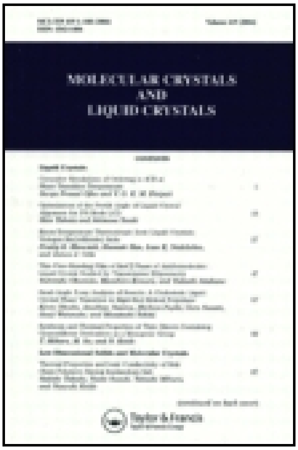

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Respective Roles of Molecular Shape and Chemical Structure on the Symmetries of Mesophases

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Respective Roles of Molecular Shape and Chemical Structure on the Symmetries of Mesophases

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Analogies between thermotropic and lyotropic Liquid Crystals were underlined at the earliest time of their investigation, since "smectic" is an old concept shared by the two domains. However, during the last decades, the differences between thermotropic and lyotropic systems were emphasized more than their similarities. As an example, the structural description is completely different for the two classes of mesophases. On one hand, the thermotropic systems are considered as close packed assemblies of rigid molecules, rods or discs, while on the other, the lyotropic systems appear as assemblies of aggregates with various shapes which mainly depend on the chemical structures and associated properties of the molecules.

Recently, important progress in the synthesis of mesogens have brought new results. Taking these into account, it appears that the gap between the two classes of materials is vanishing and that the primitive analogy might be viewed in a more general frame. The wide variety of structures might be considered within a unique description in terms of a two media organization (paraffinic/polar or aromatic) separated by interfaces, where the nature of the interactions (ionic force or chemical linkage) is an important factor of structural modulation.

1. INTRODUCTION

Two distinct classes of liquid crystals exist, the thermotropic and lyotropic. The structure of the mesophases involves two major aspects. Macroscopically, the structure corresponds to a space group which describes the symmetry properties and deals with the crystalline character of the phase. Microscopically, it is concerned with the organization and conformation of the molecules. The disordering which always exists at this level is responsible of the liquid character of the mesophases. Both thermotropic and lyotropic molecules give rise to several mesophases which may be classified according the same space groups. Nevertheless from a microscopic point of view, the thermotropic and lyotropic molecules are quite different owing to their shape and chemical structure.

The molecular shape is the most important feature of the molecules forming thermotropic mesophases. The earliest studied molecules of such mesophases can be considered as rigid rods. Later, it was shown that rigid discs generate also mesophases. The organizations of both kinds of molecules have symmetries compatible with the individual molecular properties and the shape and anisometry of the involved molecules. These properties have introduced the name "mesogen" which applies to components which form mesophases and which we will restrict to the components forming thermotropic mesophases.

In the opposite way, the chemical structure is the most important feature of molecules forming lyotropic mesophases in presence of a solvent. One part of such molecules has a great affinity with the solvent while the other part is excluded from it. Therefore these molecules, called "amphiphilic molecules," form interfaces between two media. One of them contains the solvent and those parts of the molecules which are soluble in the solvent, the other contains only the parts of the molecules which are excluded from it. The interfaces can be organized in periodic structures with lattice parameters large compared to the dimension of the molecules, *i.e.*, the molecules lose their individuality.

In the last few years new thermotropic mesogenic molecules have been synthesized and the gap between the polymorphism of the two classes of liquid crystalline phases has been reduced. The similarities between the structures or molecular organizations of both classes of mesophases has become more obvious.

This will be presented and discussed in several steps. We will first compare the thermotropic smectic and lyotropic lamellar phases. Secondly, we will show how the polymorphism of the disc-like thermotropic mesogens recall that of lyotropic systems. Finally we will point out that the concept of mesophases made of aggregates, so far restricted to the lyotropic liquid crystalline phases, may be extended to the thermotropic ones.

