \) | \( p\)-\( n\)-Octyloxybenzolic acid | 106-147 |
| Smectic D: | | |
| \( n\cdot\text{C}_6\text{H}_5\text{O} \) \( \text{NO}_2 \) \( \text{COOH} \) | \( 4'\)-Octadeoxy-3'-nitro-diphenyl-4-carboxylic acid | 159-195 |
| Smectic E: | | |
| \( \text{C}_6\text{H}_5\text{OOC} \) \( \text{N}=\text{N} \) \( \text{C} \) \( \text{H}=\text{CH} \) \( \text{COOC}_6\text{H}_5 \) | Diethyl-\( p\)-terphenyl-\( p\)-\( p'\)-carboxylate | 173-189 |
| Smectic F and G: | | |
| \( n\cdot\text{C}_6\text{H}_5\text{O} \) \( \text{N}=\text{N} \) \( \text{C} \) \( \text{H}=\text{CH} \) | 2-(\( p\)-Pentyphenyl)-5-(\( p\)-pentyloxyphenyl)pyrimidine | 103-114 (F) 79-103 (G) |
| Smectic H: | | |
| \( \text{C}_6\text{H}_5\text{O} \) \( \text{N}=\text{N} \) \( \text{C} \) \( \text{H}=\text{CH} \) | 4-Butyloxybenzal-4-ethylaniline | 40.5-65.5 |
| Smectic I | | |
| \( n\cdot\text{C}_6\text{H}_5\text{O} \) \( \text{N}=\text{N} \) \( \text{C} \) \( \text{H}=\text{CH} \) | \( n\)-Pentyl-4-(\( 4'\)-\( n\)-decyloxybenzylidene amino)cinnamate | 73.8-97.0 |

| **DISCOTIC LIQUID CRYSTALS** | | |
| \( \text{C}_6\text{H}_5\text{O} \) \( \text{OCH}_3 \) | Hexabutoxytriphenylene | 88.6-145.6 |
relatively small disc-like molecules prepared in the laboratory were benzenehexa-alkanoates and hexa-alkoxytriphenylenes. This type of liquid crystal has been given several names; “discotic” will be used in this paper. A skeletal structure of hexaalkoxytriphenylene is shown in the table.

Thermotropic Liquid Crystals

Thousands of organic compounds show liquid crystallinity on heating. These are referred to as thermotropic liquid crystals. The table includes an abbreviated collection of thermotropic liquid crystals.

Thermotropic liquid crystals can be further classified as nematic and smectic structures. Although there are several types of nematic liquid crystals, our discussion will be limited to the ordinary and cholesteric structures.

Ordinary Nematic Structure

The arrangement of molecules in the ordinary nematic liquid crystal is represented schematically in Figure 1a. The lines in the figure represent the molecules within the structure. The direction in space of the principal axis of the molecules (the director \( n \)) is arbitrary with the only structural restriction being that the long axes of the molecules maintain a parallel or nearly parallel arrangement. This has been identified as one-dimensional packing.

Liquid crystals in the nematic phase can be transformed on heating to an isotropic liquid. This is a first order transition, the enthalpy of which is generally between 0.1 and 1.0 kcal/mole. Although the orientation of the molecules in a nematic liquid crystal is incomplete, the measure of the degree of orientation can be reasonably expressed by a single-order parameter (\( S \)).

\[
S = \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)
\]

where \( \theta \) denotes the angle between the long molecular axis and the nematic symmetry axis. Experimental values of \( S \) (order parameter) range from near 0.4 at the nematic-isotropic point to near 0.6 in the lower temperature. \( S \) is equal to 1 when the molecules are completely oriented and when their long axes are all parallel.

Cholesteric Structures

A common packing of the molecules in the cholesteric phase is helical. In a qualitative way, this molecular packing can be described as a layer packing of the molecules followed by a superimposed twist which generates a helix. You will note in Figure 1b that the molecules in the lower layer have the long axes directed so that the long axes lie essentially parallel to one another. If you look at the second layer, you will notice that the director of the molecule has its long axis parallel to its neighbor. If one continues packing these layers one on top of another while superimposing a twist, one finally completes a structure which is like a winding staircase. This is referred to as a helical packing. An interesting item to focus on at this point is that this helix diffracts light. It has been known for a long time that a solid such as salt will diffract x-radiation, but the diffraction of molecular packing which occurs in visible light has almost been ignored.

