

Shashi Chandra
Book

Additional material
only for Reference.

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Liquid Crystals

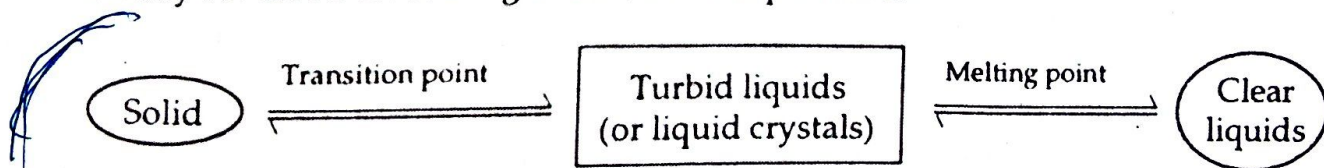
"The study of chemistry is profitable not only in as much as it promotes the material interest of mankind, but also because it furnishes us with insight into those wonders of creation, which immediately surround us and with which our existence, life and development, are most closely connected."

1 INTRODUCTION

A state of matter that is intermediate between the solid crystalline and the ordinary (isotropic) liquid phases is known as **mesomorphic state** (meaning intermediate form, in Greek) or **liquid crystals**.

Liquid crystals flow like ordinary liquids, they adopt the shape of their container but they exhibit anisotropic (i.e., different properties in different directions) properties as do solid crystals in the same thermodynamically stable phase.

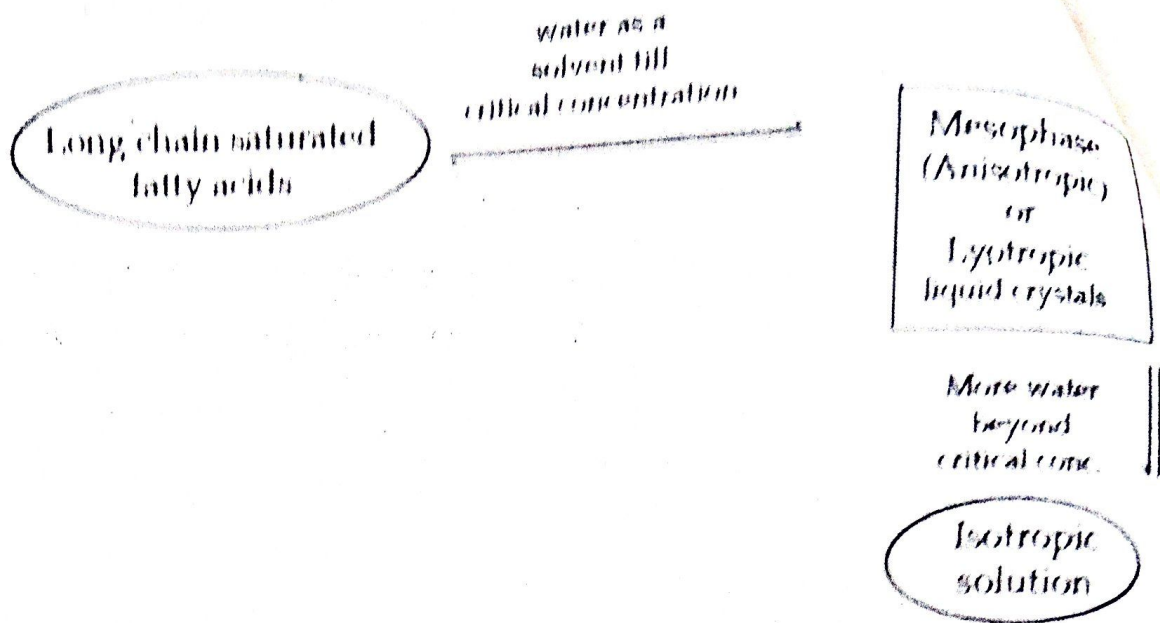
On heating, certain solids undergo two sharp phase transformations : first they fuse sharply yielding turbid liquids (at a characteristic temperature, known as **transition point**) and then again equally sharply, they yield clear liquids (at some higher characteristic temperature, known as **melting point**). These changes are exactly reversed on cooling at the same temperatures.



The intermediate phase exhibits anisotropy in its properties so it is known as **mesomorphic state** or **liquid crystalline state**.