2. LAYERED PHASES

The layered phases form one of the most common classes of mesophases. They are encountered both for thermotropic and for lyotropic liquid crystals (LC). Before there were any structural investigations at the molecular scale, G. Friedel[1] derived the existence of the layer structure from textural observations and gave the name "smectic" to the thermotropic layered mesophases by reference to the soaps, underlining the similarities of the two kinds of mesophases. Such phases are made of 1D periodical stacks of infinite, planar lamellae. In a thermotropic lamellar phase each lamella is an assembly of parallel molecules that can be packed without any periodical translational order parallel to the lamellar plane. If the long axis of the molecule, *i.e.*, the director, is perpendicular to the lamellar plane, this phase is optically uniaxial since in general the molecule undergoes an uniaxial rotation around its long axis. This is the Smectic A (Sm A) phase shown in Figure 1a. The long axis of the molecule can be tilted, and one obtains a Smectic C (Sm C) which is optically biaxial, as shown in Figure 1b. In lyotropic systems the lamellar L_α phase (using Luzzati's notation[2]) has the same symmetry as the Sm A phase. Nevertheless, the structure is different at a local scale. A lyotropic is at least a two component system made of an amphiphilic molecule and a solvent (oil or water). In general we will restrict ourselves to mixtures of amphiphilic molecules with water that illustrate the polymorphism of lyotropic liquid crystals. The L_α phase of amphiphilic molecules in presence of water is that of a periodical stacking along one dimension of alternate homogeneous layers of amphiphilic molecules and water with flat interfaces.[3] The hydrophobic part of the amphiphilic molecules are located inside the lipid layers while the

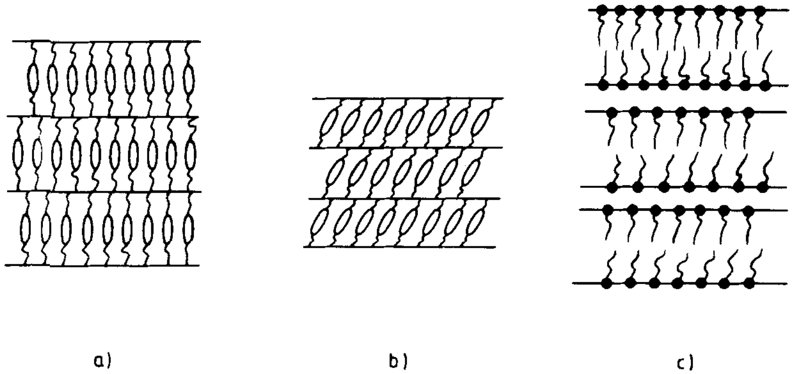


FIGURE 1 Schematic representation of the molecular organization in lamellar fluid mesophases:
a) SmA, b) SmC, c) Lα.

hydrophilic part is located at the surface of the layers (amphiphile/water interface). The water medium has only a weak anisotropy and the lipid medium is uniaxial as shown in Figure 1c. No tilted equivalent of the L_α phase exists, but in both classes of mesophases one encounters layered structures in which a 2D crystalline ordering takes place in each layer.

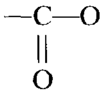
In fact, knowing the configuration of the molecules, one can easily understand how this configuration acts upon the molecular organizations in the mesophases. Therefore we will develop this idea through:

1) the comparison of the properties of the perfect Sm A and L_α phases;

2) the comparison of the other layered phases obtained in both systems and,

3) the occurrence of structural fluctuations in layered phases.

2.1. Comparison of the Smectic A and L_α phases

Let us first look at the mesogenic molecules. A smectogenic molecule[4] is built with a semi flexible rod-like core, usually phenyl rings linked together by more or less flexible links such as:  $-\underset{\underset{\displaystyle O}{\|}}{C}-O$, $-CH{=}N-$, $-CH{=}CH-$, $-CH_2-CH_2-$, etc.; and one or two paraffinic chains whose length is usually between 1 and 20 carbon atoms grafted in para positions. The stability of the Sm A phase is increased with increasing length of the paraffinic chains. In this paper we do not intend to discuss in detail the different molecules that could form a Sm A phase. The crude description given above and the examples in Figure 2 are sufficient for our understanding of the interactions that imply a Sm A phase: *first*, the long axis of the molecules need to be more or less parallel to each other (high orientational order parameter) and, *second*, the segregation between aromatic and aliphatic parts due to the weak amphiphilic character of the smectogenic molecules drive their lamellar organization. In lyotropic systems the amphipatic character of the molecules is of importance. The hydrophobic part of amphiphilic molecules is generally an alkyl chain of the order of 8–20 carbon atoms; the hydrophilic part is either a anionic or cationic polar group or a non-ionic one, for example an alcohol function or a polyoxyethylene group $(CH_2-CH_2-O)_x$.[5] The earliest studied lyotropic systems are those of soaps whose molecules are alkali salts of fatty acids. Amphiphilic molecules can form mesophases when they are mixed with water according their hydrophobic-