The pitch, \( p \), and hence the reflection color of this helix is strongly temperature-dependent. Thin, homogeneously aligned layers of these cholesteric-nematic compounds are good temperature sensors. Usually the pitch decreases as the temperature increases, and the reflection bands are shifted to shorter wavelengths (toward blue). The temperature sensitivity is extremely strong in the neighborhood of a cholesteric to smectic phase transition. Cholesteric compounds with pitches less than about 700 nm have recently been observed to exhibit a “blue phase” between the isotropic and cholesteric regions.

Smectic Liquid Crystals

Over the last few years, research activity with the smectic type of liquid crystals has increased greatly. There are at least nine classes of smectic liquid crystals. Of these, eight have molecular packings arranged in layers with characteristic packings between and within layers. The remaining smectic structure, known as \( S_{xy} \), is isotropic. It does not show layer packing but rather cubic packing. The molecular packing of smectic A is shown in Figure 1c and smectic C in Figure 1d.

Structure of Lyotropic Liquid Crystals

The second category of liquid crystals, known as the lyotropic, is generated by mixing two or more substances, one of which is generally quite polar (e.g., water).

Lyotropic liquid crystals are commonly prepared by the action of a “solvent” on a solid. Lyotropic liquid crystals are divided into categories based primarily on their structure. This discussion of lyotropic liquid crystals will emphasize two-component systems composed of water and amphiphilic compounds. An example in living systems would be lecithin, cholesterol, bile salts, and water. Amphiphilic compounds have a polar head (ionic) which tends to dissolve in water (hydrophilic) and an organic tail (hydrophobic) which is not soluble in water. The molecular geometries found in amphiphilic compounds are of two common types. Sodium stearate is a typical Type 1 molecule. In this type of molecule the polar head is attached to a long hydrophobic tail (water insoluble).

\[
\text{CH}_3-(\text{CH}_2)_7-\text{CH}-(\text{CH}_2)_2-\text{OOC}-\text{CH}_2
\]

Type 2 molecules have the polar head attached to two hy-

![Figure 1](image_url)
drophobic tails. The hydrophobic groups generally lie either side-by-side and form a “clothespin” structure, or are at an acute angle to each other forming peg-shaped molecules. Aerosol OT and phospholipids are examples of Type 2 molecules. The formula for Aerosol OT is

\[ 	ext{H}_2\text{O} \]

By addition of water to the crystalline form of an amphi- phile, a series of structures can be generated. With certain combinations, the polymorphic mesophases formed will show lamellar molecular packing (packing in layers known as the neat phase), cubic molecular packing (the viscous phase), and hexagonal molecular packing (the middle phase). Removing water can reverse the order of mesophase formation. These statements can be represented schematically as follows:

\[
\begin{align*}
\text{Lamellar} & \quad \text{Cubic} & \quad \text{Hexagonal} \\
\downarrow \text{Solid} & \quad \downarrow \text{Liquid} & \quad \downarrow \text{Liquid} \\
& \quad \downarrow \text{-H}_2\text{O} & \quad \downarrow \text{-H}_2\text{O} \\
& \quad \downarrow \text{Crystal} & \quad \downarrow \text{Crystal} \\
& \quad \downarrow \text{Micellar} & \quad \downarrow \text{Homogeneous} \\
& \quad \downarrow \text{-H}_2\text{O} & \quad \downarrow \text{-H}_2\text{O} \\
& \quad \downarrow \text{Solution} &
\end{align*}
\]

Structures Formed From Amphiphiles and Water

1. The lamellar structure (the “neat” or “G” phase)
   It is generally agreed that this phase is smectic in character, with the amphiphilic molecules packed parallel to each other with water to form a lamellar (layer-like) packing. Molecules with lamellar packing can be tilted to the planes of the layer. See Figure 2a.

2. The hexagonal structure (the “middle” or “M1” phase)
   This structure is stable at higher water concentrations or at higher temperatures than its lamellar structure. X-ray diffraction studies show that the amphiphilic molecules are grouped into rod-like clusters of indefinite length, which, in turn, are arranged side-by-side in a hexagonal packing. See Figure 2b.

3. The cubic structure (the viscous “isotropic” or “V1” phase)

In some systems there is an intermediate between stable G and M1 phases. Ordinary optical observations can give no information on the structure of this phase beyond showing that it is isotropic. X-ray diffraction studies indicate that the molecules pack in spheres and the spheres then pack in a cubic lattice (micelle). See Figure 2c.

An inverted structure is commonly found in lyotropic sys- tems. In this structure the polar groups are directed inward and enclosed in a water core. The medium between the rods is of hydrocarbon composition. See Figure 2d.

