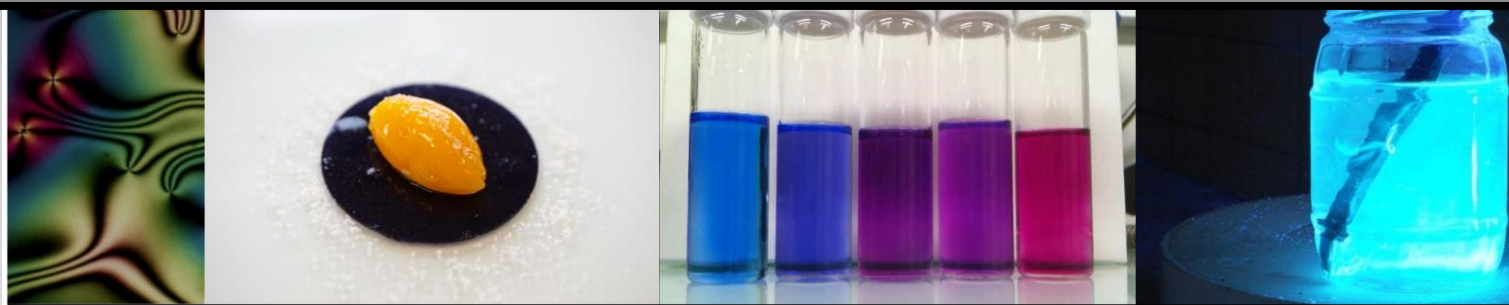


Cours de Chimie

L3 Phytem - 3 avril 2013



Jonathan Piard (jonathan.piard@ens-cachan.fr)

Thèmes possibles

————— Cristaux liquides

Photophysique —————

————— Nanomatériaux

Cuisine moléculaire —————

————— Cristallographie

Autres —————

Programme de Prépa

_____ Classification périodique

_____ Modèle quantique de l'atome

_____ Modèle de Lewis

_____ Structure électronique des molécules diatomiques

_____ Cinétique chimie micro et macroscopique

_____ Thermodynamique

_____ Chimie des solutions

_____ Chimie organique

_____ Diagrammes binaires

_____ Spectroscopie

_____ Cristallographie

_____ Polymères

Cristaux liquides

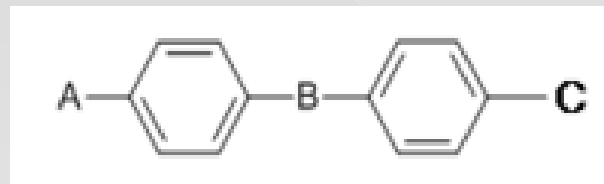
Un **cristal liquide** est un état de la matière qui combine des propriétés d'un liquide conventionnel et celles d'un solide cristallisé.

On exprime son état par le terme de mésophase ou état mésomorphe (du grec « de forme intermédiaire »).

La nature de la mésophase diffère suivant la nature et la structure du mésogène, molécule à l'origine de la mésophase, ainsi que des conditions de température, de pression et de concentration.

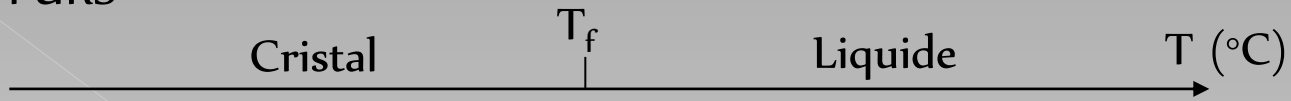
L'existence des mésophases est fondamentalement due à l'anisotropie des mésogènes:

- Anisotropie géométrique
- Anisotropie chimique



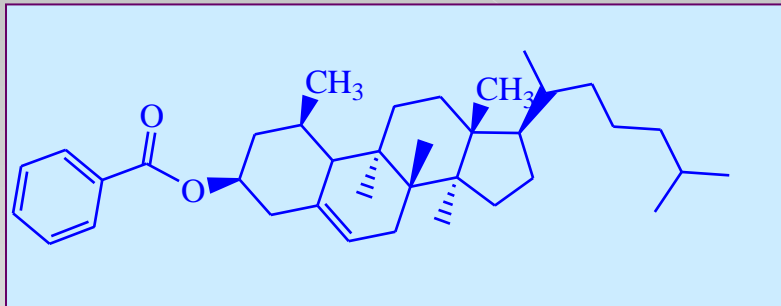
Cristaux liquides

CORPS PURS



MESOGENES THERMOTROPES

* 1888 F. Reinitzer



Friedrich Reinitzer
(1857-1927)

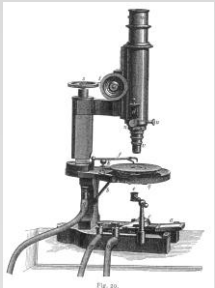
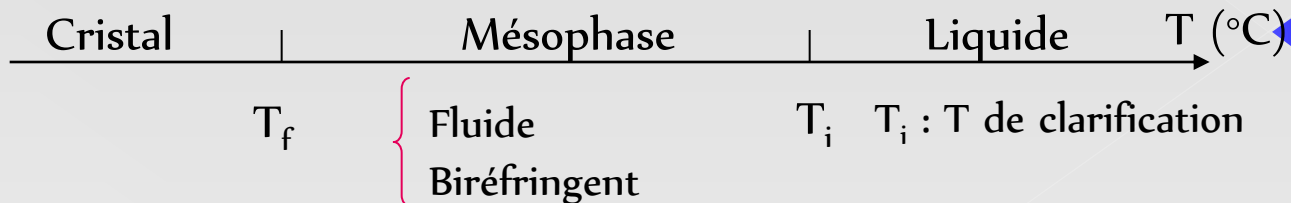
Benzoate de cholestérol

* 1889 O. Lehmann → cristaux coulants

* 1890 O. Lehmann → liquides cristallins



Otto Lehmann
(1855-1922)



Cristaux liquides

- * 1890 Gattermann → phénomènes analogues observés sur un composé de synthèse
- * 1900 O. Lehmann → cristaux liquides
- * 1902 2 élèves de Vorländer synthétisent des composés ayant un comportement différent → polymorphisme
- * 1922 G. Friedel → classification (nématique, smectique, cholestérique)
→ mésophase
- * 1975 P. G. de Gennes → théorie des cristaux liquides



Ludwig Gatterman
(1860-1920)



Daniel Vorländer
(1869-1941)



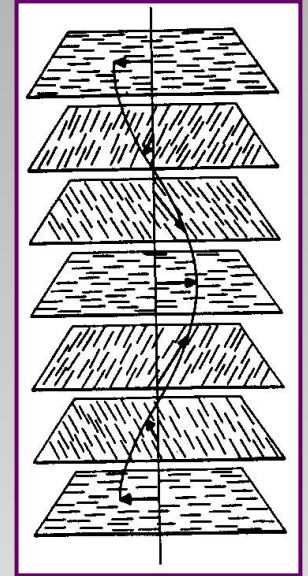
Georges Friedel
(1865-1933)

Cristaux liquides

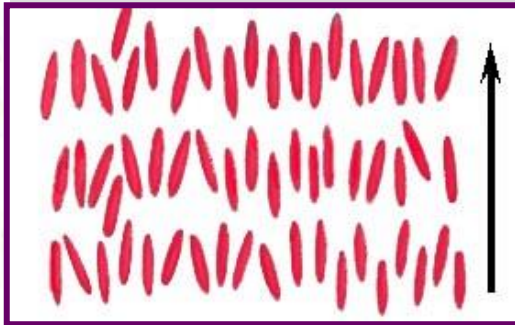
Phase nématique N



Phase cholestérique N*



Phases smectique A



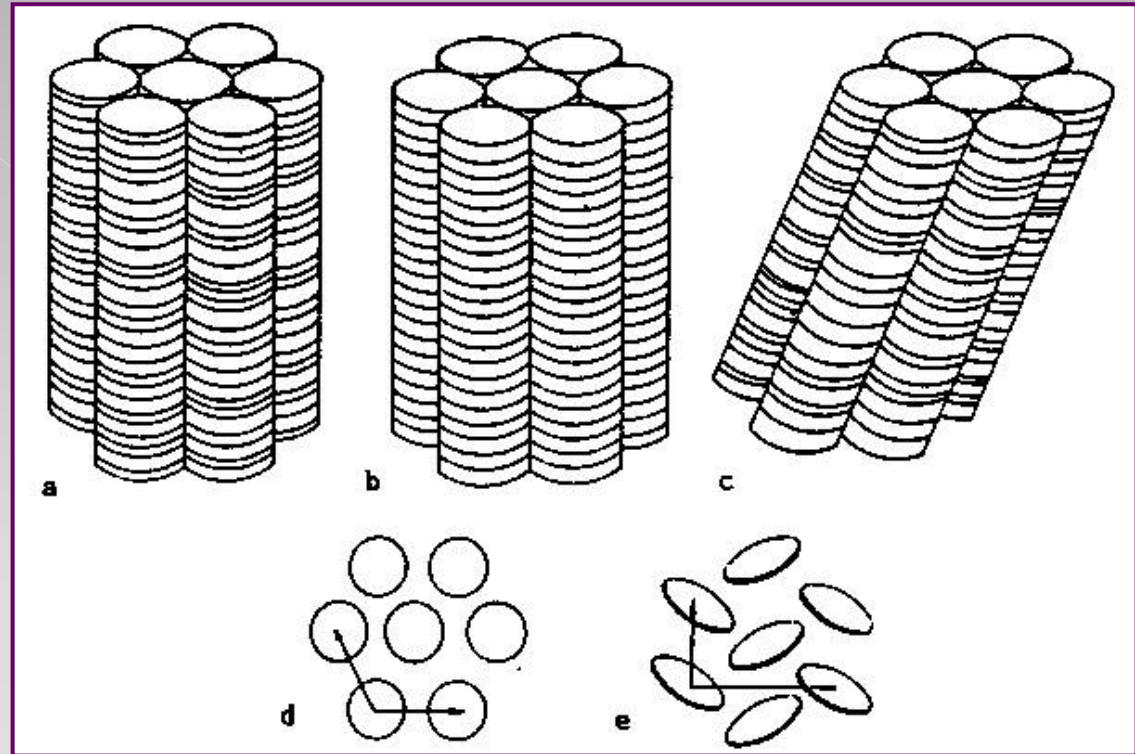
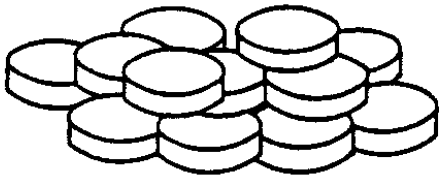
Phases smectique C