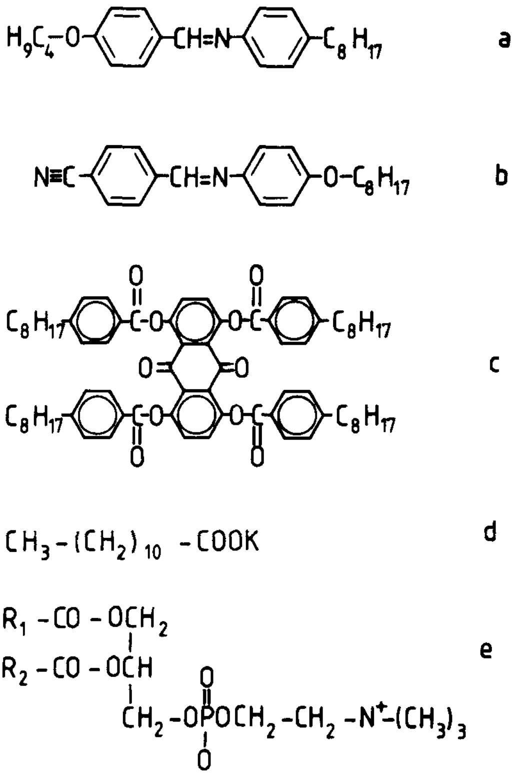


FIGURE 2 Examples of mesogenic molecules

a) Typical smectogenic molecule.
   The polymorphism is: Cr ↔ SmB ↔ SmA ↔ N ↔ I.
b) Molecule bearing a high longitudinal dipole with a Cr ↔ SmA ↔ N ↔ I polymorphism.
c) Lath-shaped molecule[53] which behaves as two linked rod-like molecules.
d) Alkali soap.
e) Typical lipid of biological interest: lecithins. R_1 and R_2 are hydrocarbon chains.

lipophilic balance. Some biological lipids[2] that are the constituents of the membranes and form an important class of lyotropic molecules have two paraffinic chains grafted on one polar head (for instance phosphatidyl choline). Furthermore, block copolymers[6] can form mesophases with a preferential solvent of only one of the two components. The most important parameter of a lyotropic mesophase and, specially, of a lamellar one is the mean area per molecule at the amphiphile/water interface. This depends on the polar interactions at the interface, on the concentration of the lipid in the solvent, and on the temperature. Typical examples of amphiphilic molecules are given in Figure 2.

A comparison between the results of similar experiments sensitive to the local organization, such as X-ray diffraction or NMR studies of Sm A and L_α phases, give an idea of the difference of behavior of the two phases due to the differences in their components. If we look for the layering organization (X-ray diffraction) both the periodicity and the electronic density profile along the normal to the layers are different. In Sm A phases the periodicity is given by the molecular size, in general equal to the length of the rod like molecules. However, in some cases for assymetric molecules ended by only one paraffinic chain, one has a bilayer structure with a head to head, tail to tail array or with interdigitation of aromatic cores due to some dipolar interactions. The periodicity is then respectively equal to twice the molecular length or approximatively to one core length plus two chain lengths.[7] In both cases the Sm A layer can be divided into one aromatic central sublayer surrounded by two paraffinic sublayers. In lyotropic systems the lipidic sublayer has a thickness which is less than twice the length of the hydrocarbon chain while the periodicity can vary with the amount of solvent. In thermotropic Sm A phases it lies between 2 and 6 nm and the boundary between aromatic and paraffinic sublayers is smooth. The electronic density profile can be described in first approximation by a sinusoidal function[8] of the coordinate perpendicular to the layer plane, since only one Bragg reflection order is seen. In lyotropic lamellar phases the periodicity exceeds in some cases a few tens of nm. The segregation between the solvent and the hydrophobic part of the molecule is nearly perfect: the description of the electronic density profile along the coordinate perpendicular to the layer plane needs the use of several harmonics,[9] and two or three reflection orders are currently observed.

