Science Update Programme

Liquid Crystals and Their Applications

Education Bureau, HKSAR

Department of Chemistry
University of Hong Kong

Education Bureau
The Government of the Hong Kong Special Administrative Region

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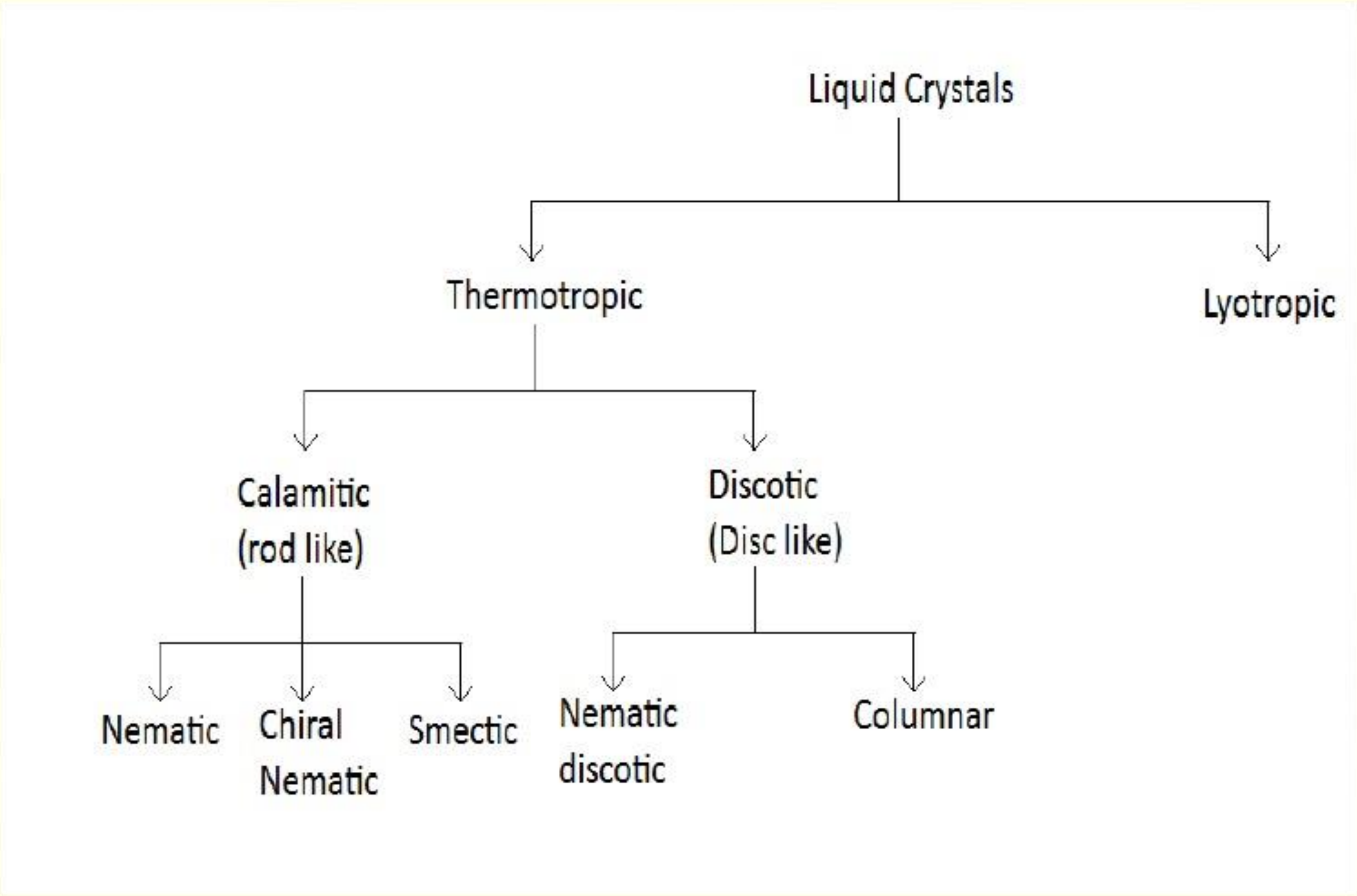
References

1. P. J. Collings "Liquid Crystals: Nature's Delicate Phase of Matter" Princeton University Press, Princeton, 1990.
2. P. J. Collings and M. Hird "Introduction to Liquid Crystals Chemistry and Physics" Taylor& Francis, London, 1997.
3. "Handbook of Liquid Crystal Research" P. J. Collings and J. S. Patel Eds., Oxford University Press, New York, 1997.
4. S.-T. Wu and D.-K. Yang "Reflective Liquid Crystal Displays" Wiley, New York, 2001.
5. Resources for more information about liquid crystals:

   http://webphysics.davidson.edu/Alumni/BeDenius/liqcry/sourcepg.htm

Classification of Liquid Crystals



What is Liquid Crystal?

Solid Phase

- Molecules with both orientation and positional orders, and are held to each other strongly

Liquid Phase

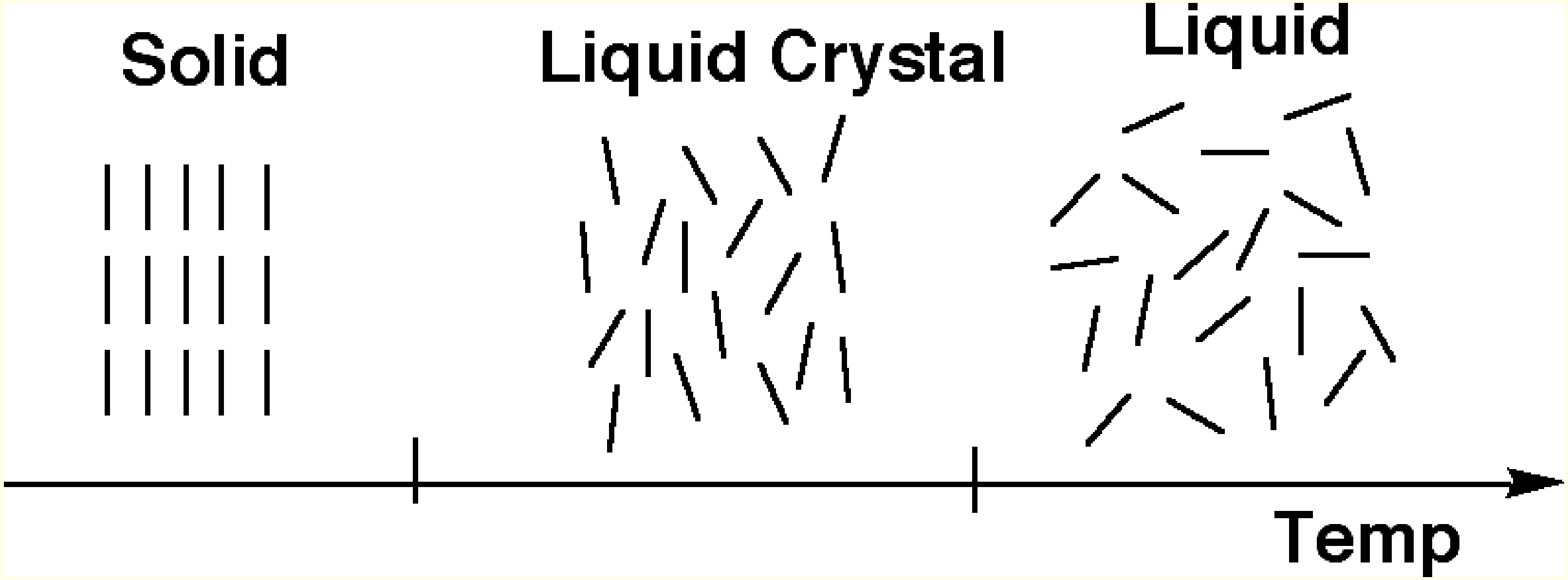
- Molecules with no orientation and positional orders, but are held together by weak intermolecular forces

Gas Phase

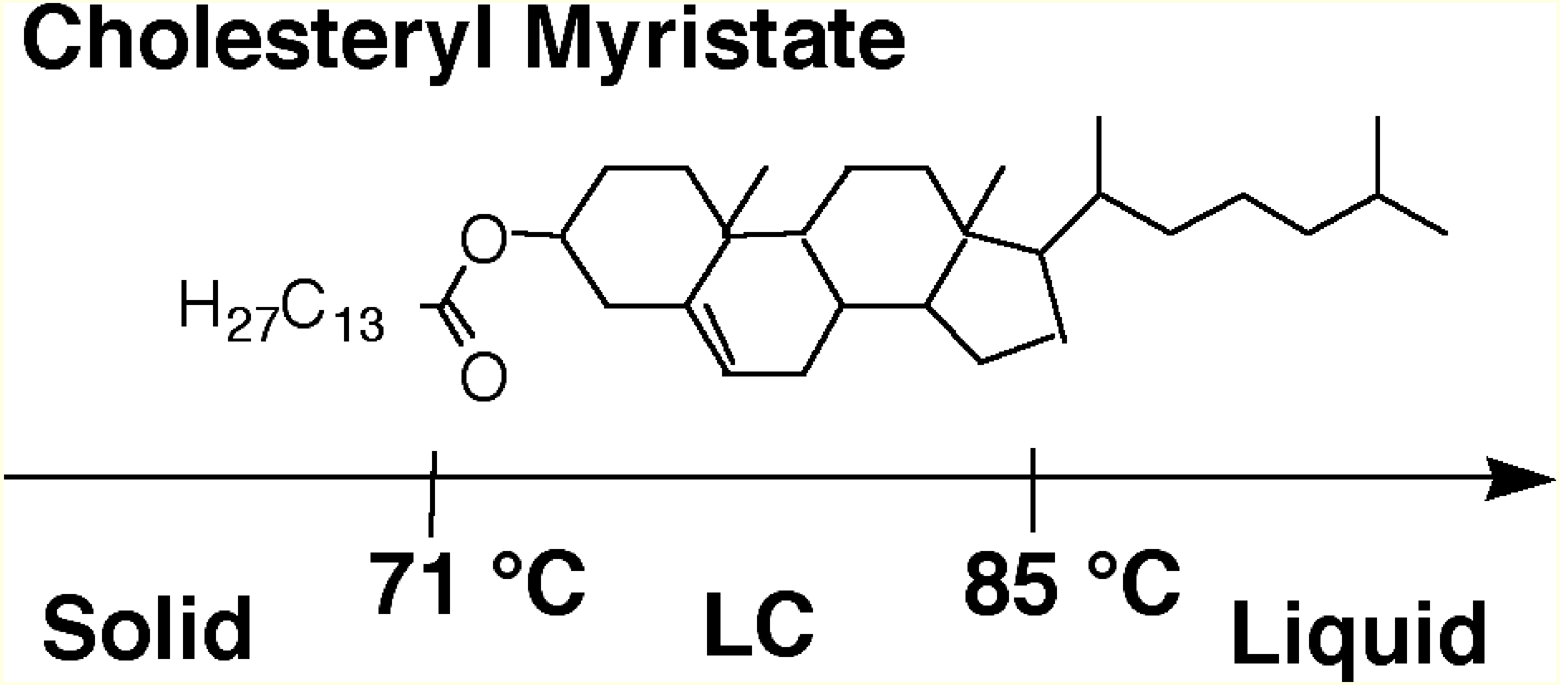
- No ordering, no intermolecular attraction