Cristaux liquides

Columnar discotic

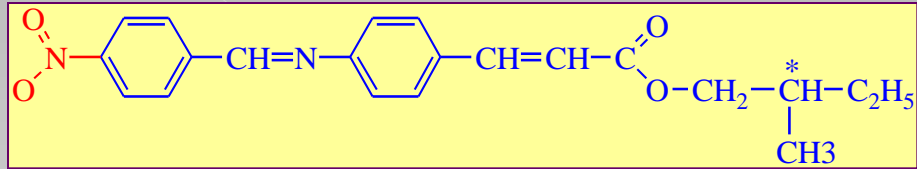
Nematic discotic



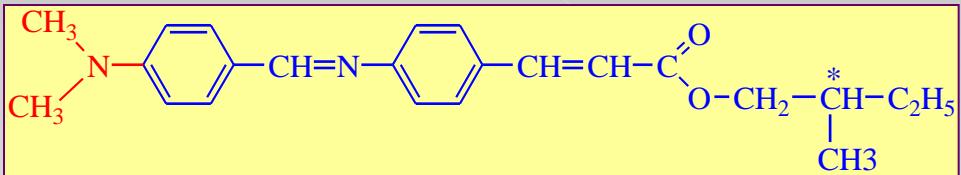
a) disordered, b) ordered, c) tilted, d) hexagonal

Cristaux liquides

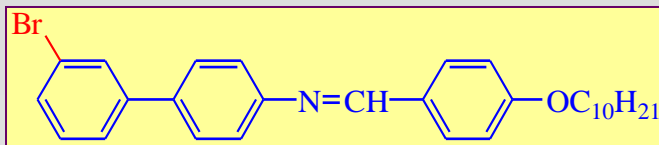
Un faible changement dans la structure moléculaire peut avoir des conséquences importantes sur le comportement mésomorphe du composé



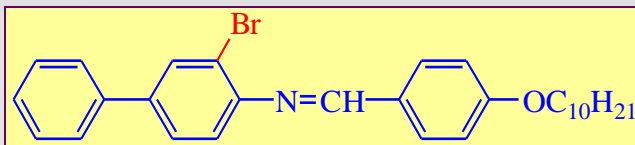
Nématique



Smectique



Smectique



Nématique

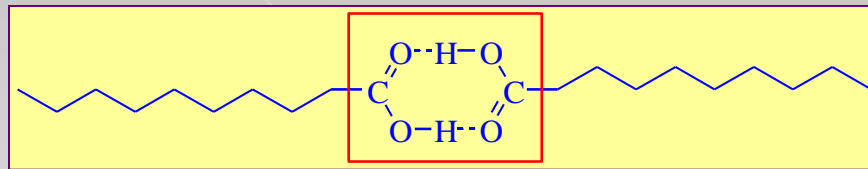
Cristaux liquides

Les alcanes :



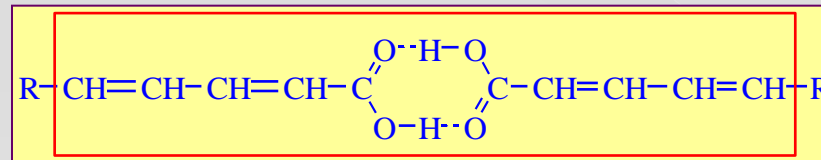
Ne sont pas mésomorphes

Les acides carboxyliques :



Ne sont pas mésomorphes

Mais :

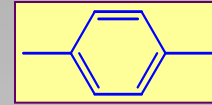


Nématique

Cristaux liquides

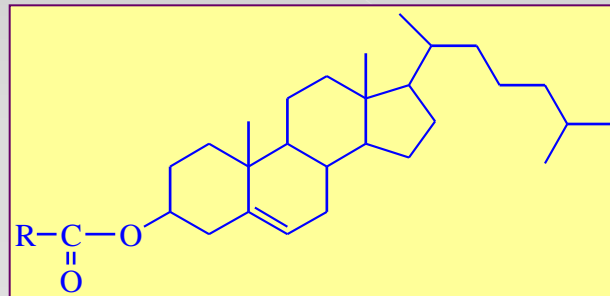
Noyaux aromatiques :

- * plan
- * polarisable
- * rigide
- * chimie (réactions de substitution)

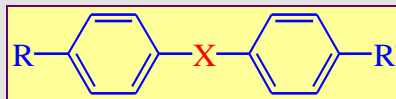


→ entités chimiques particulièrement attractives pour obtenir des C.L.

→ à l'exception des dérivés du cholestérol

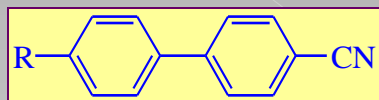


la majorité des molécules de cristal liquide a été construite selon l'architecture suivante :

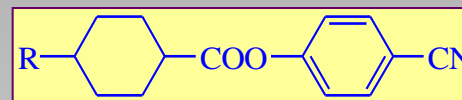


Cristaux liquides

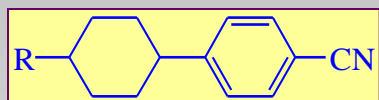
Le groupement central X n'est pas une nécessité