If we now give a tentative description of the intra layer ordering, the two phases also appear different. In many descriptions of the Sm A ordering the molecule (aromatic core and paraffinic chain) is generally considered as a unique entity while in lyotropic systems the two media (solvent and lipid layer) behave differently. On the X-ray diffraction pattern of an oriented sample of Sm A, shown in Figure 3a, one can see a broad diffuse scattering with a crescent shape; the maximum of intensity is found in the equatorial plane perpendicular to the director at a scattering vector of the order of $2\pi/0.45\ \mathrm{nm}^{-1}$. This scattered intensity occurs from C—C interferences whose main contribution arises from pairs of atoms belonging to parallel close neighboring molecules. No distinction can be made between carbon pairs issued from the aromatic medium and pairs belonging to the paraffinic medium. The

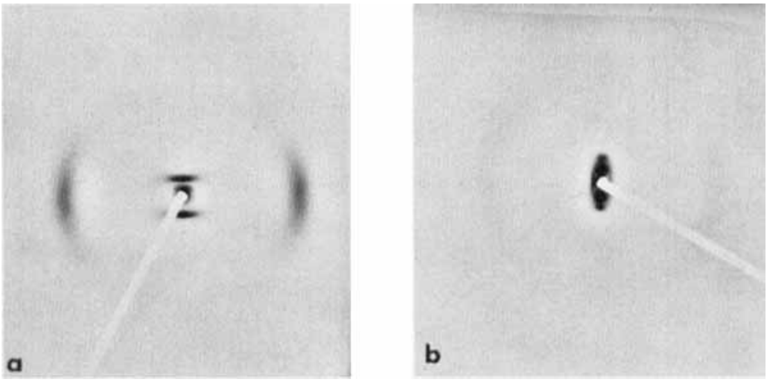


FIGURE 3 X-ray diffraction patterns of oriented samples of the lamellar phases.
a) SmA molecule: Figure 2a; T = 56°C.
The Bragg reflections on the layer planes are overexposed and surrounded by an elongated diffuse zone corresponding to X-rays scattered by the undulation modes of the layers.
b) Lα phase: decylammonium chloride/H_2O/NH_4Cl T = 32°C.
Two Bragg peaks are visible at small angle. The diffuse scattered intensity by undulation modes is weak and not seen here.

angular extension of the crescents give a measure of the global order parameter; its value is comparable to those extracted from dielectric (optical) or diamagnetic measurements which give the core order parameter.[10] Moreover it is obvious that the two moities of a molecule, occupy a cylindrical volume of the same section at least if the layer thickness is equal to one or twice times the molecular length. The mean area per molecule is about 0.25 nm^2.[11] In a lyotropic L_α phase the solvent medium is nearly locally isotropic and gives an isotropic ring for a scattering vector $2\pi/0.32\ \mathrm{nm}^{-1}$ while the chains give a diffuse ring similar in position to that observed for a Sm A phase at a scattering vector equal to $2\pi/0.45\ \mathrm{nm}^{-1}$: Figure 3b. The mean area per chain is deduced from the thickness of the amphiphilic layer which can be deduced from the periodicity of the phase, knowing the concentrations and molar specific volumes of the amphiphilic molecules and water.[3]

Nuclear magnetic resonance experiments on perdeuteriated chains[12,13] give information on the order parameter of the deuteriated methylene and methyl chains links, *i.e.*, about the conformational state of the chains. As illustrated in Figure 4, from the order parameter curve of the paraffinic chains in a Sm A phase compared to that of the paraffinic chains with similar length in an L_α phase, we may infer that, in both cases, the paraffinic chains have a similar behavior.