Liquid Crystal Phase

- A fluid phase in which a liquid crystal flows and will take the shape of its container. It differs from liquid that there are still some orientational order possessed by the molecules

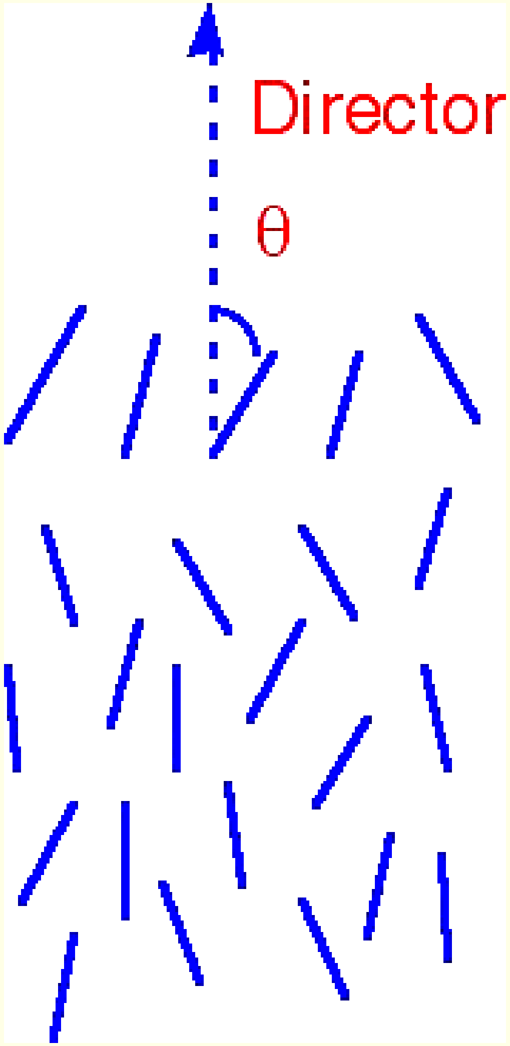


- A phase that exists between solid and liquid
- Discovered in 19th century when studying a cholesterol derivative



Orientational Order

- Assuming that the direction of preferred orientation in a liquid crystal (LC) is ↑, this direction can be represented by an arrow, called the *director* of the LC.



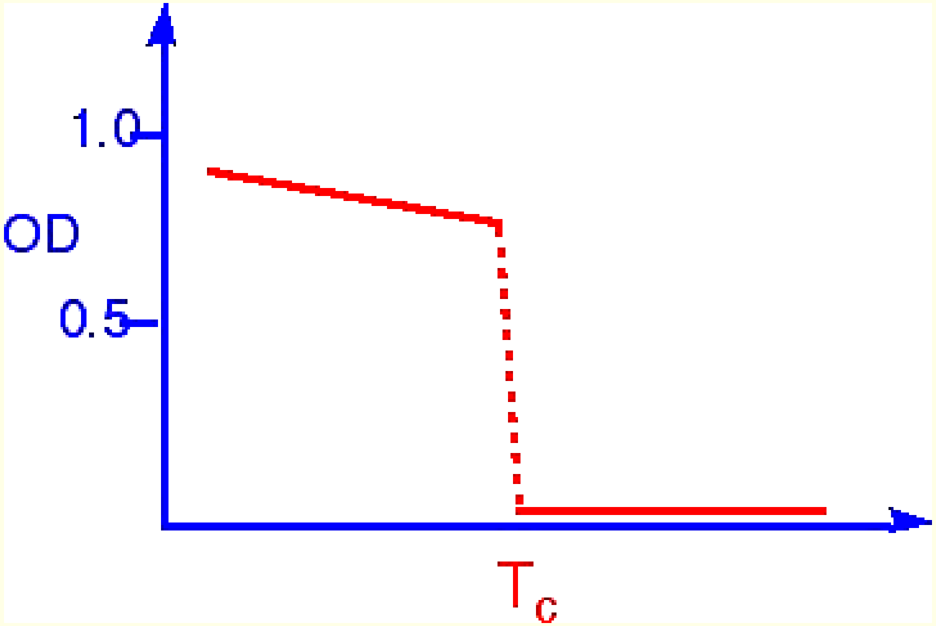
- Each molecule is orientated at some angle to the director
- We could measure all the angles and obtain the average angle as a measure of the degree of orientational order, which increases as $\theta \rightarrow 0$.

Order parameter (OD): $\left\langle \frac{3\cos^2 - 1}{2} \right\rangle$

Perfect orientation: θ for all molecules = 0°, OD = 1

Completely random orientation: OD = 0

- The order parameter decreases as the temperature is increased
- Typical values of OD are ~ 0.3 to 0.9



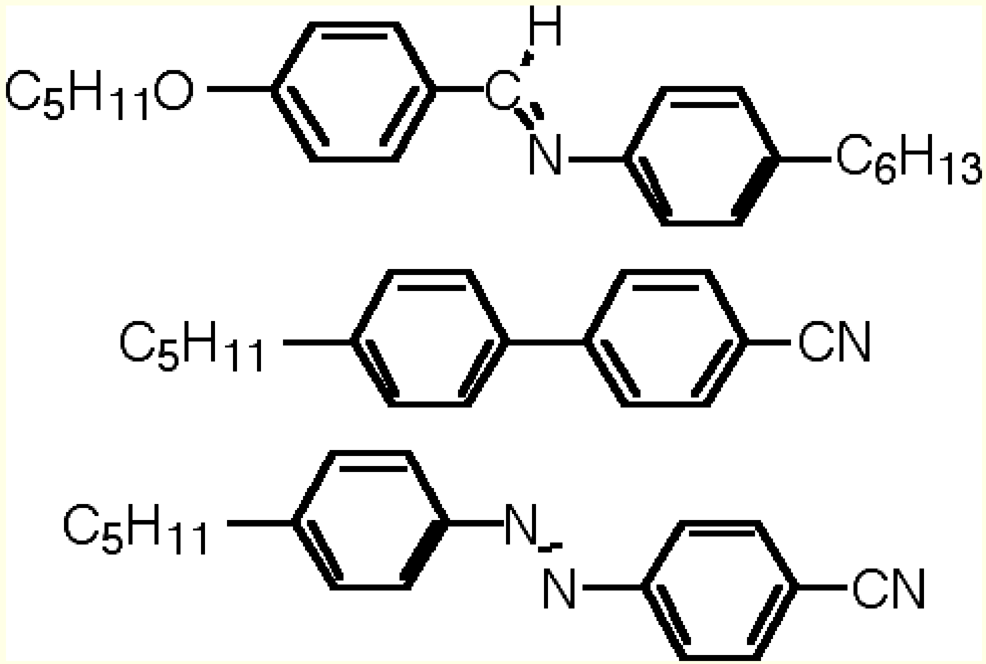
Temp.

T_c: transition temperature from LC to liquid state

Criteria for a molecule being liquid crystalline

- The molecule must be elongated in shape-length should be significantly greater than its width
- Molecule must have some rigidity in its central region
- The ends of the molecule are somewhat flexible

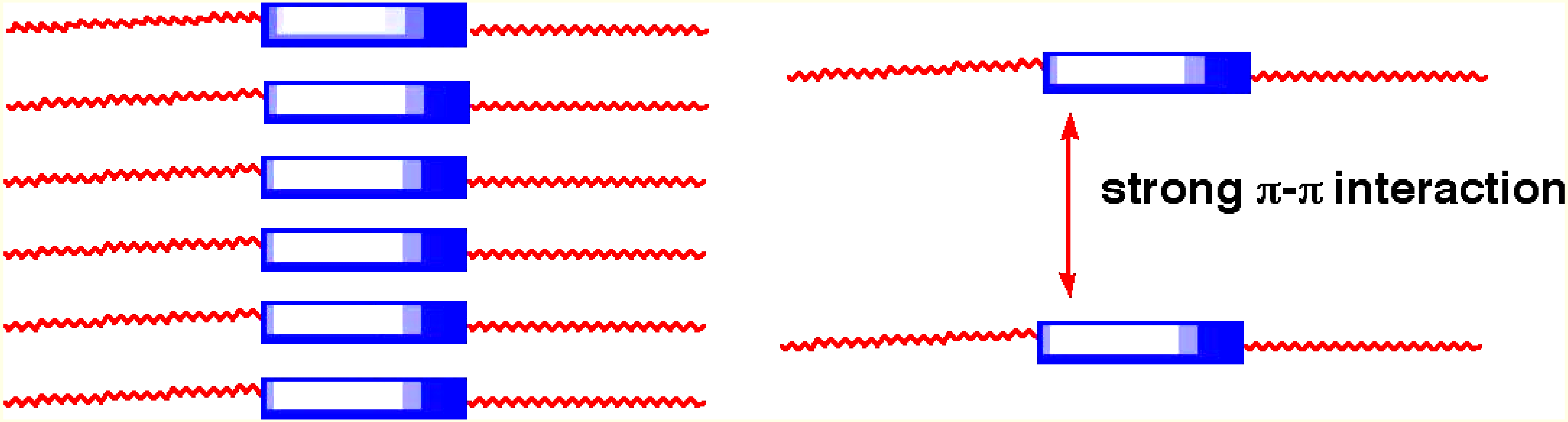
Typical representation of a LC molecule



Mesogens

Note: these molecules possess very strong dipole moment

The liquid crystal molecules prefer to align parallel to each other because of the strong intermolecular attraction (**π-π interaction**)



Those LC exhibited by these rod-like molecules with one molecular axis much longer than the other two are called *calamitic liquid crystals*