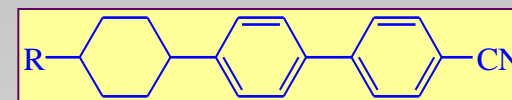
CB 1973



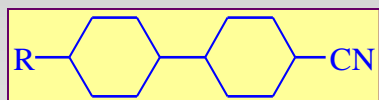
1973



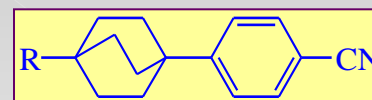
PCH 1977



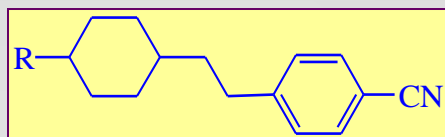
BCH



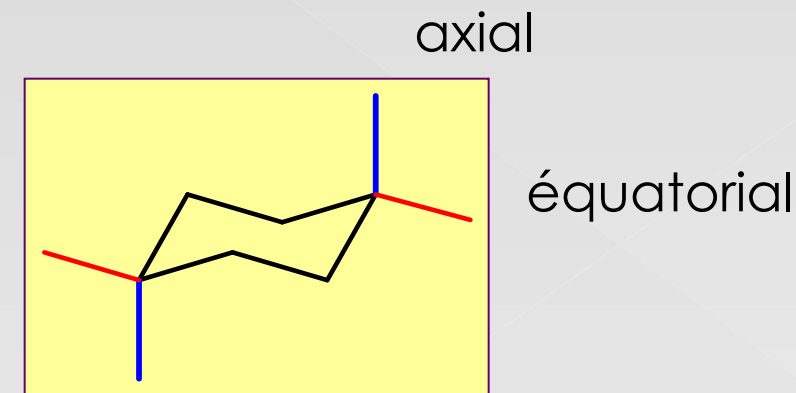
CCH 1978



1979

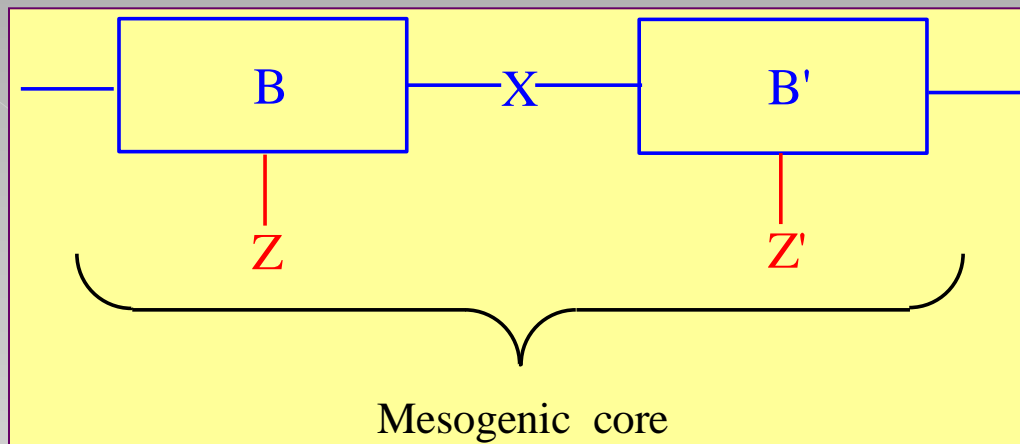


PECH 1983



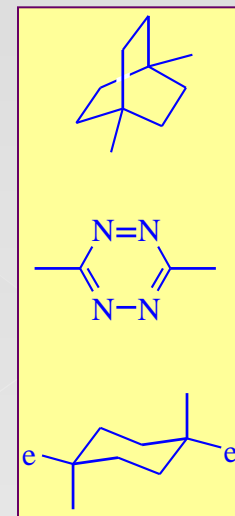
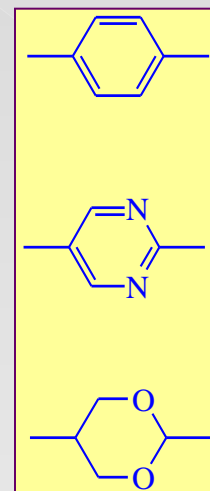
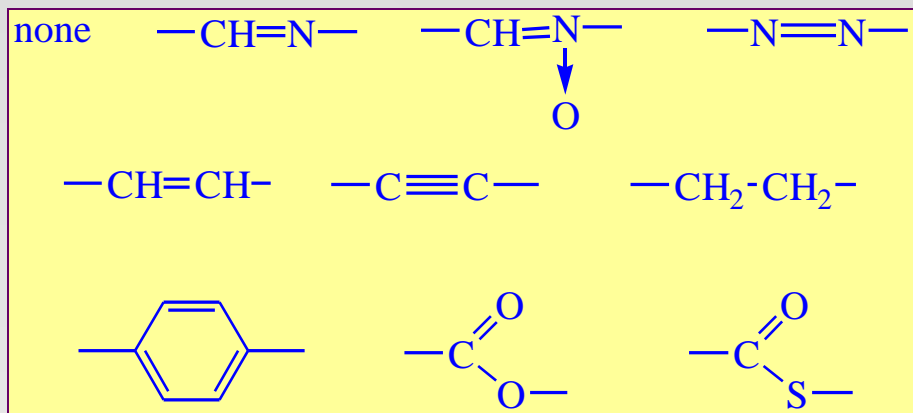
Cristaux liquides

CŒUR MESOGENE



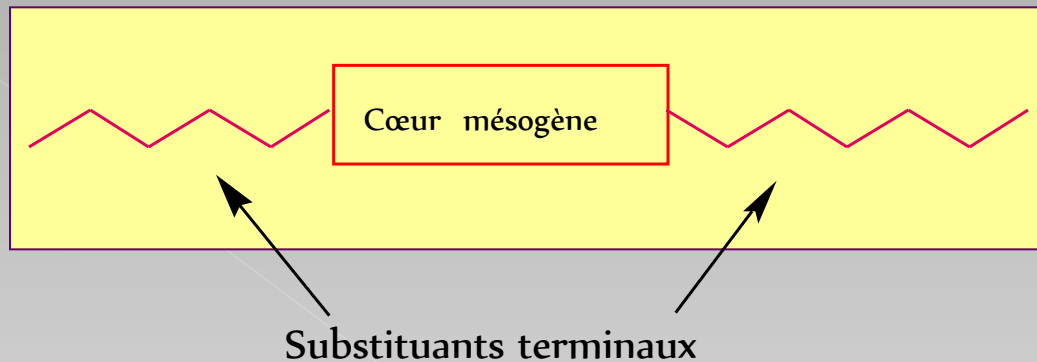
X

B B'

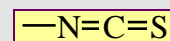
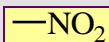
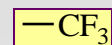
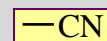
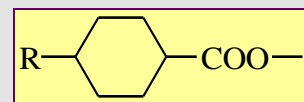
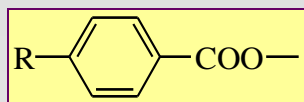
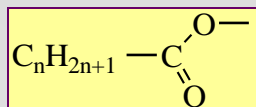
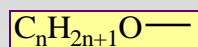
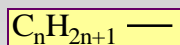


Cristaux liquides

STRUCTURE CHIMIQUE DES MOLECULES CALAMITIQUES

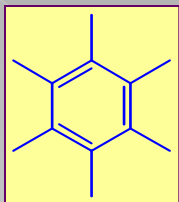


Exemples de substituants terminaux :

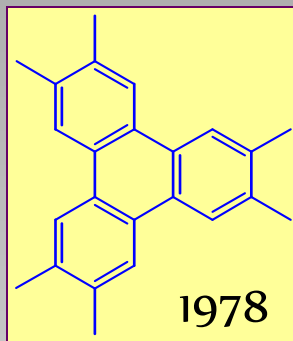


Cristaux liquides

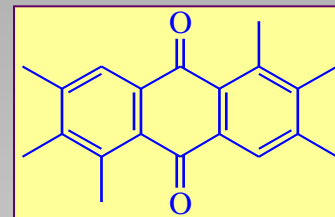
Discotiques



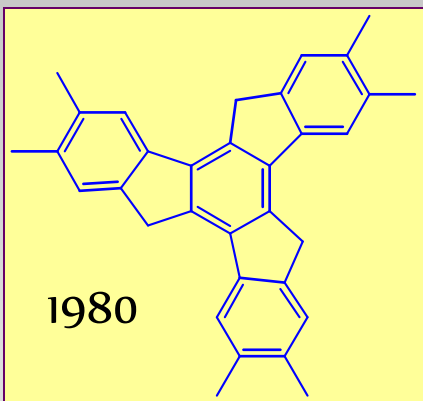
1977



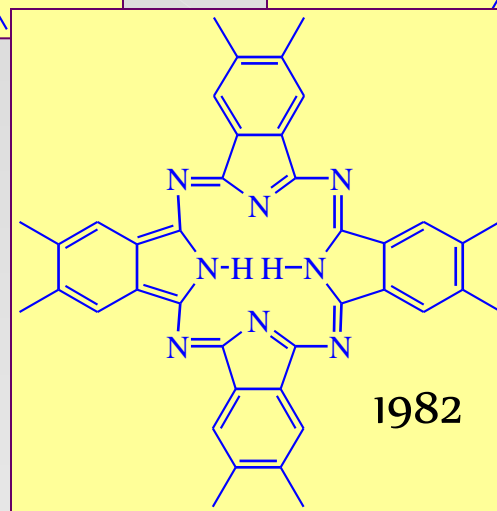
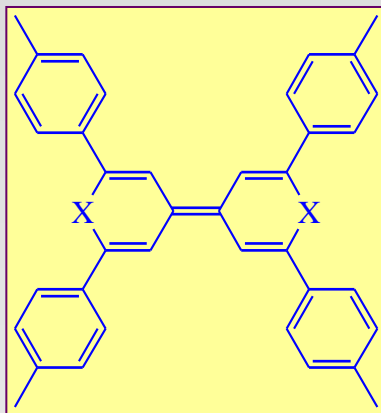
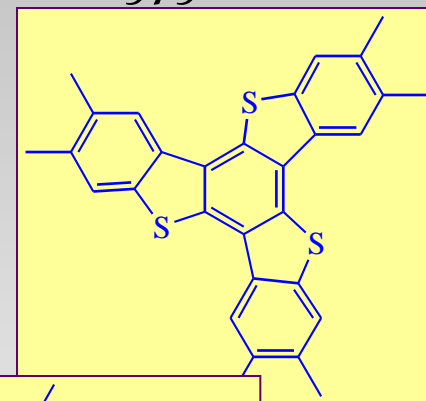
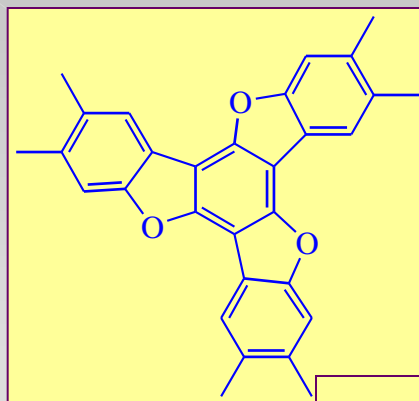
1978