Thus **liquid crystals** can be defined as "Condensed fluid phases with spontaneous anisotropy". On heating, such compounds undergo a change from highly ordered arrangement in solids to disordered isotropic liquids through *anisotropic* liquid crystal state. Such liquid crystals which are formed when the temperature is varied are called **thermotropic liquid crystals**.

In contrast, when a solvent is added to some substances they first form a mesophase. Further increasing the amount of solvent beyond a critical concentration leads to a transformation to an isotropic liquid. Mesomorphic phases of this kind are called **lyotropic liquid crystals**.



Comparison of liquid crystalline phase with solid and liquid phases :

Characteristic	Solid Phase	Liquid Crystalline Phase	Liquid Phase
Positional order	Present	Absent	Absent
Orientalional order	Present	Present	Absent
Mobility	Immobile	Mobile	Mobile
Structure (molecules are represented as thin rectangles)	Fig. 1(a)	Fig. 1(b)	Fig. 1(c)

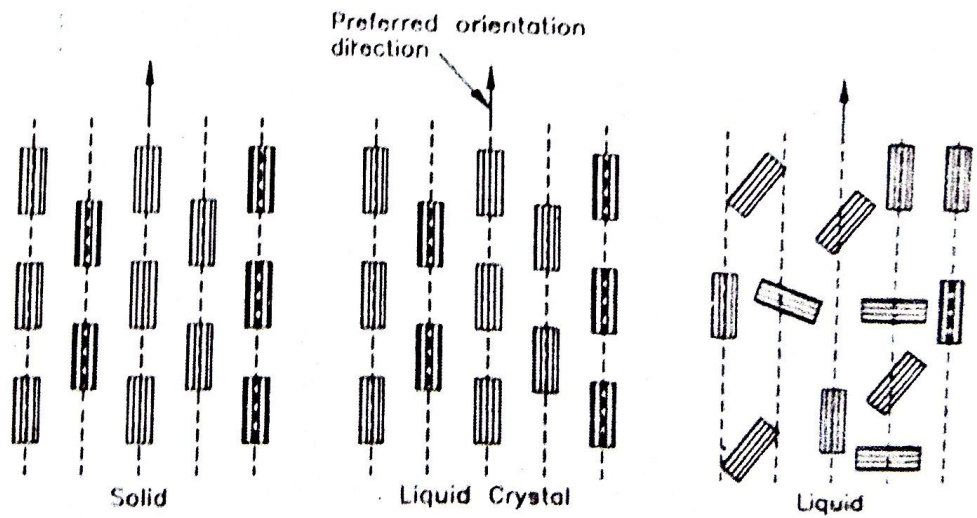


Fig. 1.

The solid phase possesses both positional as well as orientational order and is immobile. In contrast, liquid phase possesses neither positional order nor orientational order. Intermediate between the two is liquid crystalline phase which has some orientational order but no positional order. Thus, the molecules in a liquid crystal tend to remain oriented in a particular direction. The direction of preferred orientation in a liquid crystal is called the **director** (\hat{n}).

g. general shape :



(i) Commonly used
Terminal groups are :

- R (alkyl)

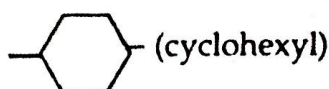
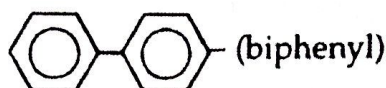
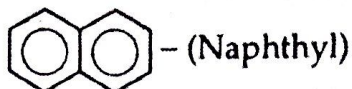
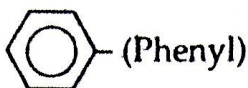
- OR (alkoxy)

- NO₂ (Nitro)

$\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{R} \end{array}$ (carboxyl)

$\begin{array}{c} \text{O} \\ || \\ -\text{O}-\text{C}-\text{R} \end{array}$ (Ester)

(ii) Commonly used
Rigid groups are :



(iii) Commonly used
Bridging groups are :

- C \equiv C -
(Acetylene)

- N = N -
(azo)

- N = N -
↓
O

- CH = N -
(schiff base)

- The bridging group induces anisotropic melt characteristics.
- The type and chain length of the terminal groups determine which mesophase the compound exhibits.
- The mesophase formation is possible only if the benzene rings are linked through para substituents. Linkage through meta or ortho positions is not favourable.
- The mesophase formation is also possible when two benzene rings are linked directly as in substituted biphenyls.