Types of Liquid Crystals

Thermotropic Liquid Crystals

- LC phase transitions resulted from temperature changes

Lytropic Liquid Crystals

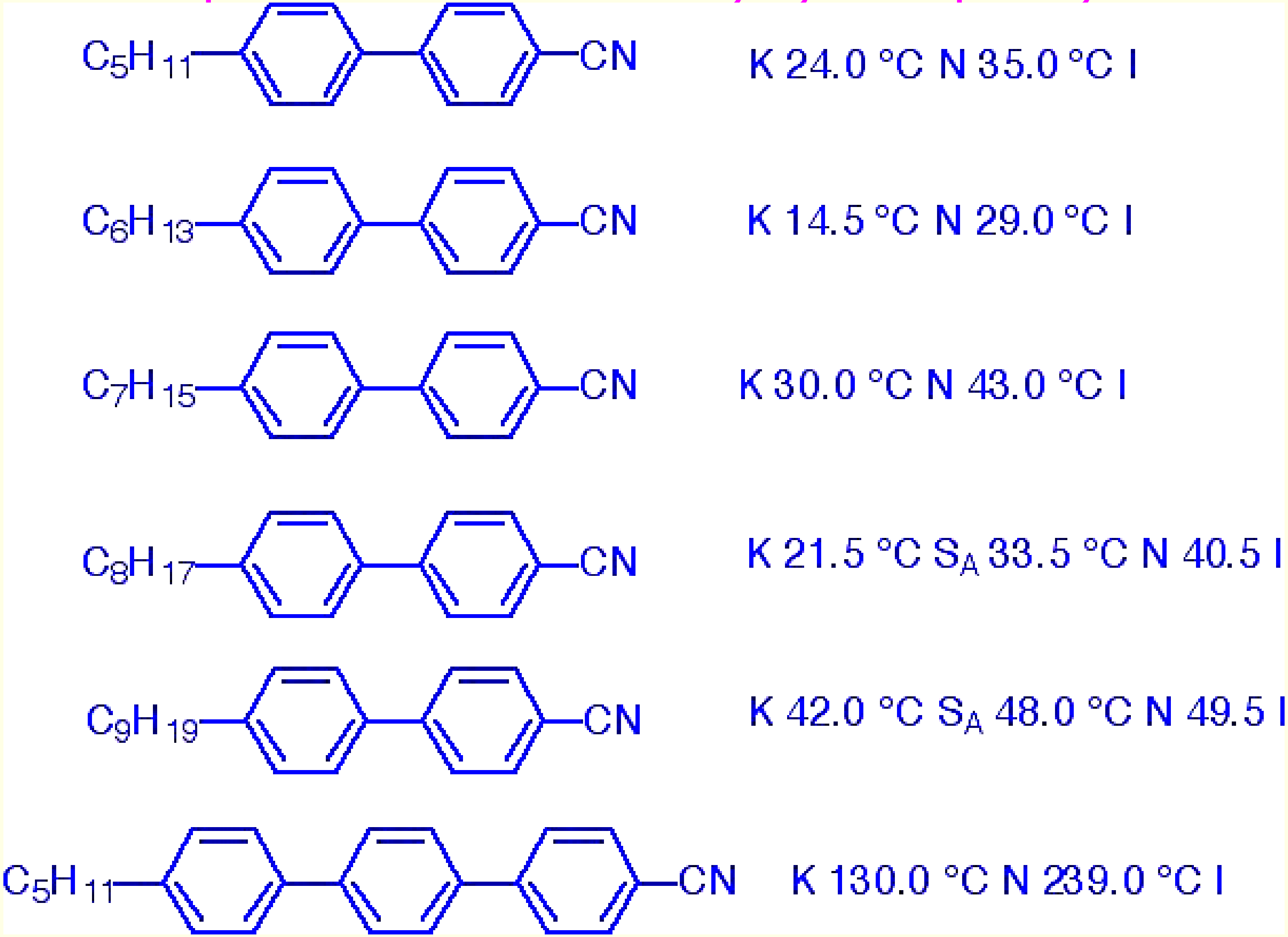
- LC phase is formed when a molecule is dissolved in a suitable solvent (with specific concentration at a particular temperature)

Different Liquid Crystal Phases (Mesophases)

Nematic Liquid Crystal

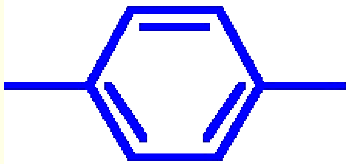
- Derived from a Greek word for thread
- The simplest LC phase
- The molecules maintain a preferred orientational direction as they diffuse throughout the sample (in a fluid phase)

Transition temperatures of some alkylcyanobiphenyl homologues

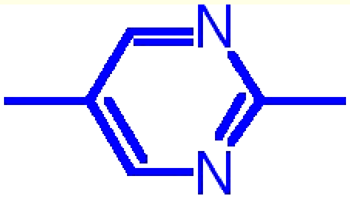


K: Crystalline phase
N: Nematic liquid crystal phase
S_A: Smectic A liquid crystal phase
I: Isotropic phase (liquid phase)

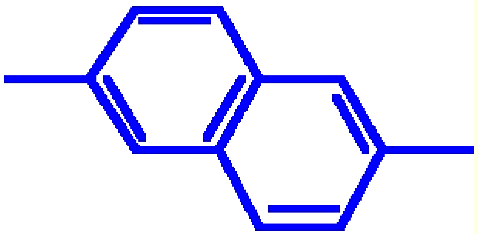
Other examples of core structures



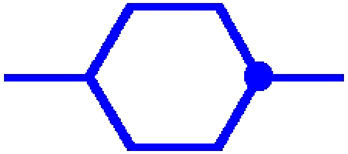
1,4-phenyl



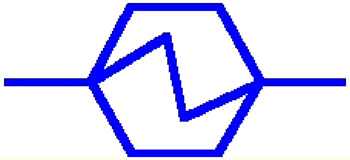
2,5-pyrimidinyl



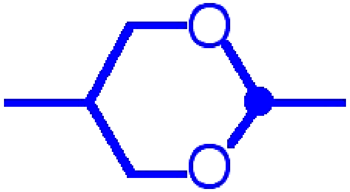
2,6-naphthyl



trans-1,4-cyclohexyl



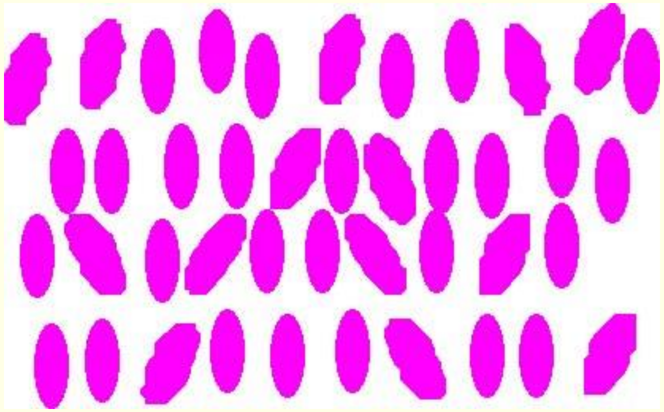
1,4-bicyclo[2.2.2]octyl



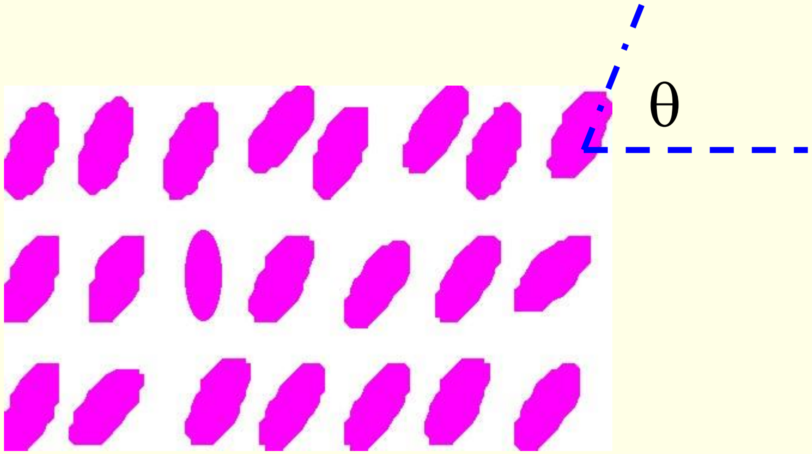
trans-2,6-decalinyl

Smectic Phase

- Besides orientation order, there also some positional order present in this phase
- Smectic A to K phases have been discovered