1979



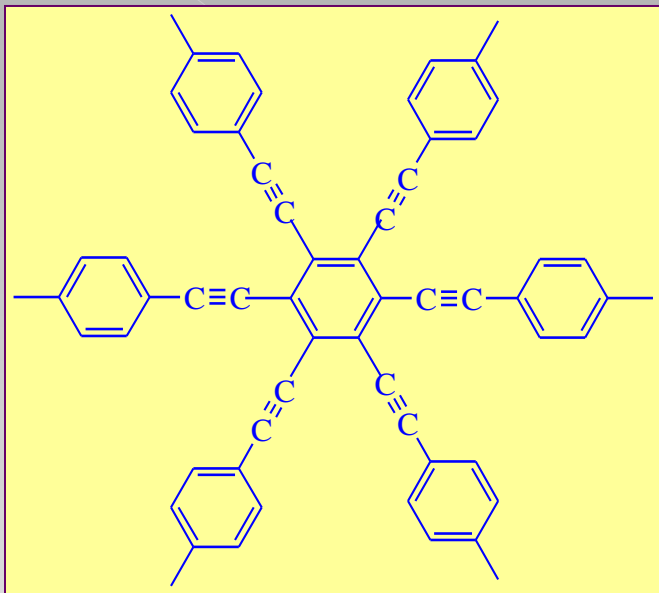
1980



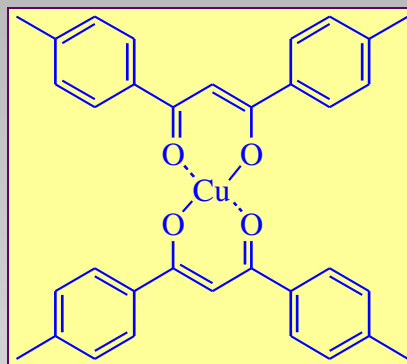
1982

Cristaux liquides

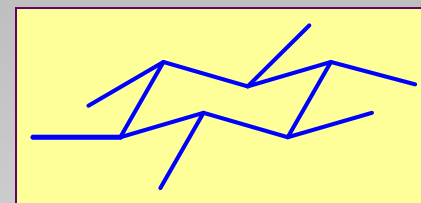
Discotiques



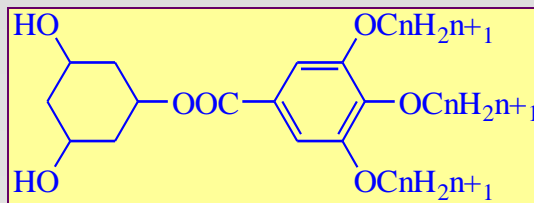
1987



1986



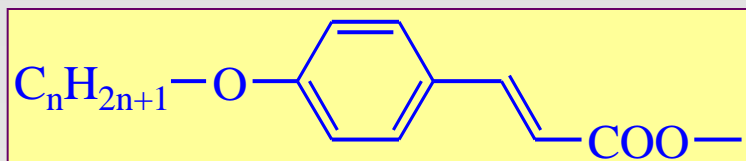
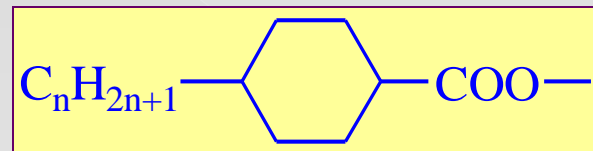
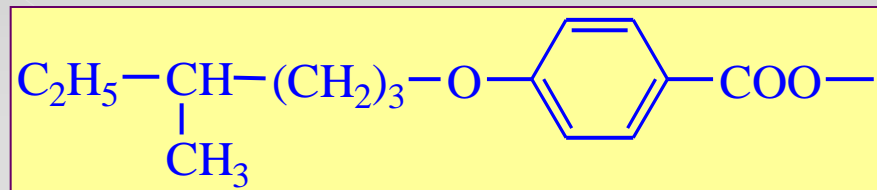
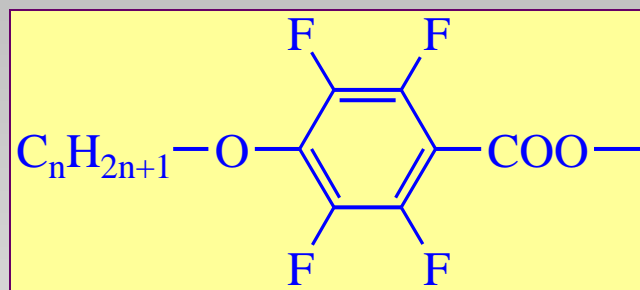
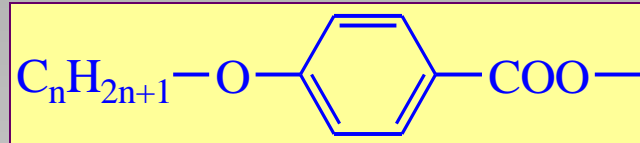
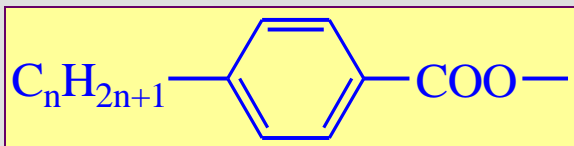
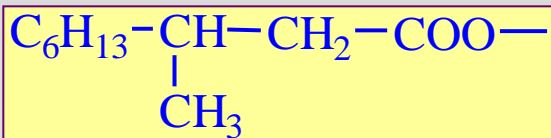
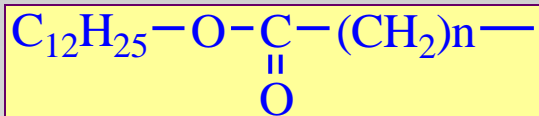
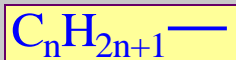
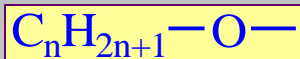
1984



1990

Cristaux liquides

Chaînes latérales

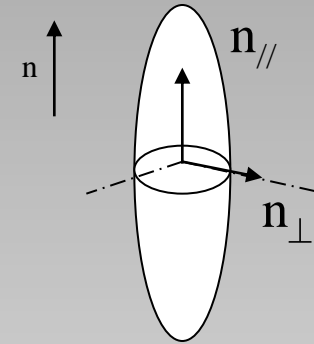


Cristaux liquides

Biréfringence optique

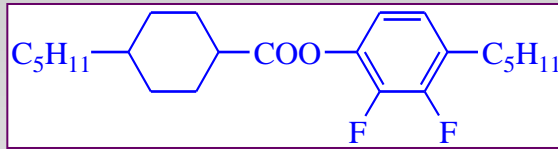
$$\Delta n = n_{//} - n_{\perp} \quad 0,05 < \Delta n < 0,45$$

Δn peut être relié à $\Delta\alpha$, mais aux fréquences optiques



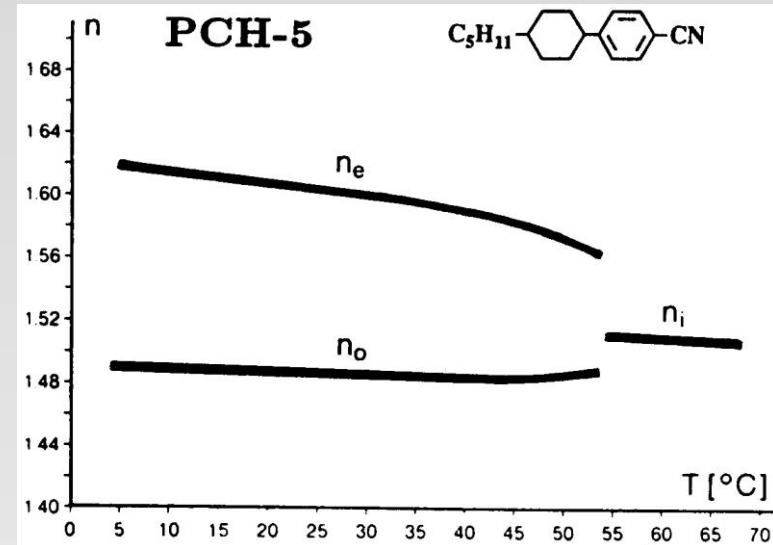
Δn est dû à la présence d'électrons délocalisés et d'électrons Π

$$n_o \sim 1,5$$



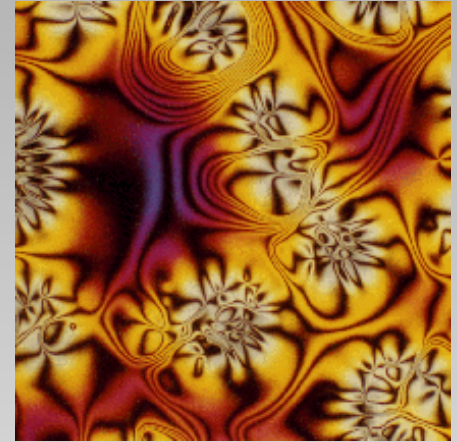
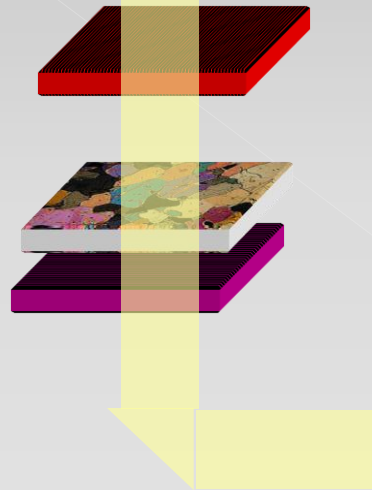
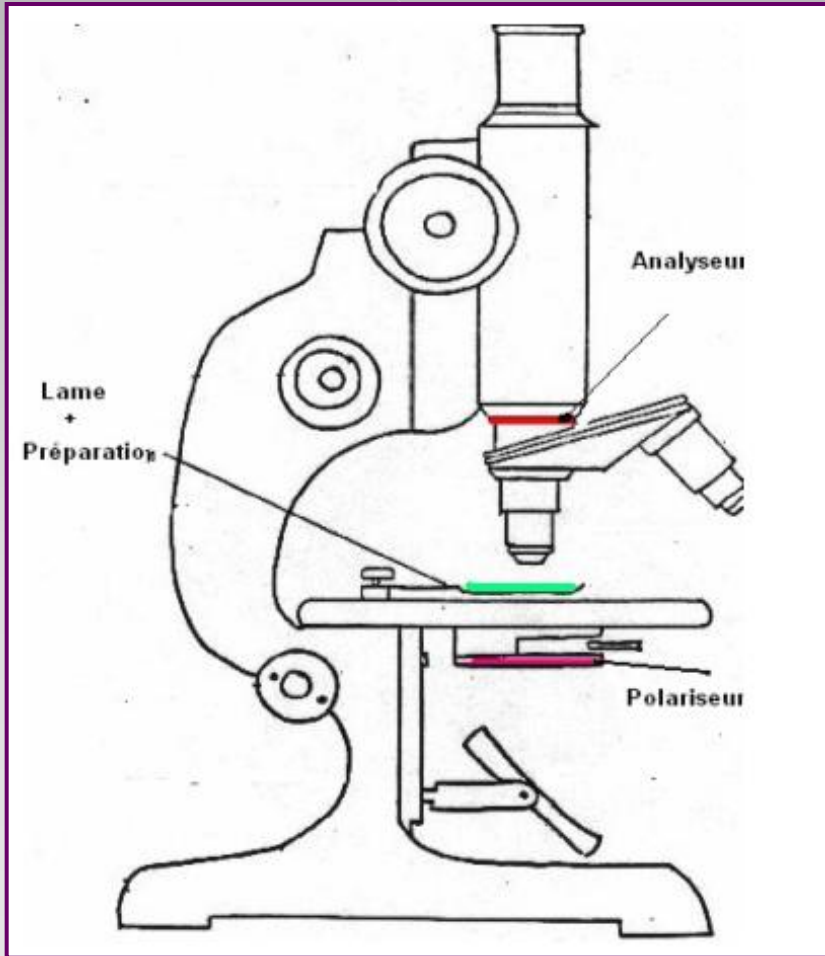
$$n_e = 1.529 \quad n_o = 1.472 \quad \Delta n = 0.057$$