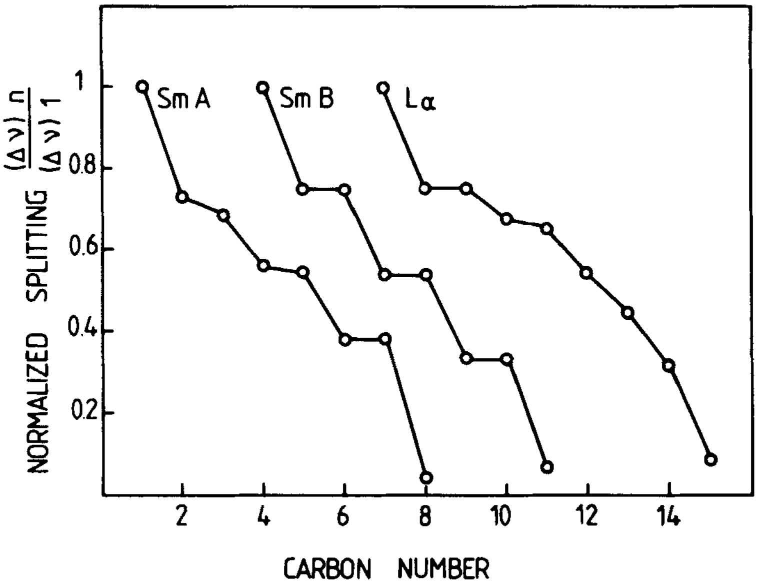


FIGURE 4 DMR measurements.
SmA: T = 55°C; SmB: T = 45°C; molecule: Figure 2a. L_α: T = 70°C; molecule: CH_3—$(CH_2)_8$—COOK
Evolution of the orientational disorder $(\Delta\nu)_n/(\Delta\nu)_1$ of the chain links as a function of the carbon number along the chains. (L_α, carbon number from polar head). The abscis scale of the SmB and L_α phases has been shifted.

We can summarize the comparison between Sm A and L_α phases as follows: the two phases have the same symmetry; the characteristic lengths are nearly the same for all Sm A phases while they vary in a large extent in lyotropic L_α phases; the organization in lamellae is a consequence of the amphipatic character of the two kinds of molecules but the segregation in a Sm A phase is less important than in a lyotropic lamellar phase where the segregation between the polar and apolar groups is complete; the conformation of the paraffinic chains is similar into both mesophases, but in Sm A phases the packing of rod like cores plays an important role while in the L_α phases the conformation of the chains is driven by the fact the chains are linked to the polar groups anchored at the amphiphile/water interface, and they become more disordered when the mean area per polar group increases. At last, in the lyotropic lamellar phases, the solvent will necessarily play a role on the interactions between adjacent layers.

It is clear that the molecular shape of the mesogens drives the smectic organization while the chemical structure of the amphiphilic molecules, and, specifically, the nature of their polar groups, are the main factors that act upon the structural features of the lyotropic L_α phases. We will see in the following section how the problems of shape and chemical structure act on the polymorphism of the mesophases obtained with each kind of molecule.

2.2. Other layered phases

Several other lamellar phases are seen as well for thermotropic mesogens (smectic phases) as for lyotropic ones. First of all, a tilted *fluid* smectic phase is seen in thermotropic liquid crystals. As we have already explained, the intralayer ordering is similar in Sm C and Sm A phases except that the director is tilted with respect to the normal to the layer in a Sm C phase. The tilt angle can vary from zero starting at a Sm A–Sm C transition up to a large limit value (~50°). Different kinds of interactions have been proposed in order to explain this phase *which has no equivalent in lyotropic systems.* Meyer and Mac Millan[14] had underlined the importance of dipolar interactions, but it appears that the molecules undergo a quasi-uniaxial rotation along their long axis and dipolar interactions are nearly cancelled except if the molecules are chiral.[15] However it has been recently pointed out by Barbero and Durand[16] that a quadrupolar gradient (related to the order parameter gradient) induces dipoles. The depolarizing field associated with these dipoles minimizes the energy by tilting the molecules. Such a gradient exists at an interface and in a modulated (*i.e.* lamellar) liquid. The occurrence of a Sm C phase is a consequence of these interactions ("ordoelectricity"). Nevertheless, one can also think that steric interactions exist between the semi flexible rod-like cores.

The occurrence of periodical stacks of 2D ordered layers is general. We will discuss mainly the case of the hexagonal lattice in the layer which is encountered in both thermotropic[17] and lyotropic[18] mesophases. A lowering of the entropy of the system can act first on the in-plane ordering of the molecules. If the uniaxial rotation of the molecules is maintained and if their long axis is perpendicular to the layer plane, then the molecular array becomes hexagonal inside each layer. These phases are the Smectic B (Sm B) phase for thermotropic mesogens and the L_β phase[9] for lyotropic systems. In both cases, tilted equivalents of these phases exist. The lattice is then centered rectangular but corresponds to a quasi-hexagonal array of parallel molecules. However, the analogy between the symmetries of the two kinds of mesophases masks a noticeable difference in the local organization.

Considering the transition Sm A–Sm B, no drastic changes in the conformation of the paraffinic chains occur (Figure 4). The transition affects mainly the core ordering while the chains keep their melted state. Nevertheless, some three-dimensional correlations can exist between the in plane positions of molecules belonging to adjacent layers. In a given smectogenic series these correlations vanish with increasing chain length and true 2D ordering is generally seen for long paraffinic chains while the so-called crystalline Sm B, which is in fact an orientationally disordered crystal, exists for very short chain lengths, even if there is no Sm A phase.