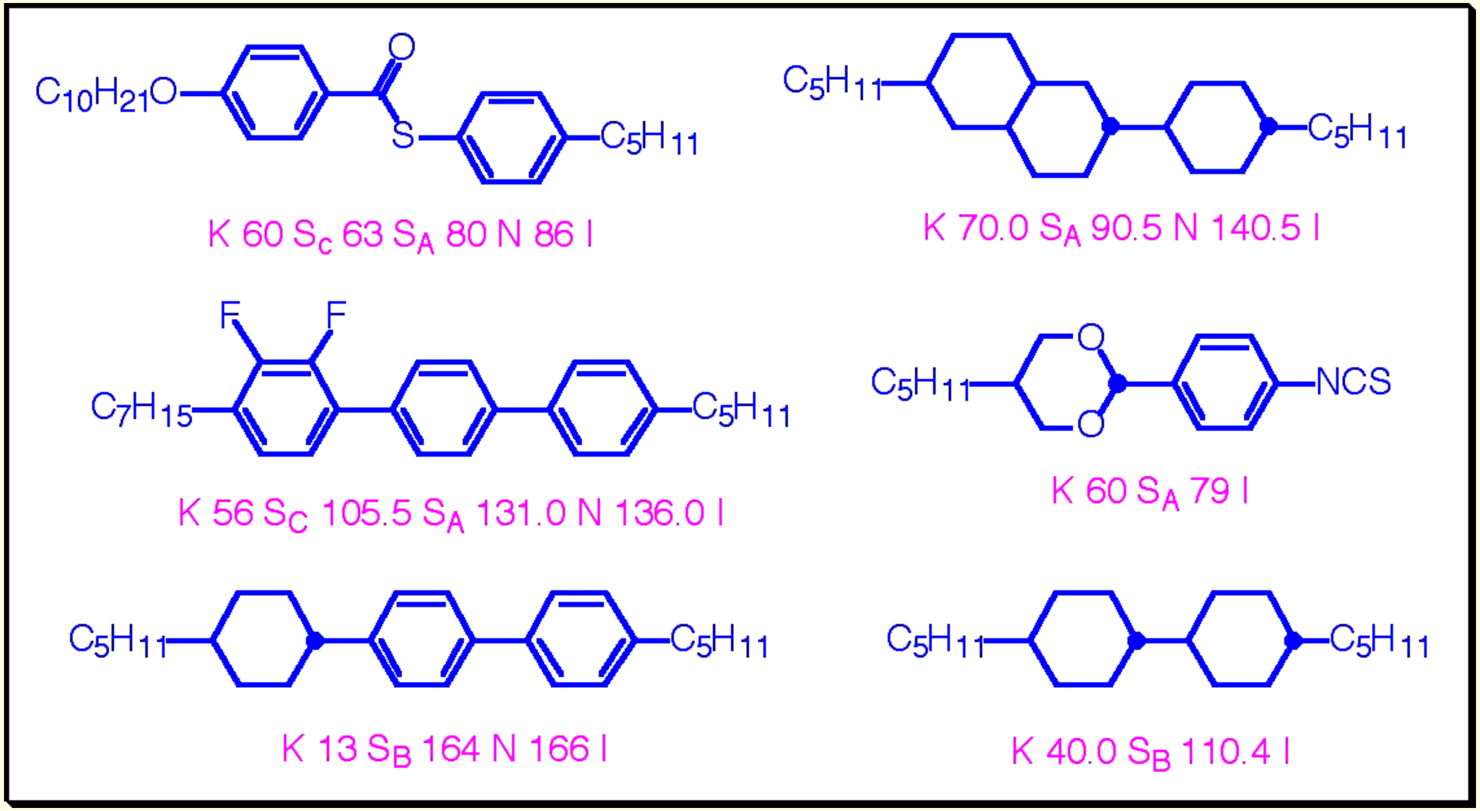


Smectic A phase: Director perpendicular to the plane

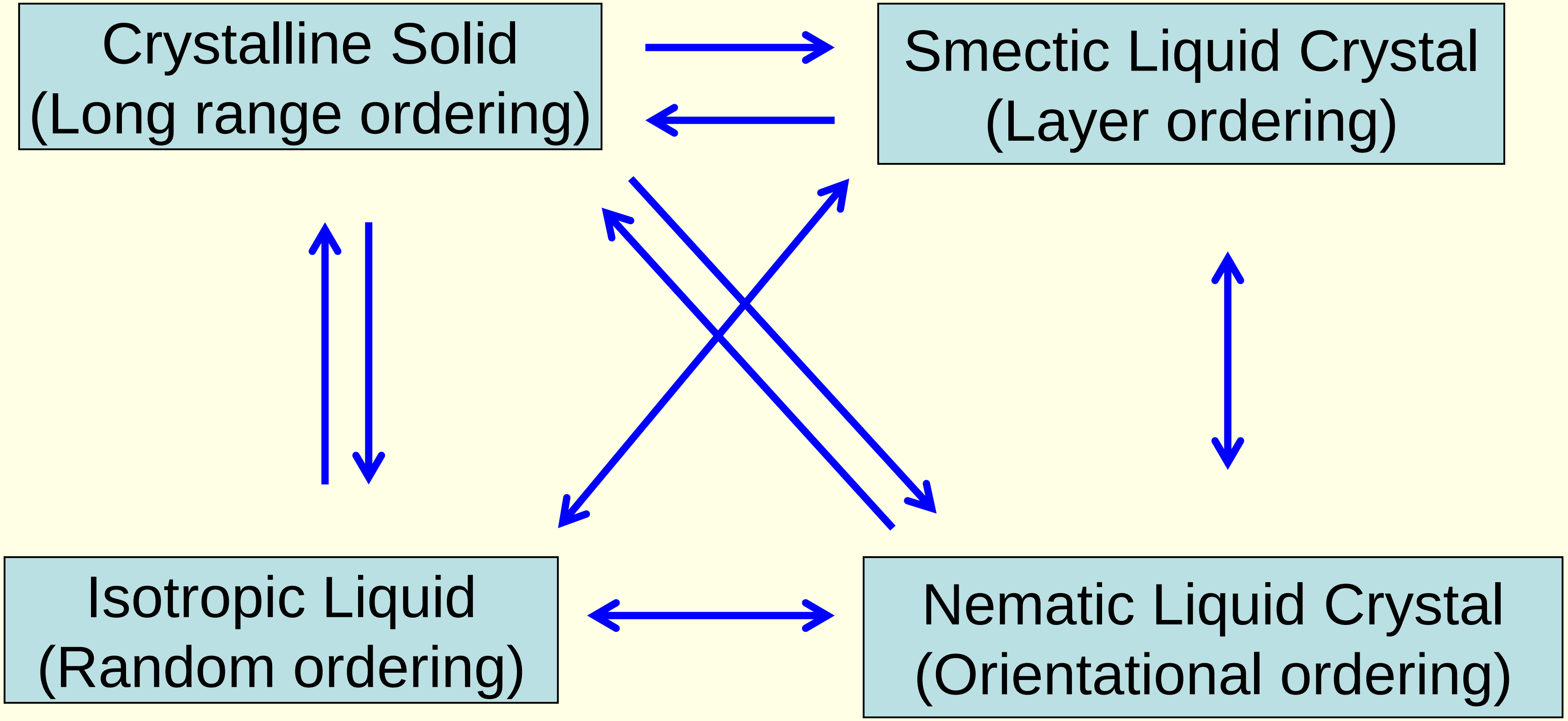


Smectic C phase: director makes an angle with the plane

- Other smectic LC phases exist in which the molecules exhibit orders within each plane
- Many molecules exhibit more than one LC phases



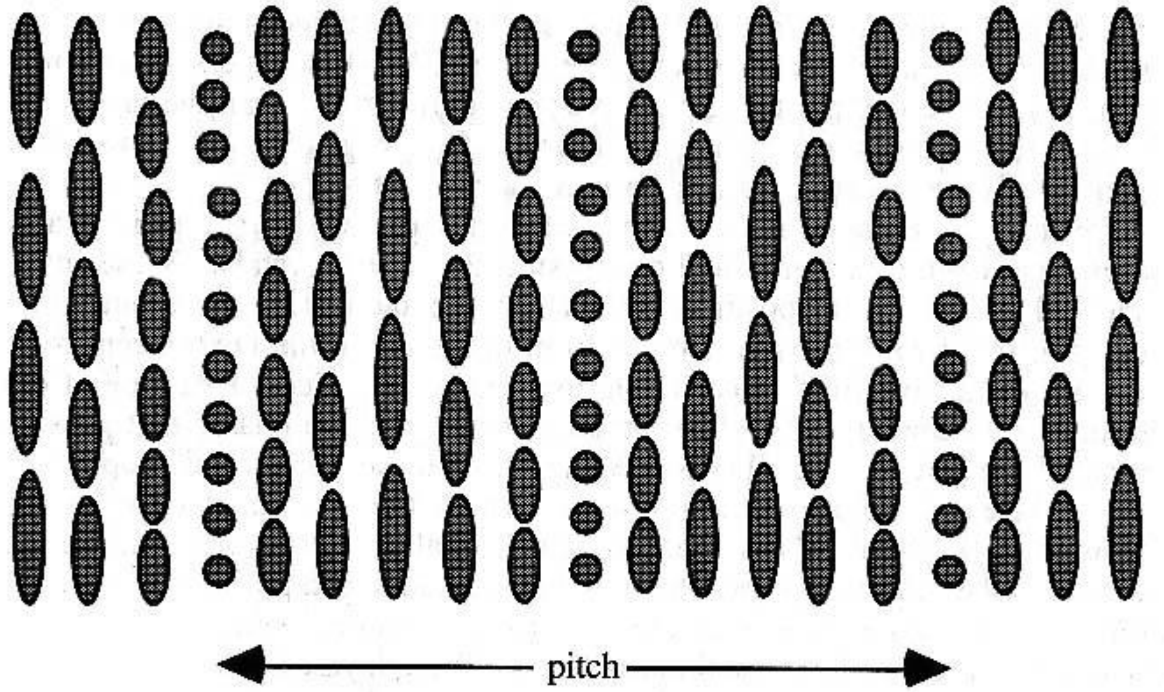
Possible thermal transitions between different LC phases



Cholesteric Liquid Crystal (Chiral Nematic Phase)

- Molecules with intermolecular forces that favor alignment between molecules at a slight angle to one another
- The director is not fixed in space as in a nematic phase, it rotates throughout the sample

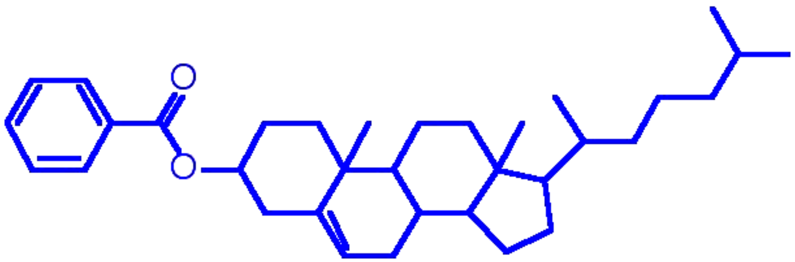
Structure of a chiral nematic phase



Structure of the chiral nematic phase.

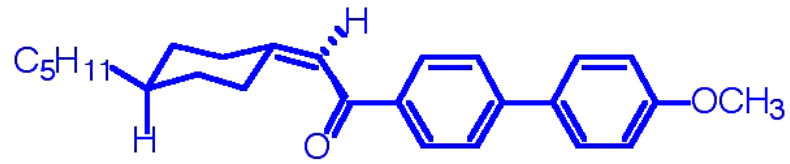
The director rotates about a horizontal axis. The distance for one full rotation is called a *pitch*.

Examples of some molecules with chiral nematic phase

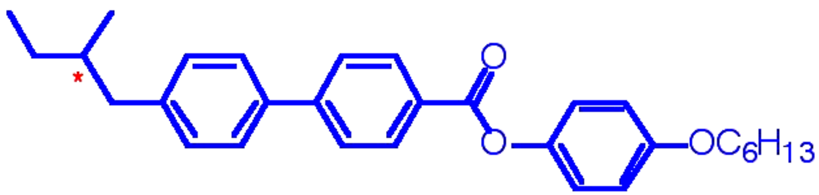


Cholesteryl benzoate

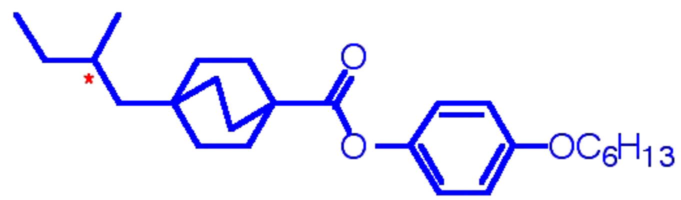
K 146 N* 178 I



K 65 N* 124 I

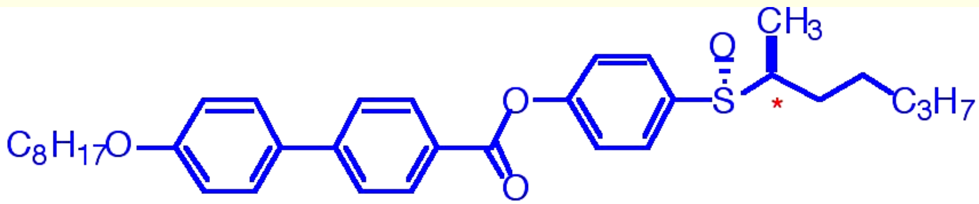


K 103 N* 115.5 I

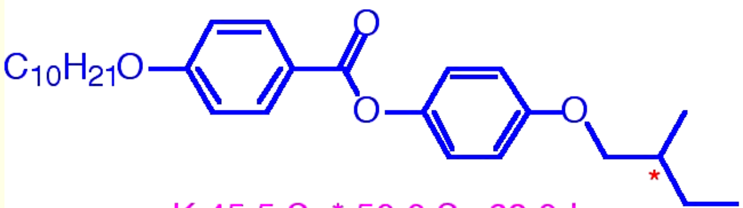


K 43.0 N* 50.0 I

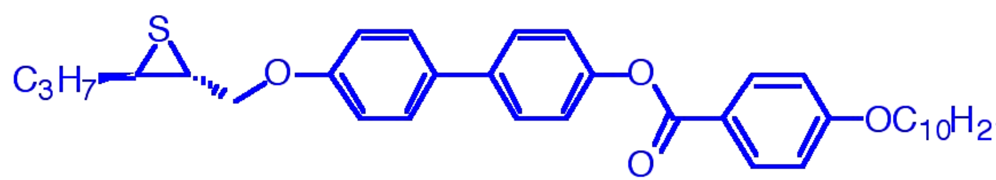
Some with both smectic and chiral nematic phases:



K 155 S_C* 158 N* 169 I



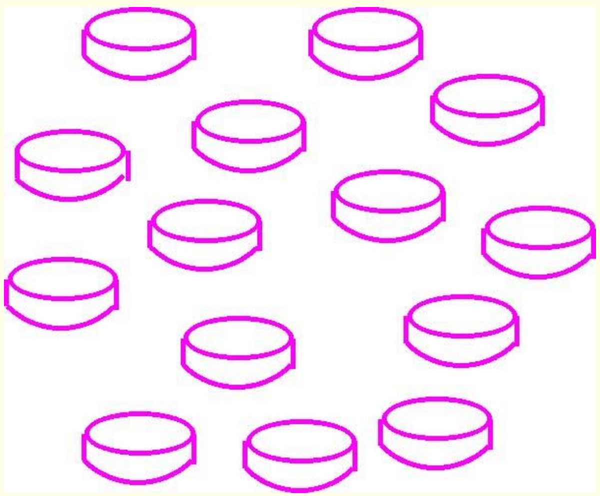
K 45.5 S_C* 50.0 S_A 63.0 I



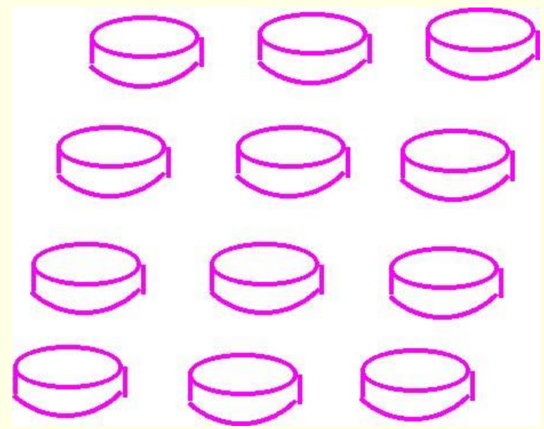
K 103 S_C* 148.5 N* 169.5 I

Discotic Liquid Crystals

- Disc-like molecules
- The axis perpendicular to the molecules tends to orient along a specific direction

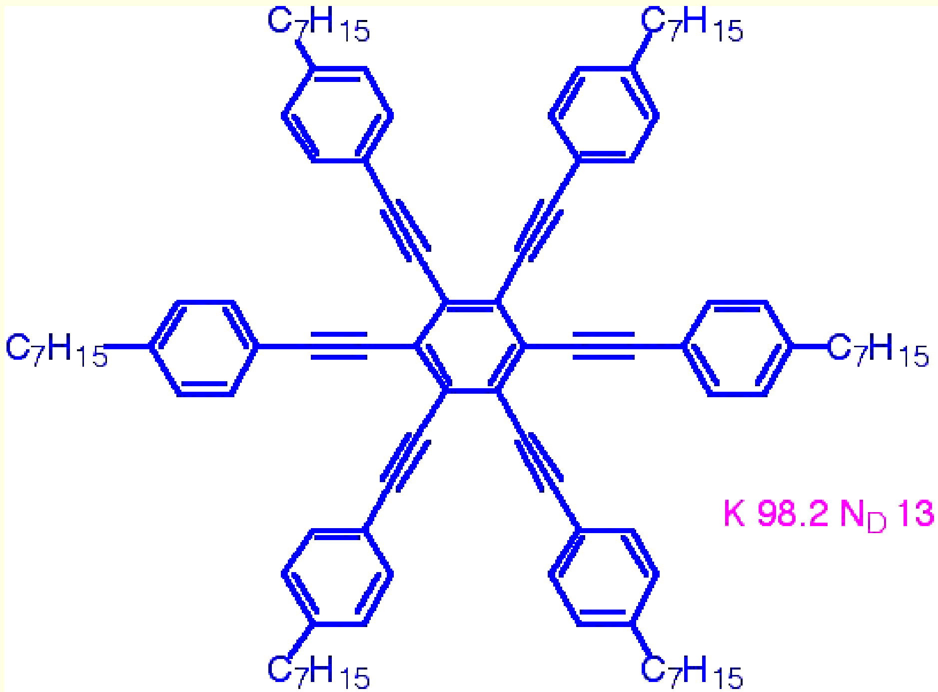


nematic

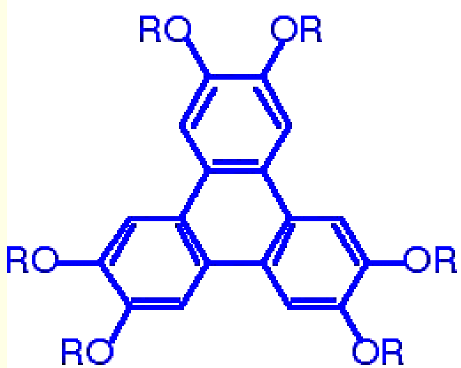


Columar discotic
(smectic discotic)
The molecules tend to position themselves in column

- In *smectic discotic* LC phase, the columns are arranged in a hexagonal or rectangular lattice (coins stacked in columns can be used to simulate the structures of various columnar mesophases.
- *Chiral nematic discotic* LC phase also exists-the director rotates in a helical fashion
- LC molecules: disc-shaped central core with some flexible peripheral moieties

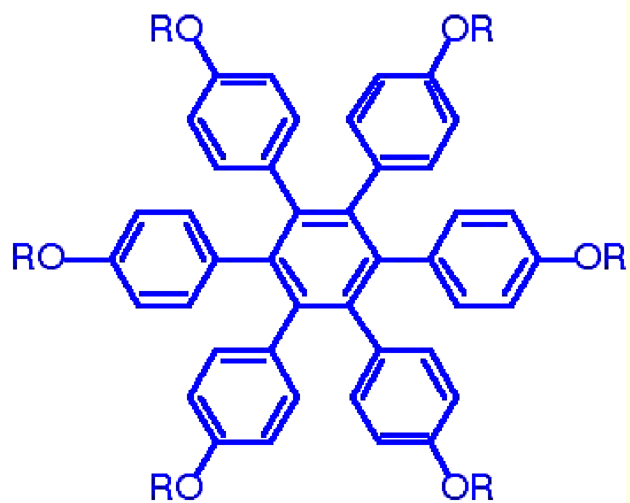


K 98.2 N_D 131.2 I



R = C_5H_{11}

K 40.0 D_{ho} 79 I

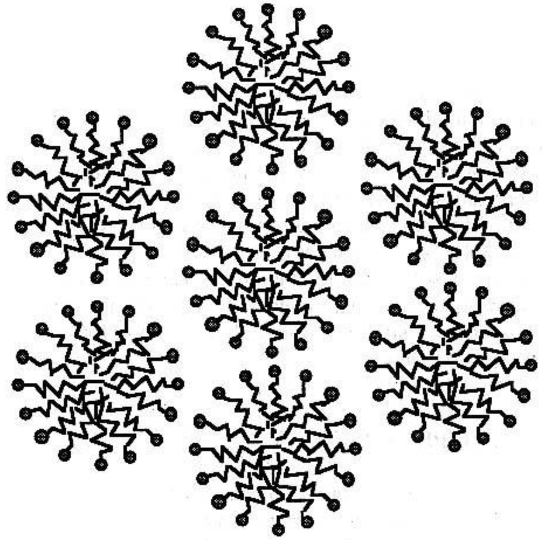


R = OC_5H_{11}

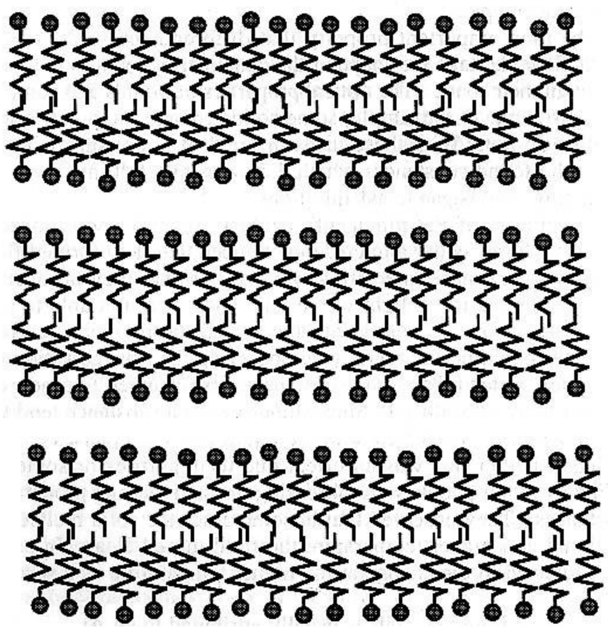
K 68.0 D_{rd} 97.0 I

Lyotropic Liquid Crystals

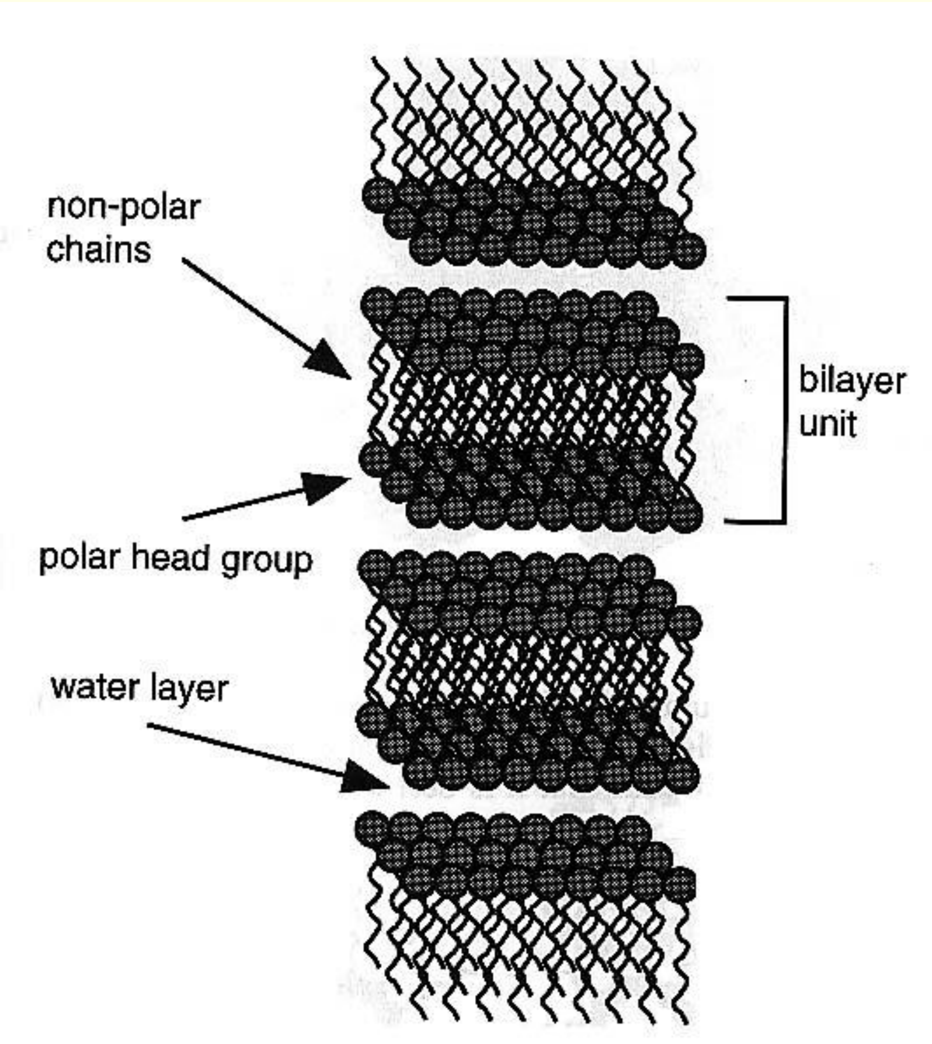
- When two different substances are mixed together, the mixture can exhibit different phases not only as the temperature is changed, but also as the concentration of one component of the mixture is varied.
- Example: a molecule that has end groups with different properties (one is hydrophobic and the other is hydrophilic