Structure	ϵ_{\parallel}	ϵ_{\perp}	$\Delta\epsilon$	n_o	n_e	Δn	ν [mm ² ·s ⁻¹]
<chem>CCCCC1CC2CC(C(=O)OC3=CC=CC=C3O)CC2</chem>	2.7	3.2	-0.5	1.492	1.550	0.063	8
<chem>CCCCC1CC2CC(C#CC3=CC=CC=C3O)CC2</chem>	3.0	2.8	0.2	1.503	1.635	0.132	23
<chem>CCCCC1=CC=C(C#CC2=CC=CC=C2O)C=C1</chem>	3.4	3.4	0.0	1.527	1.783	0.256	20
<chem>CCCCC1=CC=C(C#CC2=CC=CC=C2C#CC3=CC=CC=C3)C=C1</chem>	3.2	2.4	0.8	1.518	1.880	0.362	32

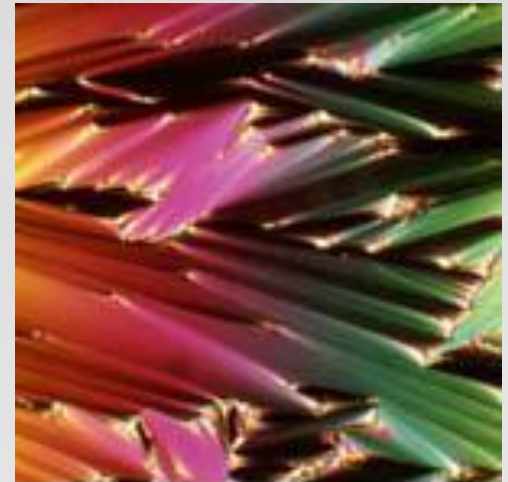


Cristaux liquides

Microscopie en polarisation



La biréfringence des zone CL joue le rôle de multiple lame d'onde.



*Photo courtesy of
Dr. Mary Neubert LCI-KSU*

Cristaux liquides

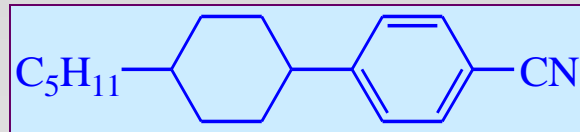
Ordre de grandeur

Enthalpies de transition

$$\Delta H_f \sim 10 \Delta H_C$$

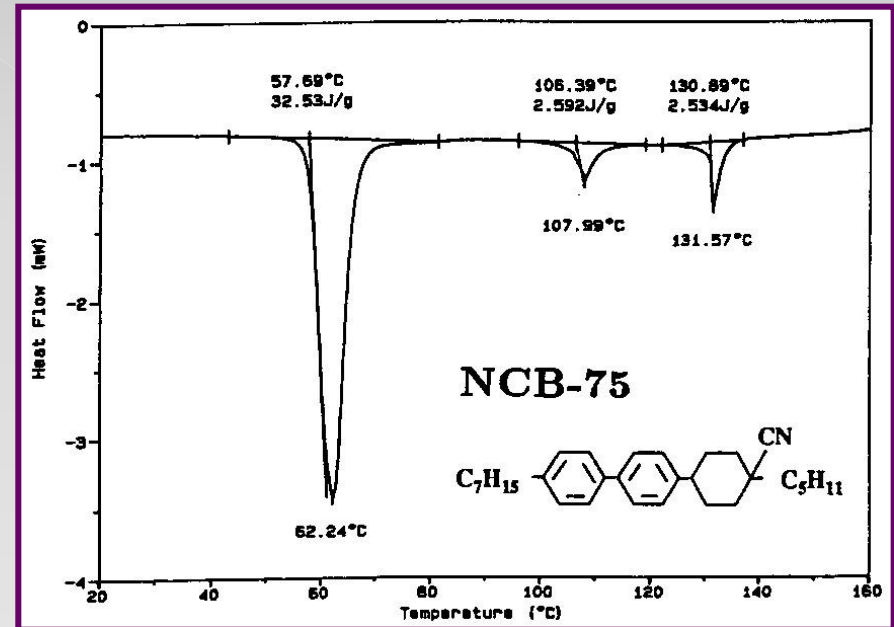
La transition C \rightarrow N est du premier ordre

ΔH_f CL polaires $>$ ΔH_f CL non polaires

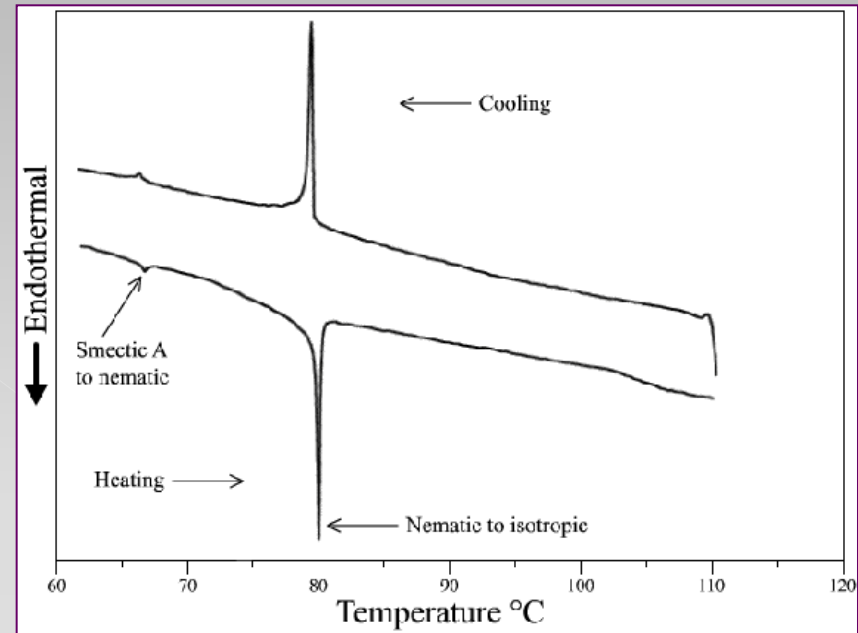
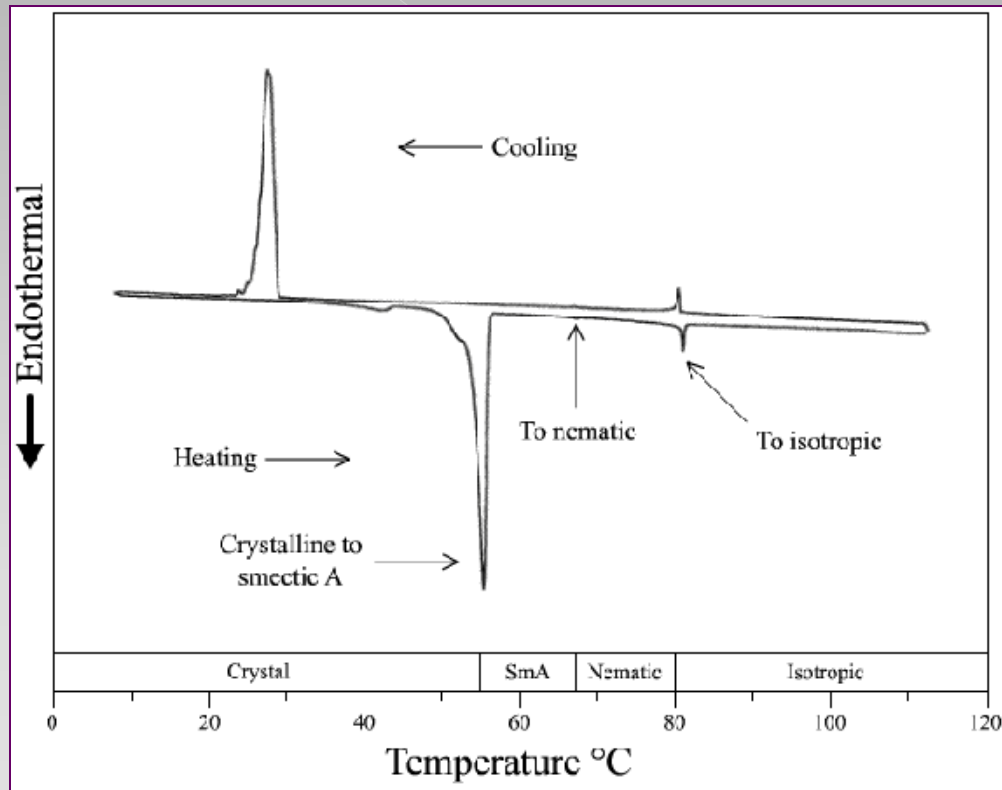