Some Properties of Thermotropic Liquid Crystals

Seven common properties attributed to liquid crystals are outlined below. When a beam of white light is shown through a crystal or liquid crystal, it divides into two beams which, refracted at different angles, are emitted parallel to each other. The two emitted beams show different colors. This property is referred to as birefringence.

Dichroism is that property of a substance which results in its showing different colors of transmitted light, depending on the length of the light path in the substance. Of liquid crystalline substances, cholesterics exhibit the most interesting dichroic properties. When white light strikes the surface of a cholesteric compound, it is separated into two components, one rotating clockwise and the other counterclockwise. Depending on the type of liquid crystal, one component reflects from the surface and is of one color, while the other component transmits from the surface and is of another color.

Cholesteric liquid crystals exhibit unusual optical activity, that is, the ability to change the direction of vibration of polarized light. This property is greater for cholesteric liquid crystals than any other known substances. For example, a 1-mm section of quartz will rotate the polarization plane of blue light some 39°, whereas a 1-mm section of isooamyl-p-(4-cyanobenzylideneamino) cinnamate will rotate the polarization plane many complete turns.

Liquid crystals are responsive to electric field effects. This is especially so for nematic and cholesteric liquid crystals. Liquid crystals also respond to a magnetic field. These properties will be discussed more fully under the Applications section.

Upon heating or addition of a second component, many thermotropic and lyotropic liquid crystals pass through more than one smectic phase. Such liquid crystalline compounds are said to exhibit polymorphism. The order of formation of the different mesophases can be predicted from the relative stabilities of these phases. (For example, we know that a smectic B is more ordered than a smectic A, and a smectic A is more ordered than a nematic structure.) Increasing the temperature of the mesogenic compound (liquid crystals) results in the progressive destruction of molecular order. Thus, the order of stability is

\[
\text{Solid} \rightarrow \text{SmB} \rightarrow \text{SmC} \rightarrow \text{SmA} \rightarrow \text{Nematic} \rightarrow \text{Isotropic} \rightarrow \text{Liquid}
\]

Liquid crystals appear in a wide variety of phases including the nematic phase, cholesteric phase, blue phase, and at least eight different smectic types. Each has its own texture. Sample preparation techniques as well as the method of obser- vation both affect the texture of the liquid crystal under consideration. For example, (in order to force liquid crystalline molecules to orient themselves perpendicular to the surface (called homeotropic alignment)) a sample can be placed between glass slides whose surfaces are treated with lecithin or organosilanes. Once a particular texture is achieved, its appearance can be further affected by the way it is illuminated and observed. The texture of a smectic A liquid crystal is shown in Figure 3 (unfortunately, you cannot see the different colors).

Molecules in a film of a nematic liquid can be oriented by
surface action. If the surface is rubbed, the molecules tend to align with their long axes parallel to the direction of rubbing. Other surface effects such as certain surfactants, may orient the molecules so that their long axes stand perpendicular to the surface. If the orientation is complete, a pseudoisotropic texture results.

Applications

A detailed description of all liquid crystal applications is quite beyond the scope of this brief review, instead we will describe the basic principles involved in their application and indicate some typical uses.

Nematics

Because of their reliability, low power consumption, versatility, and good readability, even under high ambient illumination, liquid crystals are prime candidates for the development of displays. Typically, a small amount of an ordinary nematic liquid crystal is placed in a thin flat optical cell. The cell walls, which are coated with a transparent conducting film (SnO₂ or SnO₂ and In₂O₃), are carefully treated to specify the orientation direction of the long liquid crystal molecules. Figure 4 illustrates a schematic diagram of the optics of a liquid crystal cell.

Application of an electric field changes the molecular alignment such that the polarization in the cell is not altered but light is transmitted. If a mirror is used behind the second polarizer, the cell will appear black when voltage is applied. If, in addition, one of the electrodes is shaped into a digital pattern of segments, then a numeric display will appear when the voltage is on. By changing the direction of the polarizers, the number can be made to appear white on a black background.

If a dye is dissolved in the liquid crystal, the absorption spectrum of the dye will be different with and without an electric field. To understand this property consider a liquid crystal in the nematic phase. In the absence of an electric field, the molecules of the liquid crystal have little order. If an electric field is applied, the molecules align themselves along the axes parallel to the direction of the field. The dye molecules will follow the arrangement of the liquid crystal host, that is, the long axis of the dye molecules will also be parallel to the electric field. The cell used in pleochroic dye studies is comparable to an ordinary liquid crystal display cell.