Examples of such compounds are given in table below :

S. No.	Name	Structure	Mesomorphic Range (in °C)
1.	p-azoxyanisole (PAA)	$\text{H}_3\text{C}-\text{O}-\text{C}_6\text{H}_4-\text{N}(\text{O})=\text{N}-\text{C}_6\text{H}_4-\text{OCH}_3$	118 - 136 (nematic)
2.	4-methoxy-4'-n-butyl- benzylideneaniline (MBBA)	$\text{H}_3\text{C}-\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{C}_4\text{H}_9$	21 - 48 (nematic)

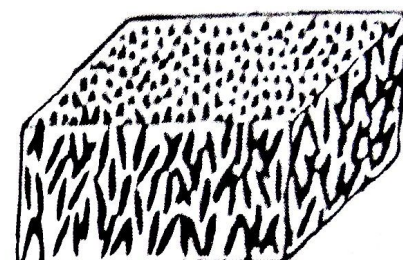
The molecules ordering in various liquid crystalline materials are discussed below :

(i) **Nematic liquid crystals.** Nematic phase is characterized by the total loss of positional order and a near normal flow behaviour similar to its liquid phase.

The molecules in the nematic liquid crystals are less ordered. They point in the same direction, but they start and stop at different positions within the liquid.

The molecules in a nematic phase appear to have a thread-like texture when observed in polarized light. Nematic in Greek means thread like, that's why they are called so. The other possible textures in these compounds are schlieren and marbled.

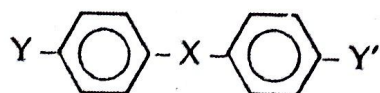
The molecules which form nematic phase have elongated shape which in most cases consist of a conjugated aromatic system. They are oriented parallel to the director. They possess enough intermolecular forces so that they stay parallel to one another. Generally, such molecules either are optically inactive or are racemic modifications. Averaged over time or space, the long molecular axes of the molecules are aligned parallel to the preferred direction. The molecules are allowed to rotate freely about their long axes.



CH₃ O — CH = N — CH₃
Nematic

Fig. 8.

Many compounds forming nematic liquid crystals have the simple structure



The most important linking groups (X) can be azo ($-\text{N}=\text{N}-$) azoxy ($-\text{N}(\text{O})=\text{N}-$), Ester ($-\text{O}-\text{C}(=\text{O})-$), schiff bases ($-\text{CH}=\text{N}-$), and unsaturated ($-\text{CH}=\text{CH}-$ or $-\text{C}\equiv\text{C}-$) groups.

The terminal groups Y and Y' are either small groups or short chains.

The examples of compounds that exhibit nematic phase are given in table below :

S.No.	Name	Structure	Nematic range (°C)
1.	p-azoxyanisole (PAA)	$\text{H}_3\text{CO} - \text{C}_6\text{H}_4 - \text{N}(\text{O})=\text{N} - \text{C}_6\text{H}_4 - \text{OCH}_3$	118 to 136
2.	4-methoxy-4-n-butylbenzylidene aniline (MBBA)	$\text{H}_3\text{CO} - \text{C}_6\text{H}_4 - \text{CH}=\text{N} - \text{C}_6\text{H}_4 - \text{C}_4\text{H}_9$	21 to 48

(ii) **Cholesteric liquid crystals.** Their name is originated from the fact that many derivatives of cholesterol form this structure. (Cholesterol itself exhibits no mesomorphic phase).

A necessary condition for the formation of the cholesteric mesophase is that the molecules are chiral. (That's why, they are referred to as the chiral nematic phase).

Their structure can be described as a twisted nematic structure. [That's why, they are also referred to as twisted nematic liquid crystal]. It means, they have a structure similar to nematic liquid crystals, but each plane of molecules is twisted slightly in relation to the plane above or below. The molecules are aligned parallel to a preferred direction \vec{L} as in a nematic phase. When proceeding in a direction normal to the plane, \vec{L} rotates continuously. The result is a **helical structure**, the axis of which can be described by a unit vector \hat{n} .