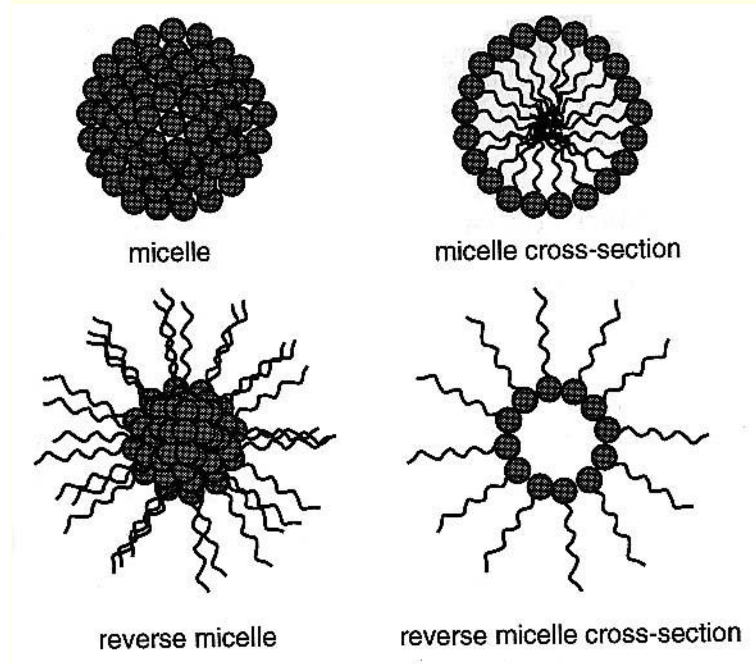


Cross-section of the hexagonal lyotropic liquid crystal phase.



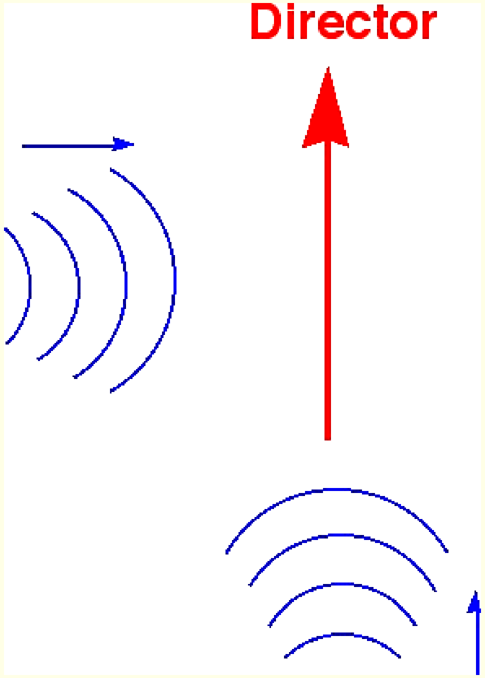
Cross-section of the lamellar lyotropic liquid crystal phase.


non-polar
chains
bilayer
unit
polar head group
water layer


micelle
micelle cross-section
reverse micelle
reverse micelle cross-section

Anisotropy in Liquid Crystals

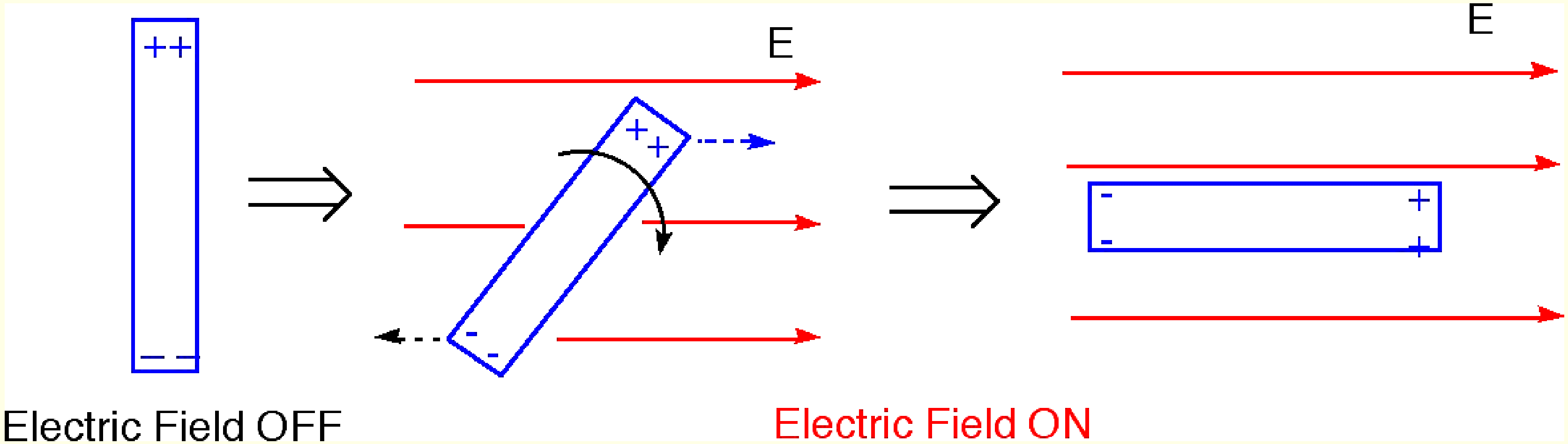
- Liquid: isotropic physical properties
- LC phases: the physical properties parallel or perpendicular to the director will be different



The speed of sound along these two directions will be different. Therefore, LC phase is also called the anisotropic phase

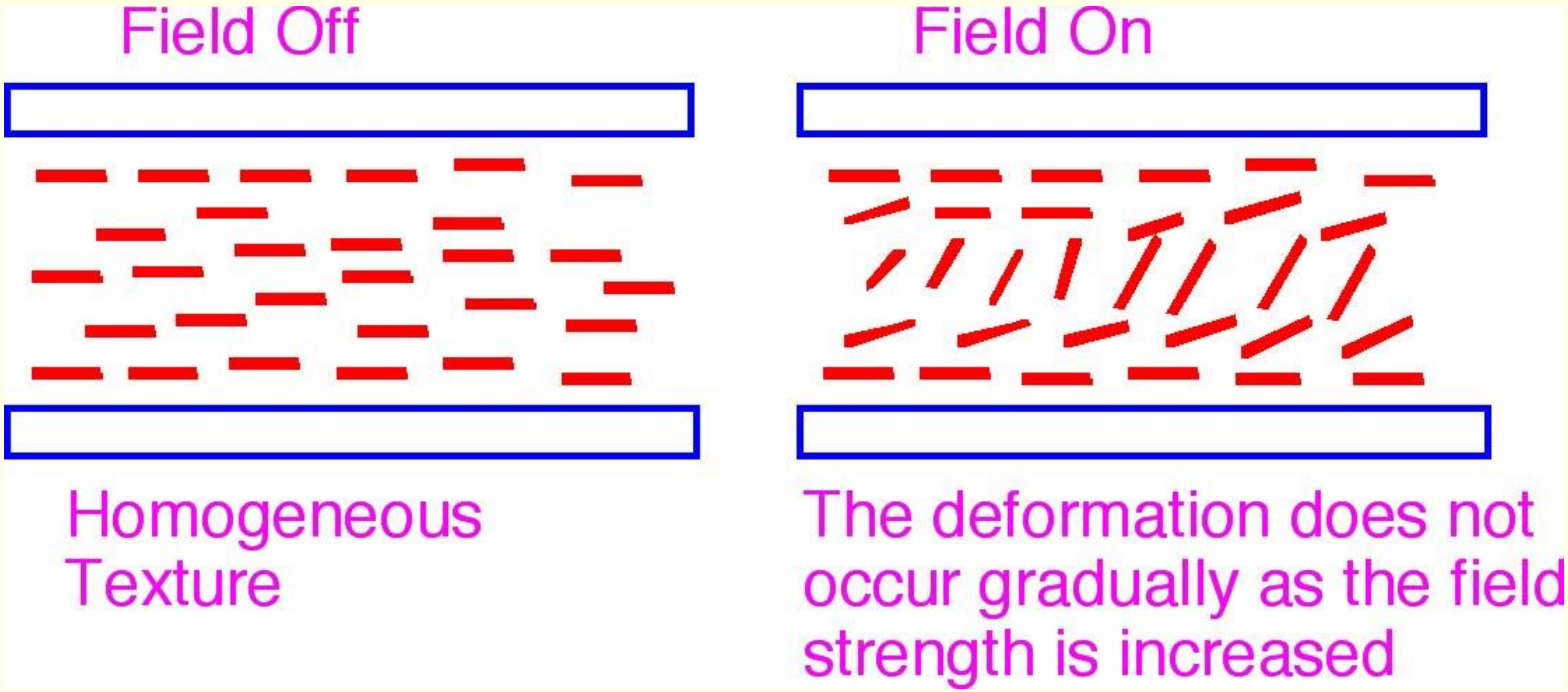
Effect of Electric Field

- Many LC molecules possess permanent electric dipole
- Under an electric field, the molecules tend to rotate until the positive and negative ends line up with the electric field

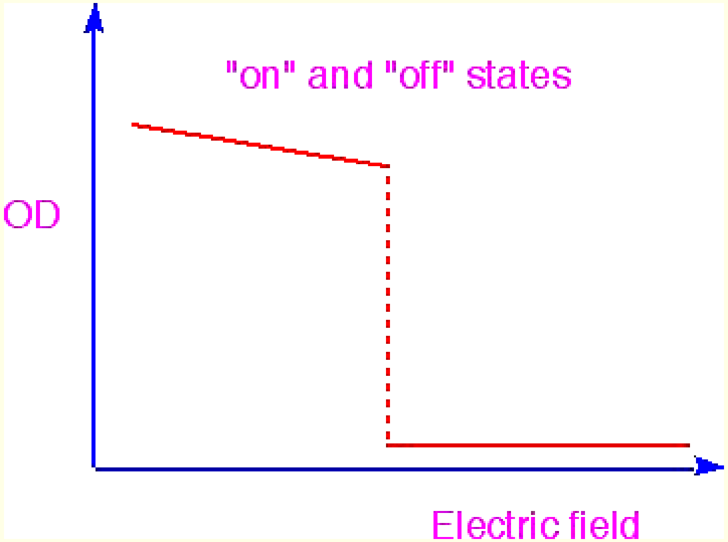


Effect of Surface

When dispersed on a substrate (e.g. glass slide, polymer film), the alignment of liquid crystal molecules can be controlled by pretreating the surface.