Cholesterics

One of the applications of cholesteric liquid crystals is temperature sensing. Cholesterics are unlike ordinary nematics in that the ordering direction spirals in space about an axis perpendicular to it. This results in a periodicity which is capable of selectively reflecting that color of light having a wavelength matching the spatial period. Since the pitch of the cholesteric spiral turns out to be sensitive to practically everything—temperature, electric fields, magnetic fields, impurity doping, and other things—the cholesteric has a display potential not possessed by ordinary nematics. Nonmedical uses of the temperature effect include fault location on printed circuit boards, in welds, and in bonded structures.

Since 1964, liquid crystals have been used as a diagnostic medical "tool." For example, detection of carcinoma of the breast, study of abnormal venous patterns including peripheral vascular disease and localization of incompetent perforator veins, placental localization, and in detecting the presence of primary or metastatic carcinoma in the skin—all utilize cholesteric liquid crystals, whose reflected color changes with temperature. Liquid crystals have been identified in sickle cell anemia, hardening of the arteries, and gallstone formation.

Fibers

Recently new research efforts are directed toward a long neglected area of polymer science—the polymeric liquid crystals. Giant molecules align spontaneously to form liquid crystals that have applications in areas ranging from electronic devices to ultra-high strength materials. Ultra-high strength polymers are characterized by their high degree of crystallinity (molecular order). Polymers that possess liquid crystalline order on their melt or solutions often exhibit exaggerated morphology in the solid state. These observations imply that the liquid crystal phase is essential to produce ultra-high strength organic materials.

A breakthrough in liquid crystal polymer research was accomplished when the du Pont Company discovered the fiber identified as Kevlar. The chemistry encountered in the Kevlar arimid fibers is quite simple. One preparation is accomplished through the reaction of 1,4-phenylenediamine and terephthaloyl chloride.

\[
\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 + \text{CO} = \text{O} \rightarrow \text{NH} - \text{C} = \text{O} + \text{COCl} \quad \text{NH} - \text{C} = \text{O}
\]

This finding has generated many new research efforts, not only using the \(p\)-aromatic polyamide but other structural units including aromatic diesters and \(p\)-hydroxybenzoic acid. Kevlar has been used in the manufacture of specialty clothing items, including bulletproof vests and tarpaulins.

Graphitic fibers can be prepared from natural pitch or from synthetic pitch both of which are liquid crystalline in nature.
The synthetic graphitic material can be prepared by heating low molecular weight aromatic hydrocarbons, such as anthracene. Fibers can then be generated from this pitch matrix. The products obtained from this chemistry have high tensile strength and are light in weight. They can be used for the construction of lightweight tools, shafts for golf clubs, etc.

**Oil Recovery**

Liquid crystal systems have also been used in oil recovery. The systems are generally tertiary in nature involving water, oil, and a surfactant. The oil is most highly solubilized at the point in which the composition and concentration of the three components form a liquid crystalline phase.

**Cell Membranes**

In living systems, cell membranes and tissues are the most commonly encountered form of liquid crystal. The model which is widely used these days in characterizing the structure of cell membranes involves the use of the lamellar structure (which is so prevalent in the surfactant industry). The skeletal structure of the membrane is essentially phospholipids which are packed into a bilayer design.

**Liquid Crystals as Solvents**

Liquid crystals are good solvents for many organic compounds. This makes them useful for such studies as chromatography, mechanism and kinetics of selected reactions, and spectroscopy studies. In chromatography, the liquid crystal functions as a packing for a column.

With nuclear magnetic resonance, it is possible to establish the structure of small organic compounds, e.g., cyclobutane in p-azoxyanisole.

**Summary**

In this brief review on liquid crystals, we have shown that one- and two-dimensional structures are found in nature. Liquid crystals bridge the gap between the rigid solid state and the essential absence of structure in the gaseous state.

A multitude of applications of liquid crystals have been developed over the past 15 years. There has been an especially rapid transition from the laboratory bench to the marketplace. Liquid crystals are second, only to the cathode ray tube, as a display medium and are widely used in digital thermometers, watches, calculators, and games. New applications will include telephones, automobiles, and television sets. Portable microprocessor-based equipment, such as computers, televisions, oscilloscopes, and other instruments, will find liquid crystal displays particularly attractive.

As more scientists, engineers, and medical researchers enter this exciting research field, new discoveries and applications will be made including those dealing with living systems. The future is full of exciting possibilities.

**Literature Cited**

**General**


(9) For a current review see Lister, J. D., and Birgeneau, R. J., *Physics Today*, 35, 26 (May 1982).


**Polymers**


**Applications**