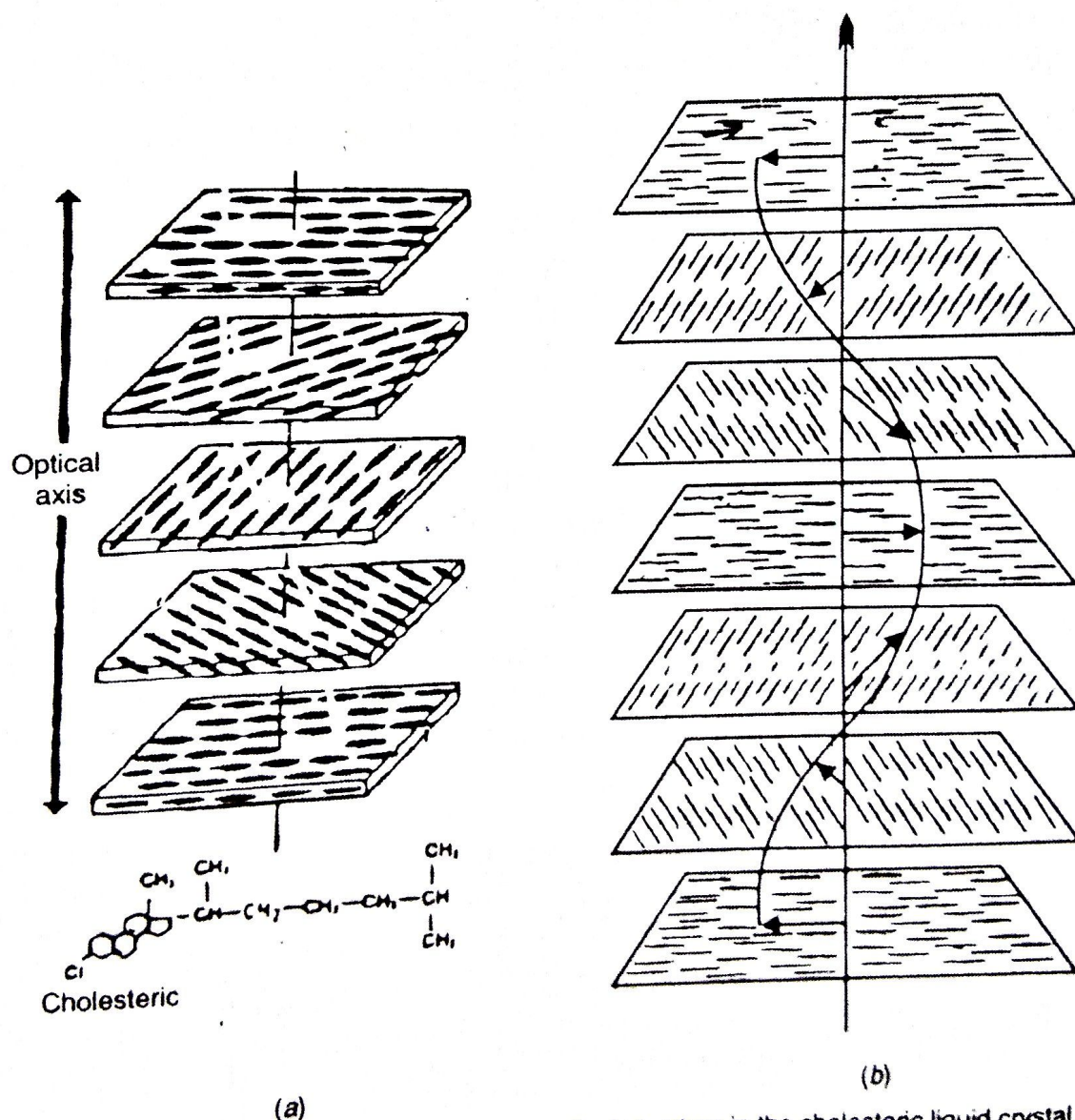


Fig. 9. Schematic representation of the helical structure in the cholesteric liquid crystal.

The **pitch** (p) of the structure is defined by the distance which is necessary to rotate \vec{L} by 180° when proceeding along \hat{n} . An infinite pitch corresponds to the nematic structure. The pitch can be adjusted to any desired value by adding