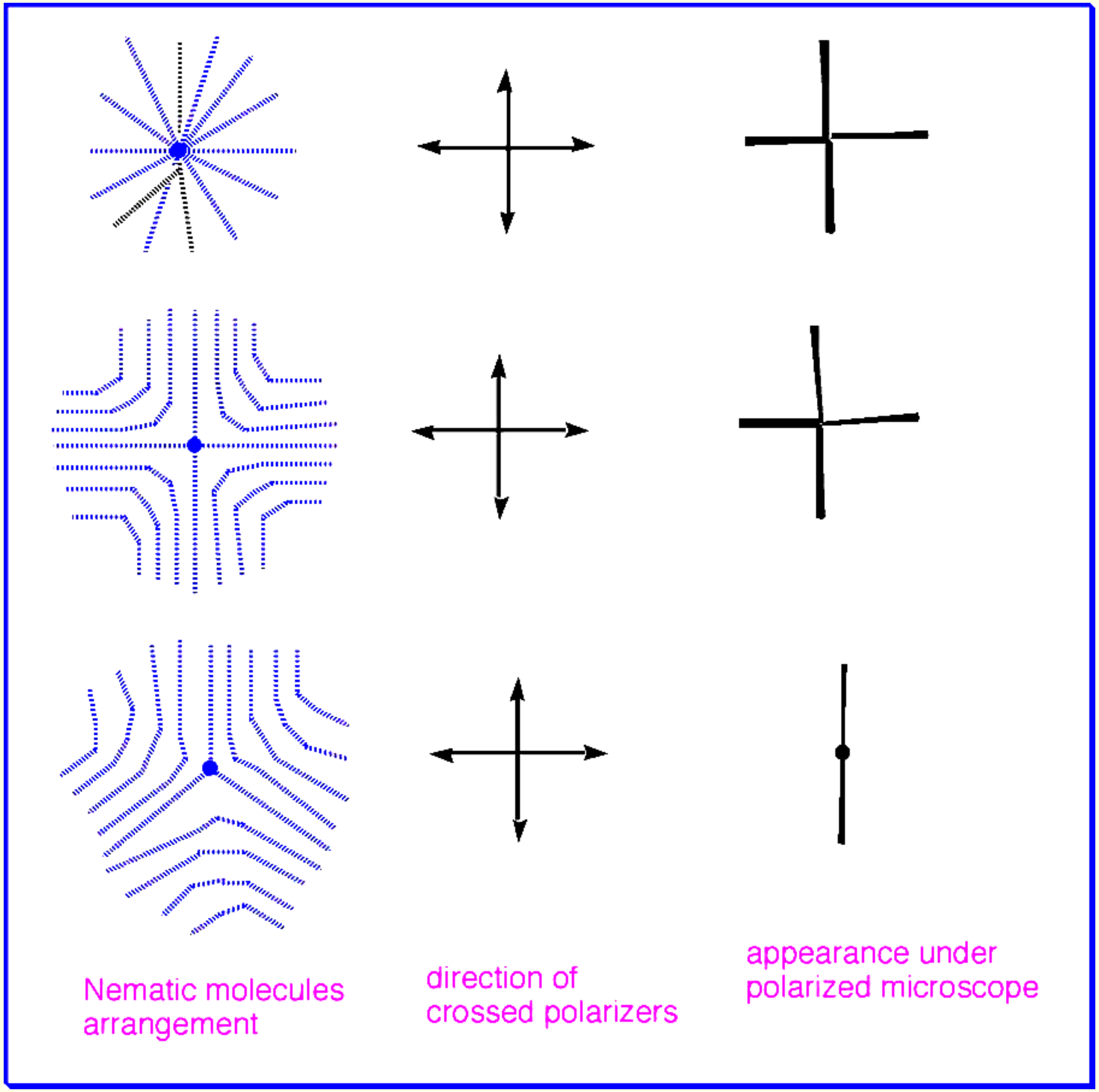
- The deformation of molecular alignment does not occur gradually as the field strength is increased
- For E-field below a threshold value, the molecules are almost completely undeformed.



Such transition is called
Freedericksz Transition

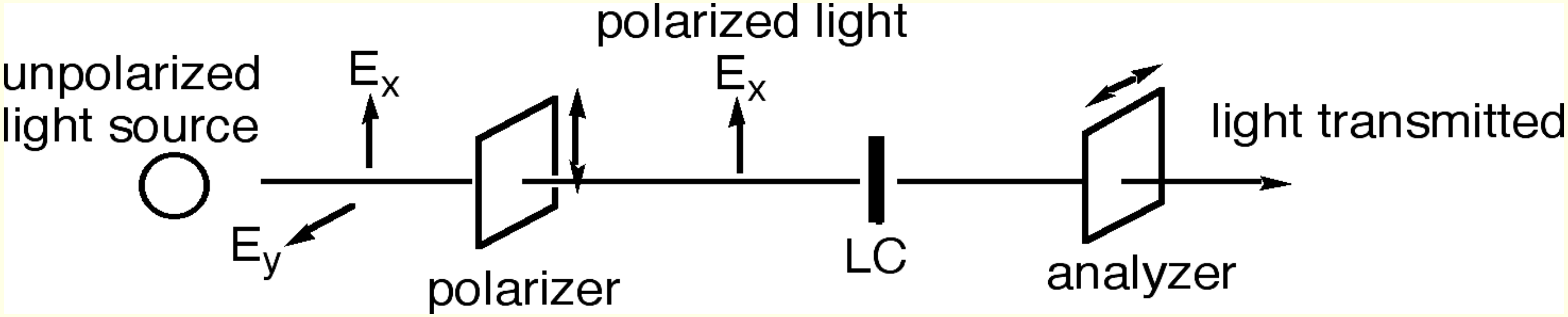
Defect in Liquid Crystals

- A normal, unaligned sample of a nematic LC does not usually have a director that points in the sample direction in all regions of the sample. The director changes throughout the sample and at positions where the director abruptly changes direction, no specific director can be defined, and a ***defect*** is generated.
- The defects can be studied by polarized microscope


Nematic molecules arrangement
direction of crossed polarizers
appearance under polarized microscope

Interaction with Polarized Light

- Since liquid crystals are anisotropic, they cause light polarized along the director to propagate at a different velocity than that polarized perpendicular to the director
- The polarization of light is rotated by the LC molecules



- If the polarized light incident on the LC has its polarization direction either *parallel or perpendicular* to the director, it will appear black under crossed polarizers
- When viewed under a microscope with the sample between two crossed polarizers, the director usually points in different directions at different points within the sample
- The *specific textures* observed under microscope give the information about the type of LC phase formed
- For more information about liquid crystal phases and their optical textures, please see: http://abalone.phys.cwru.edu/tutorial/enhanced/files/lc/phase/phase.htm

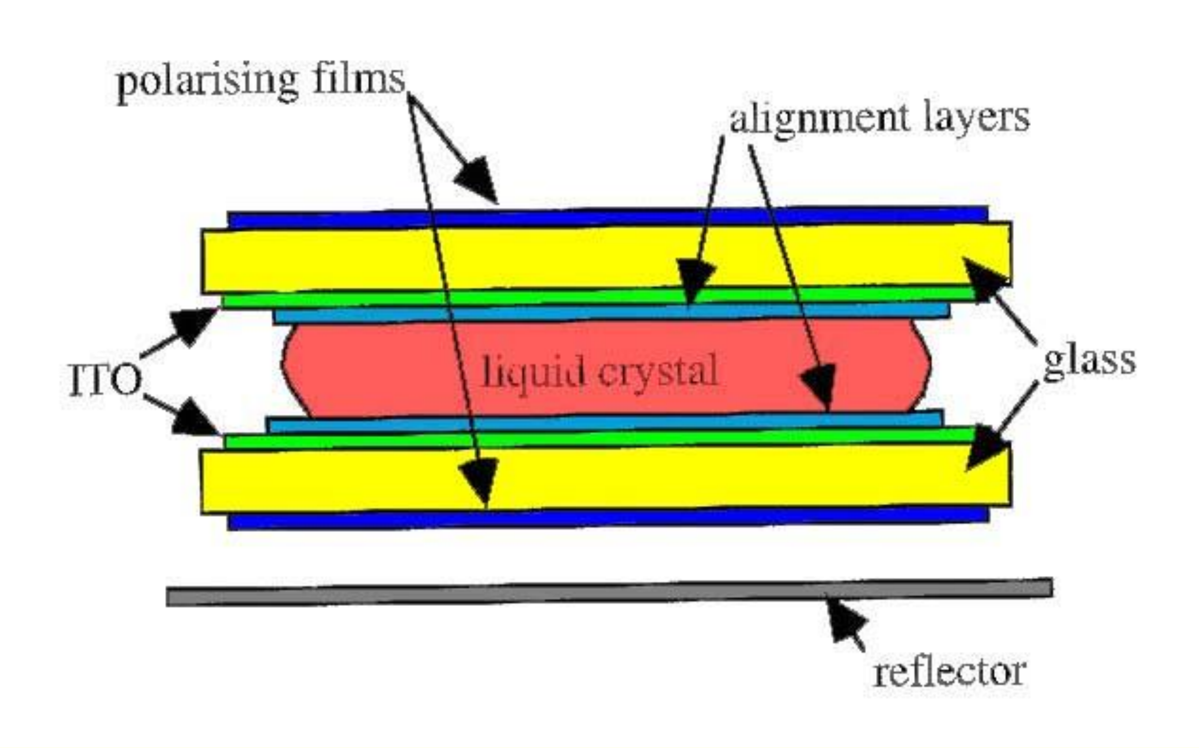
Other techniques that is commonly used in the characterization of Liquid Crystal phases

- **X-ray diffraction**
  - Structure of the LC phases
  - Presence of long range order
- **Thermal analysis**
  - e.g. Differential Scanning Calorimetry (DSC)
  - Transition temperatures
  - Enthalpy of thermal transitions

Liquid Crystal Display (LCD)