Anyway, the chain keeps a disorder conformation and a confirmation of this can be found in the diffraction pattern. When the structure is 2D hexagonal (or pseudo hexagonal), the width along the director of the diffraction peaks that characterize this hexagonal ordering is comparable to the inverse core length and does not vary with the number of carbon atoms of the paraffinic chains.[17]

The L_α–L_β transition corresponds to a crystallization of the paraffinic chains, and in the L_β phase they undergo a whole trans conformation. This appears from the structural parameters: a small area per chain ($\sim$0.195 nm^2) and a large thickness of the amphiphilic bilayer. Moreover the electron density profile along the director shows a good localization of the terminal methyl groups[9] (Figure 5). The presence of water layers between the lipid layers, wherein the molecules are organized in a hexagonal array, does not allow any positional correlation between the in-plane coordinates of molecules belonging to adjacent layers: we have a strictly 2D ordering. Another problem concerns the quality of the "2D crystalline" lattice.[17] This problem is related to the theoretical study of the melting of a 2D crystalline lattice and we will not discuss this

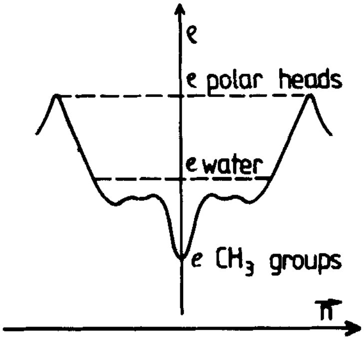


FIGURE 5 L_β phase. Electron density profile, ρ, of the amphiphilic bilayer along the director, **n**, of the phase. Reported from reference 9.

point here. The lamellar ordered phases can be considered as an alternative stacking of more or less crystalline layers with liquid ones. For thermotropic smectics the crystalline medium is constituted by the molecular cores while the paraffinic medium is made of uniaxial liquid layers. In lyotropic systems the paraffinic chains are crystallized, and the aqueous medium is fluid. Therefore there is a noticeable difference between the two phases. In Sm B phases the order is driven by the cores whose shape allows a close packing of molecules in uniaxial rotation while the chains have a less important role. In L_β phases the chains are more or less crystallized owing to interactions with the aqueous medium due to the chemical structure of the molecules. Moreover it must be emphasized that in thermotropic mesophases all crystalline layers can be derived from the same hexagonal lattice while in lyotropic mesophases, the chemical characteristics of the amphiphilic molecules may be at the origin of a diversification in 2D plane lattices.[9,18]

A survey of the layered structures in both classes of LC has underlined the differences in the behavior of the two kinds of molecules. Differences also appear in the transformations which destroy the layered structures.

2.3. Perturbations of layered structures

The most studied and also the most evident perturbation that can occur in a Sm A lies in the transition towards a Nematic. A Nematic (N) is an assembly of parallel rod like molecules with a liquid like positional order of the molecules in three directions of space. Therefore the main change occurring at a Sm–N transition occurs in the 1D periodicity. In other words the amplitude of the longitudinal fluctuations increases in Sm A phase and, finally, all correlations between the position of the centers of mass along the director axis disappear. Consequently, the segregation between cores and chains also disappears.

Contrariwise, in lyotropic systems, owing to the strong amphipatic character of the molecules made of strictly apolar and polar groups, the segregation between both parts of the molecules is always manifest. Therefore, whatever the perturbation of the lamellar structure may be, the system still exhibits hydrophobic/hydrophilic interfaces. These interfaces which are flat, *i.e.*, whose curvature is zero in the lamellar phases, can change in shape and their curvature takes values which allow other shapes for the aggregates of molecules. The aggregates may be micelles, ribbons or cylinders. The micelles can form isotropic solutions or anisotropic fluids (lyotropic nematic phases). The ribbons and cylinders are generally packed in a two dimensional lattice. We will only consider the occurrence of 2D lattices of ribbons that may be viewed as perturbations of the lamellar structure. Ribbons can be considered as limited lamellae, and ribbon phases exist for the two classes of LC.