C 30 N 54,9 L

$$\Delta H_f = 21,35 \text{ kJmol}^{-1} \quad \Delta H_C = 0,96 \text{ kJmol}^{-1}$$



Analyse par DSC

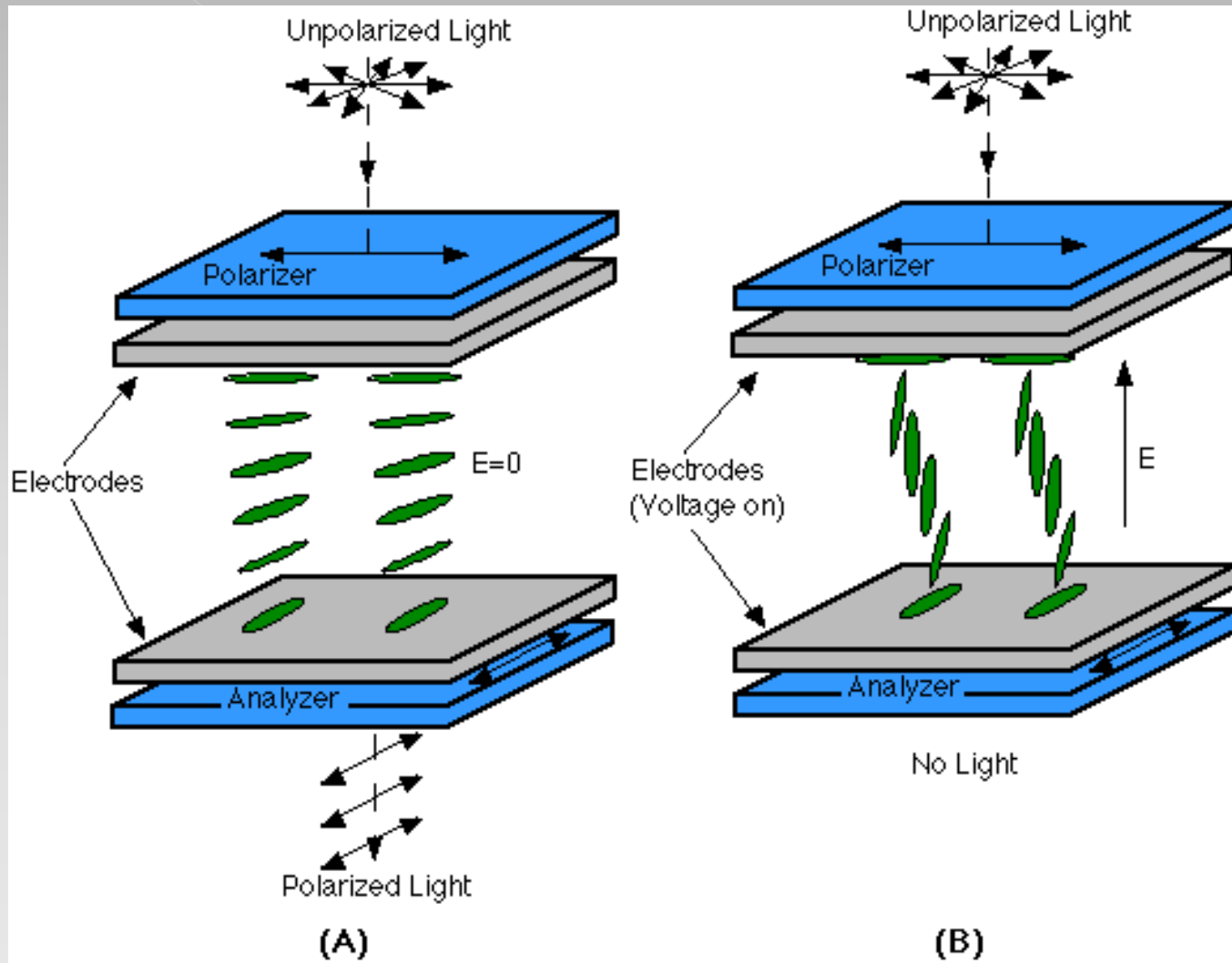


Applications

Cristaux liquides

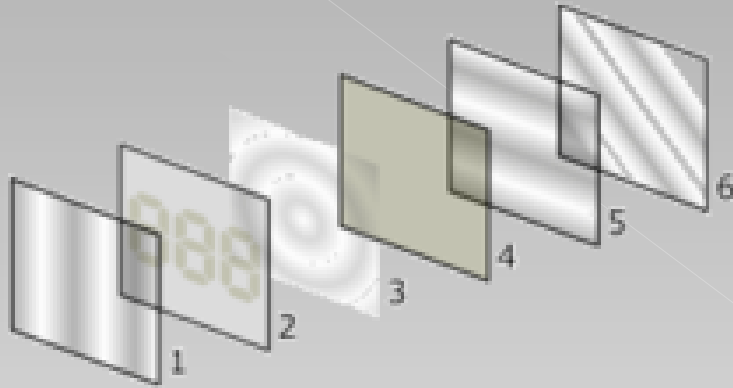
TWISTED NEMATIC EFFECT (TN)

PRINCIPLE OF OPERATION



Cristaux liquides

Écran à cristaux liquides LCD



1. Filtre de polarisation (vertical)
2. Verre avec électrodes correspondant au filtre vertical
3. Cristaux liquides
4. Verre avec électrodes correspondant au filtre horizontal
5. Filtre horizontal pour bloquer/laisser passer la lumière
6. Surface réfléchissante

Les polariseurs

Ils sont constitués de 3 films laminés

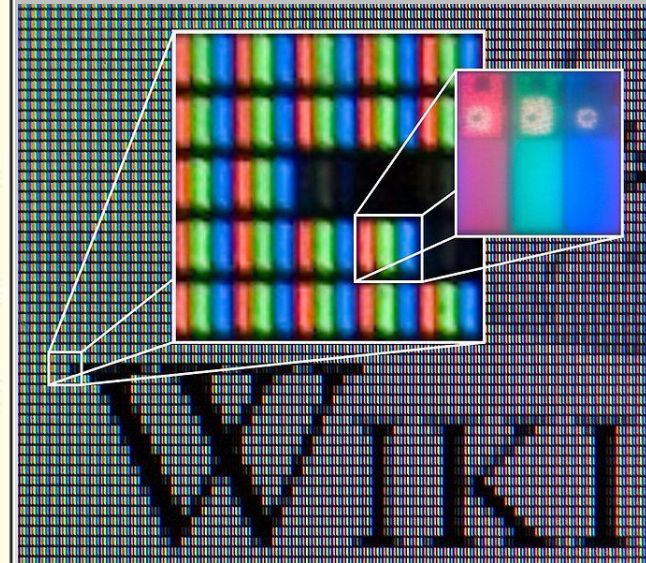
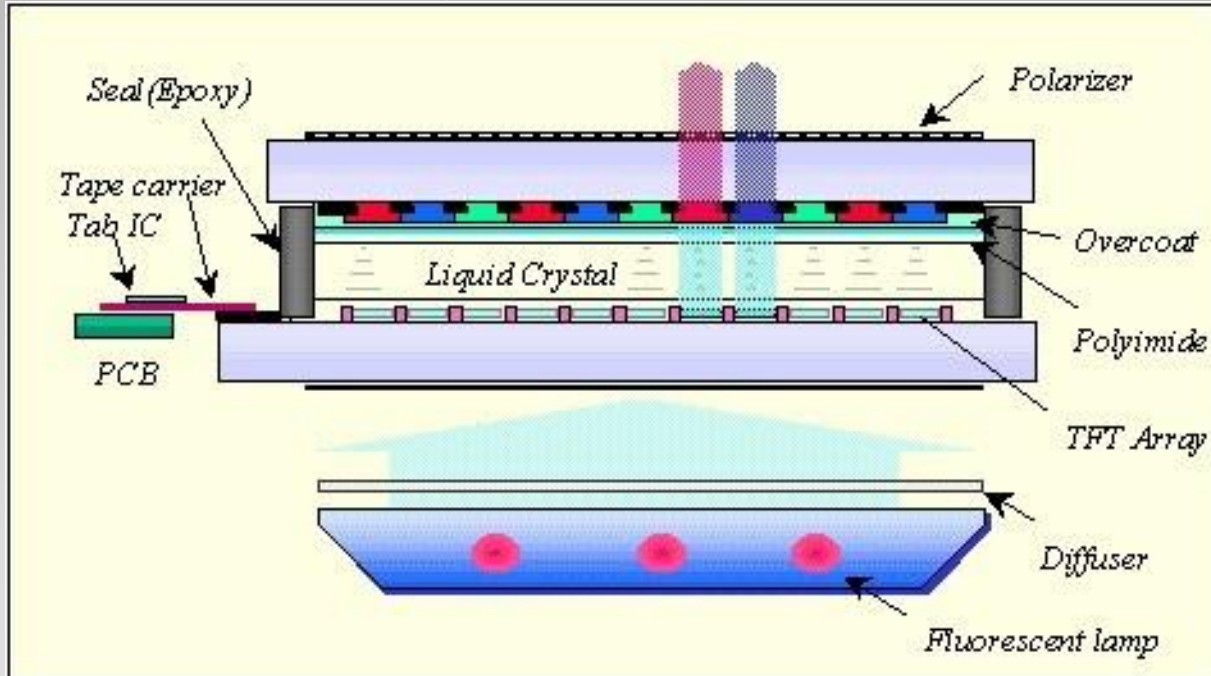
- * la couche polarisante proprement dite (film d'alcool polyvinylique contenant de l'iode ou un colorant) mince et fragile
- * la partie active est prise en sandwich entre 2 films protecteurs (polyester, acétate de cellulose)