- The simplest display device: with ON and OFF states only.
- Make use of the change in brightness of the device (Black vs. White)
- The simplest LC display: *twisted nematic mode*

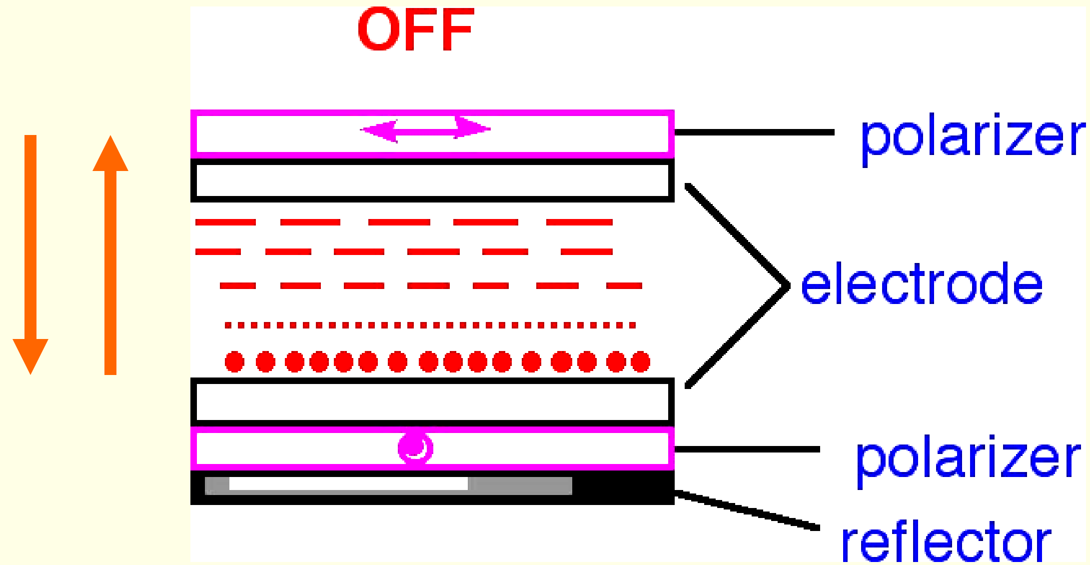
More information on LCD at:
http://abalone.cwru.edu/tutorial/enhanced/files/lcd/tn/tn.htm



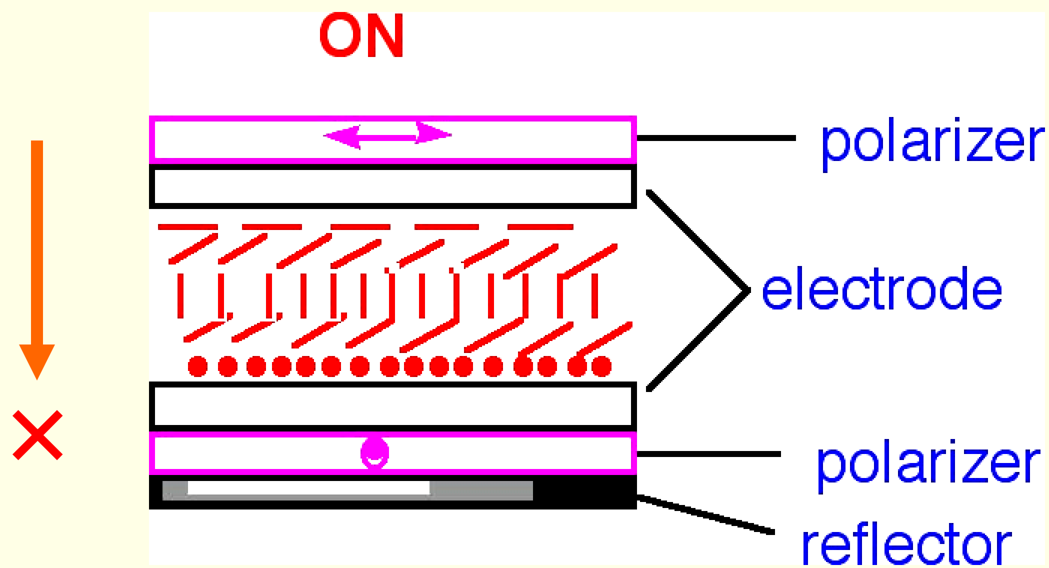
The glass surfaces have been treated so that the LC molecules prefer to align parallel to the surface

The director of the nematic LC molecules is forces to twisted through an angle of 90° within the cell
(i.e. the polarization direction of light rotates 90°)

Polarized light can enter the second polarizer and it is reflected back to the surface



Polarized light cannot enter the second polarizer. No light is reflected. A dark surface is observed.

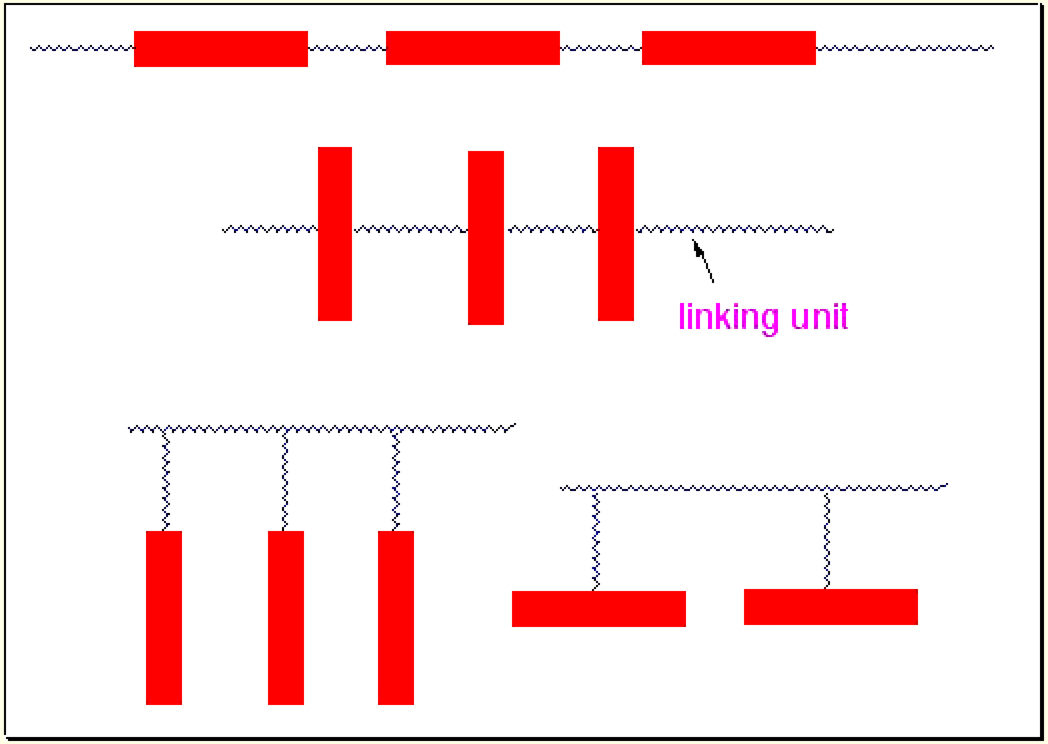


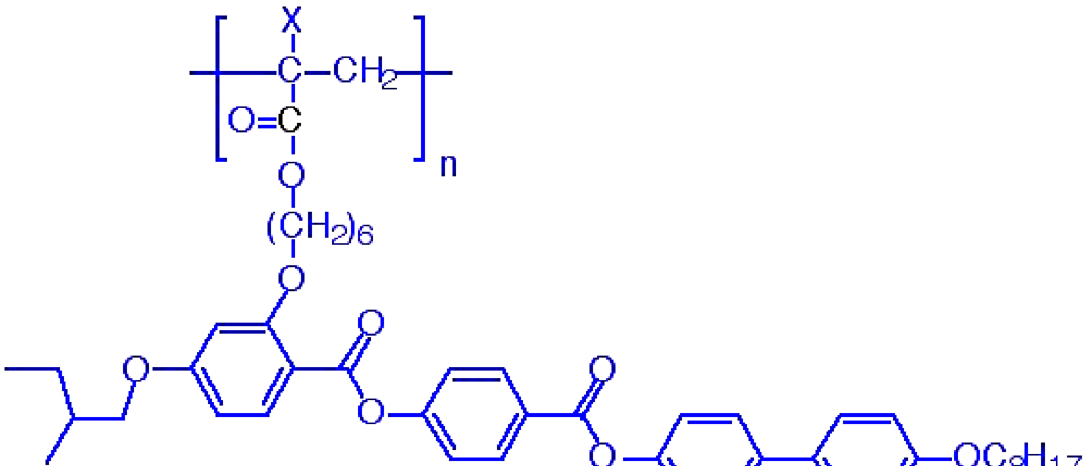
Multicolor Display

- Typically found in all laptop computers/TVs/PDAs
- Every pixel contains three color components-Red, Green, and Blue

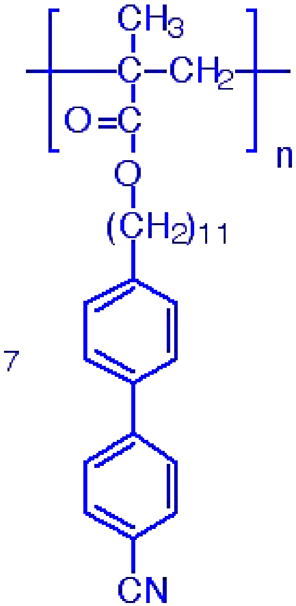
Polymer Liquid Crystals

- The mesogenic unit is incorporated into a polymer molecule
- On the main chain or side chain

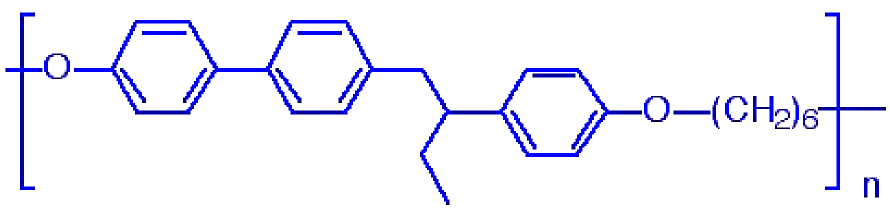




X = H: G 30.1 N* 110.8 I
X = CH_3: G 37.8 N* 101.5 I



G 30 S_A 81 I



G 65 N 135 I

Applications of Liquid Crystals

- Surface Thermometry
  - Thermochromic behavior of chiral nematic phase
- Switchable Light Panels (windows)
  - Liquid crystal droplets dispersed in a polymer film, whose optical properties change under the action of an electric field

- Spinning of fibers from polymers
  - Some aromatic polyamides form lyotropic LC phase when dissolved in suitable solvents.
  - When fibers are spun from LC solution, the molecules will have additional ordering in alignment, which give enhanced tensile strength to the fibers
  - Example: Kevlar
    - This polymer forms lyotropic LC solution in sulfuric acid