In thermotropic phases, the N phase is not only the intermediate state between the isotropic liquid and the lamellar Sm A phases, but also can be the intermediate state (reentrant N) between two Sm A (or C) phases of different periodicity, since it corresponds to the disappearance of the periodicity. Moreover, one can imagine that, if the two periods are in competition, the constraints in the lamellar phase structure can be released by nematic domains.[7] The whole system may be organized in a periodic ribbon structure. An analogy between these phases (Sm $\tilde{A}$ and Sm $\tilde{C}$) and ribbon phases in lyotropic systems can be made[19]: in both cases a periodical modulation of the intra-lamellar ordering occurs. Nevertheless, looking at precursors effects, the two systems behave differently. In smectic phases there are columns of molecules which are out of phase with the layering periodic order. These columns induce a localization of X-ray scattering intensity in discs perpendicular to the director as shown in Figure 6a.[20] When the Sm $\tilde{A}$ or the Sm $\tilde{C}$ phase is approached, correlations between the columns are established, and the scattering discs become rings. Entering in the ribbon phases the columns are developed in periodically spaced walls. In lyotropic L_α phases, inhomogeneities appear inside the lipidic bilayers. These inhomogeneities induce X-ray diffuse scattering intensity localized in a hollow cylinder of axis parallel to the director of the phase, and the latter is either a precursor of a nematic phase[21] or of a ribbon phase.[22] In this last case approaching the phase transition, the intensity vanishes in the central part of the cylinder, *i.e.*, correlations appear between layers[22] as shown in Figure 6b.

Once more it appears that both classes of mesophases behave differently. The dense packing of parallel cores is a permanent feature of the thermotropic mesogens, while the continuous amphiphile/water interface is the important feature in the lyotropic systems. Perturbations of this interface give rise to many different structures, for example several assemblies of infinite cylinders with various shape. In the case of thermotropic LC, the occurrence of infinite cylinders on a hexagonal lattice is unexpected unless one changes the structure of the molecules. The polymorphism is sensitive to specific intramolecular interactions while, in the lyotropic systems, it seems to be

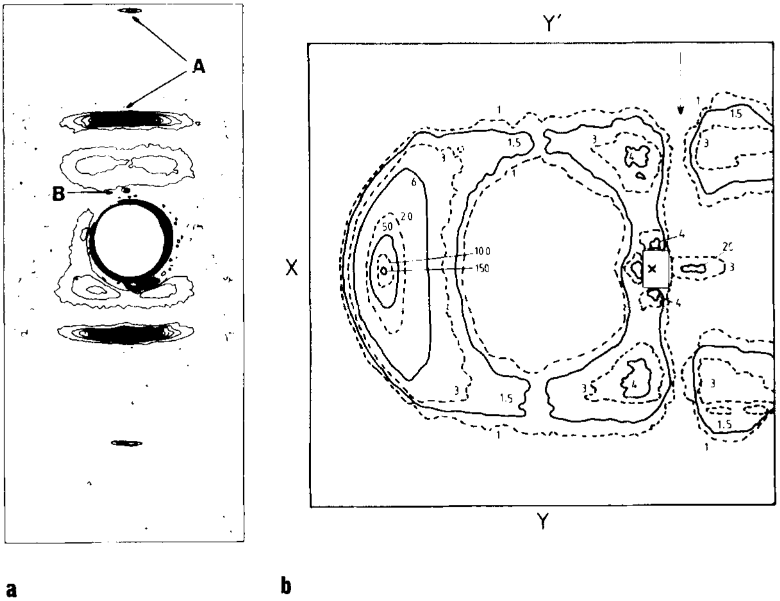


FIGURE 6 Intensity contours for the small angle area of the diffraction patterns of lamellar phases showing pretransitional features near a 2D mesophase.

a) SmA in the vicinity of a SmA–SmC̃ transition.
   C_9H_{19}—O φ − N = CH φ − O CH_2 − φ − CN. In A Bragg peaks of the layer structure surrounded by the thermal scattering intensity; in B Bragg reflection of the third harmonic wavelength. A diffuse band perpendicular to the director lies between B and the first spot A; the intensity along the band is modulated.
b) A Monocrystalline domain of a L_α phase of the SdS/1-decanol/water system (molar SdS/1-decanol ratio: 2,26). The director, **n**, of the phase is along the horizontal axis of the figure. Beside the Bragg peak, diffuse lateral scattering bands are observed along $q_\perp$ (scattering vector perpendicular to **n**).
   (The arrow indicates the extinction of scattered intensity due to sample absorption). Reported from reference 22b.

entirely explained by the interfacial behavior such that the polymorphism will be limited if one kept homogeneous interfaces.