Les polariseurs sont commercialisés sous forme de film autocollant

Le choix, le collage, la façon d'orienter les polariseurs conditionnent l'aspect final de l'écran

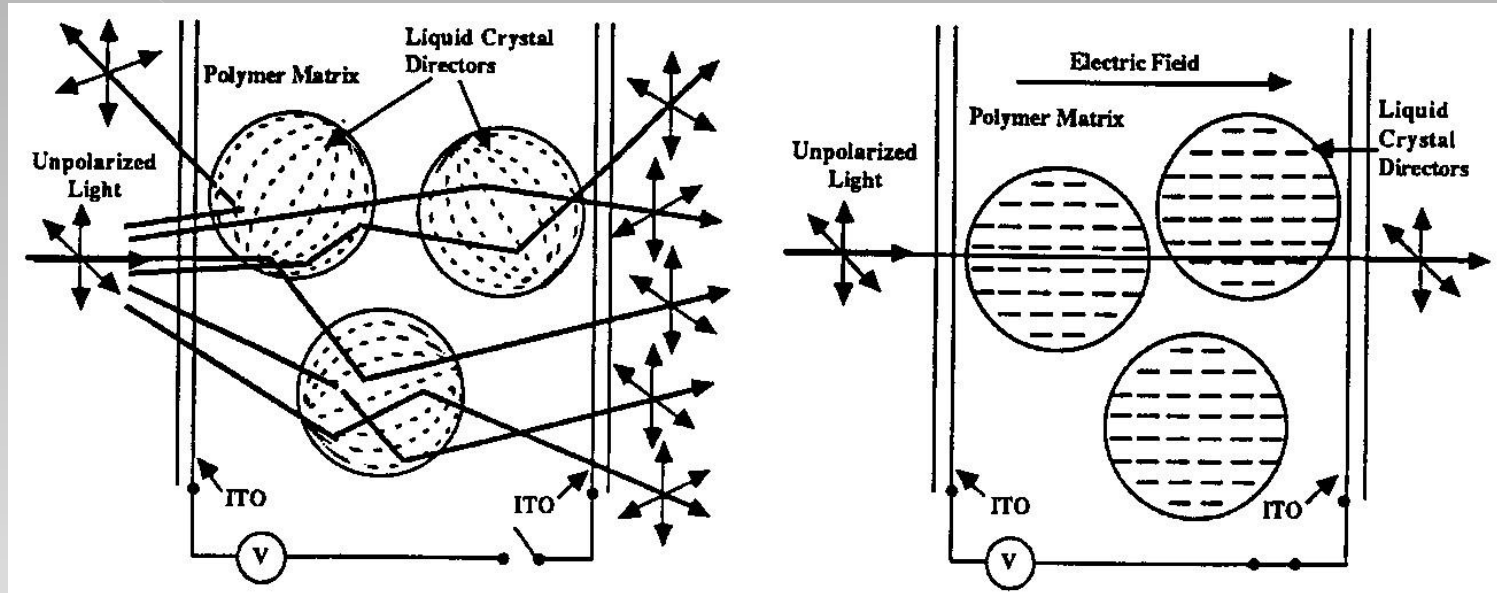
Cristaux liquides

LA COULEUR



Cristaux liquides SYSTÈME DIFFUSANT

Liquid Crystal : N $n_{//} n_{\perp} \Delta e > 0$ Polymer : n_p



The N within the cavities adopts a bipolar configuration

The N droplets within a film act as a collection of uniaxial crystals. In the unpowered film, each droplet acts as a birefringent medium with 2 refractive indexes :

- * ordinary refractive index n_0
- * extraordinary refractive index n_e

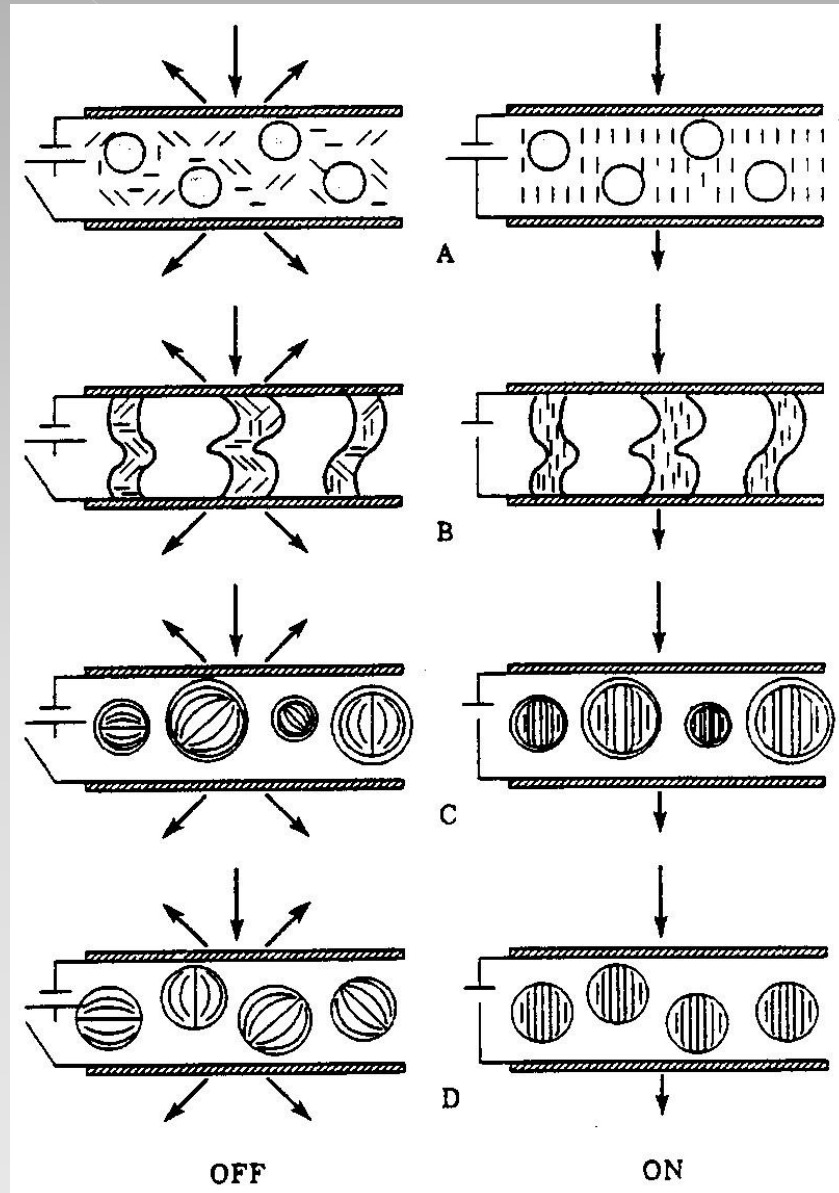
n_0 and n_p are chosen to be close in value :

$$n_0 = n_p$$

$$n_e = \frac{n_{\perp} n_{//}}{\sqrt{n_{\perp}^2 \sin^2 \theta + n_{//}^2 \cos^2 \theta}}$$

Cristaux liquides

LIQUID CRYSTAL POLYMER COMPOSITES



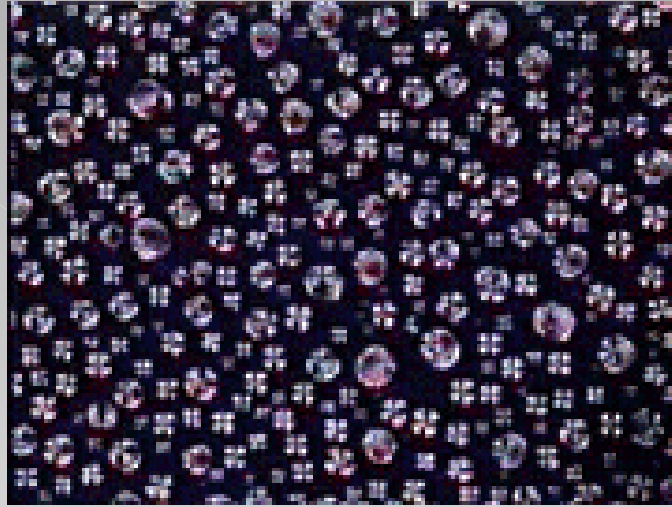
Glass beads in a LC film

LC imbedded in a microporous film

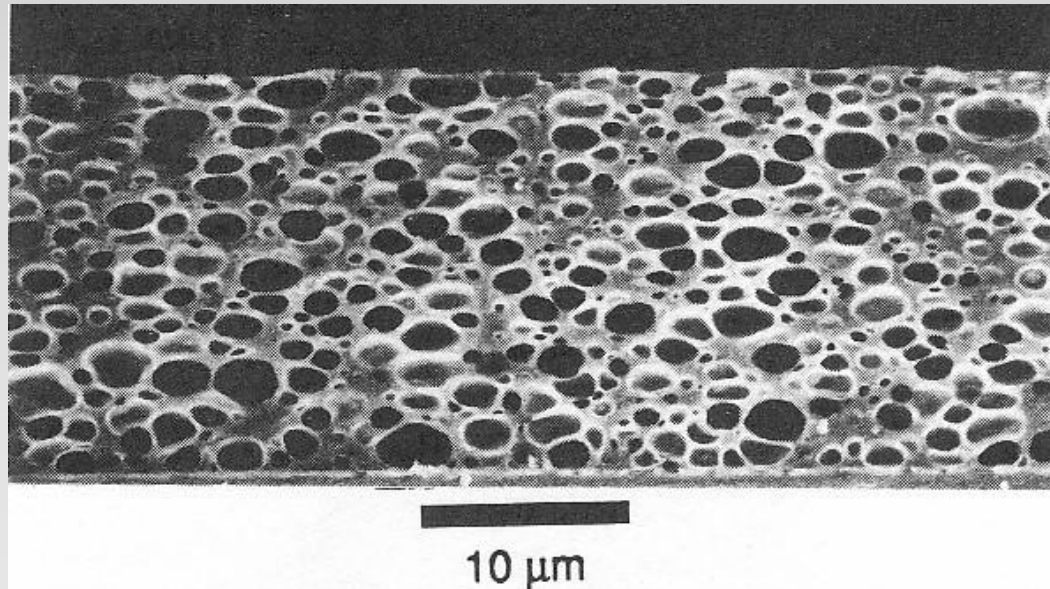
Encapsulated LC

Polymer dispersed LC

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Optical microscopy



Electron microscopy

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Smart windows

First commercial application 1m x 2.5m

Uses :

- * privacy windows in offices, airports, hospitals
- * bank teller window



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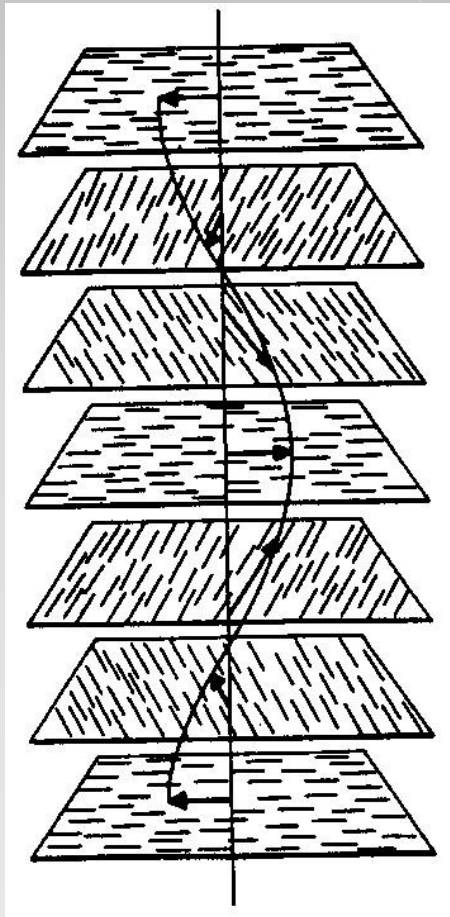
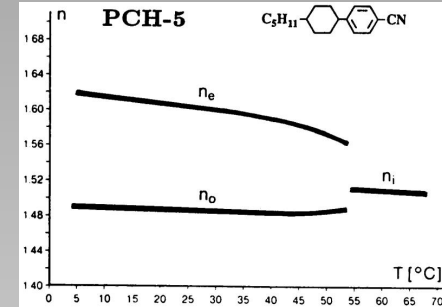
LA PHASE CHOLESTERIQUE N^*

Biréfringence circulaire $n_G -$

n_D

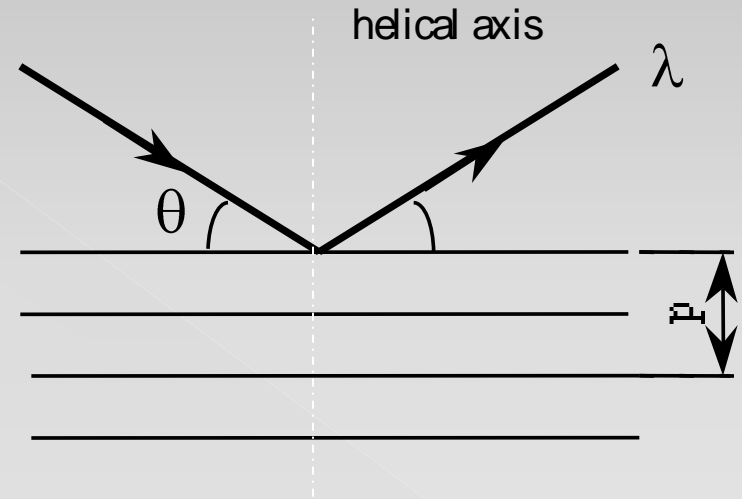
Pouvoir rotatoire

$$\alpha = \frac{\Pi \Delta n e}{\lambda}$$



N^* layers

Réflexion sélective de la lumière




$$n p \sin \theta = k \lambda$$

k : entier

n : indice de réfraction moyen

Cristaux liquides



CHATEAU
MIS EN BOUTEILLE AU CHATEAU
HOBLITZ
1985

Servir le vin à sa température idéale est un facteur essentiel du plaisir de la dégustation.
Température recommandée : de 17° à 18°.

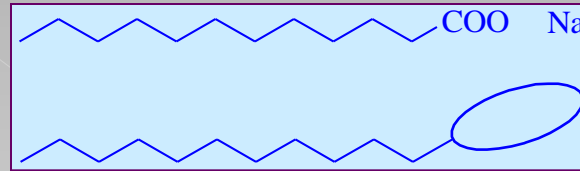
12 14 15 16 17 18 19 21 23 26 30 75cl



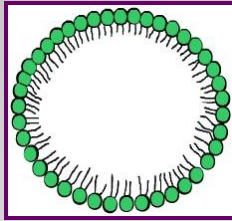
Cristaux liquides

LYOTROPIC LIQUID CRYSTALS

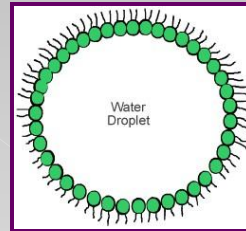
Amphiphilic molecules :



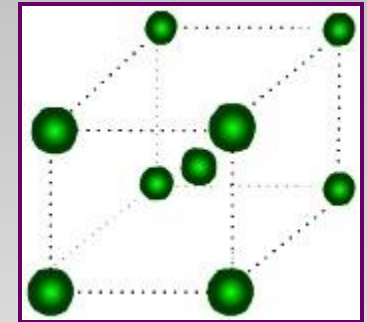
Sodium laurate



Micelle

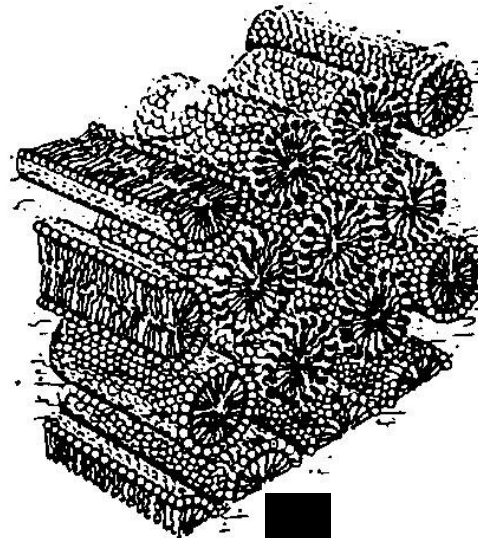
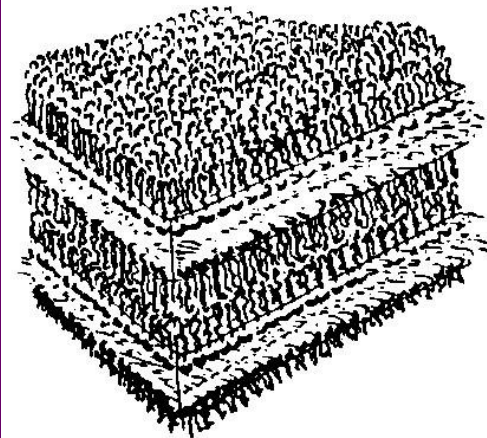


Inverted packing



Cubic packing

Lamellar packing



Hexagonal packing