3. CYLINDRICAL PHASES

In the second important class of mesophases, assemblies of parallel cylinders of infinite length form 2D networks. If the cylinders have a circular section, they form a hexagonal network of space group symmetry, P 6/m 2/m 2/m, with no periodical translational order along the six-fold axis.[23] The "hexagonal phase" is the analogue with a 2D ordering of the liquid layered Sm A and L_α phases. This hexagonal phase was first put in evidence in lyotropic systems. Other cylindrical phases with orthorhombic and monoclinic symmetries also exist, and are intermediate states between the L_α phase and the hexagonal one. Thermotropic LC are able to form phases with the same symmetry as the hexagonal one if the molecules are disc-shaped.

We will first discuss the hexagonal lyotropic mesophases and their transformations. Thereafter, we will explain how disc-like thermotropic molecules can form hexagonal phases with the same symmetry and we will compare the polymorphism obtained with a disc-like mesogen with that encountered in some lyotropic systems.

3.1. Cylindrical phases in lyotropic systems

Several studies have been devoted to the structure of the hexagonal and intermediate phases in lyotropic systems of soaps, detergents, block copolymers and lipidic molecules of biological interest. In this paper we shall deal with hexagonal phases and intermediate phases made of amphiphilic molecules in presence of water.

The hexagonal lattice is put in evidence by X-ray diffraction. It is generally assumed that the interface between the aqueous medium and the paraffinic chains has a circular symmetry. From the lattice parameter, the concentrations and the partial specific volumes of the amphiphilic molecules and water, one can derive the diameter of the circular section of the cylinders. In general it is ≤ twice the length of an extended molecule.[3] This implies that the paraffinic chains fill the inner part of the cylinders as shown in Figure 7a. These cylinders are embedded in a continuous water medium, and the phase is called "direct" or type I hexagonal phase, H_α (in Luzzati's notation[2]). If the cylinders have circular sections it implies that the curvature of the apolar/polar interface is homogeneous. The area of the polar head groups has a value intermediate between those of the lamellar and isotropic phases.

In lyotropic systems of diacylphospholipids the structure elements are infinite cylinders or rods filled with water; they contain the polar head groups and are embedded in a continuous disordered paraffinic medium such as sketched in Figure 7b. This phase is called "inverted" or type II hexagonal phases[2] (cfr. those of anhydrous divalent cation soaps which in fact have been the first and for a long time the only known thermotropic hexagonal phases[24]). Complex hexagonal phases[3] with two polar/apolar interfaces for each cylinder, as shown in Figure 7c, have also been proposed.

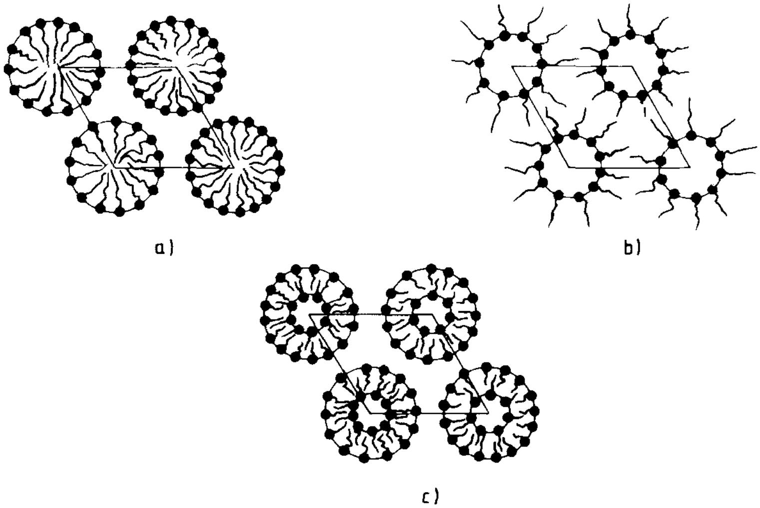


FIGURE 7 Schematic representation of the molecular organization of the lyotropic hexagonal mesophases:
a) direct, b) inverted, c) complex.

The paraffinic chains are always in a liquid-like state as opposed to the paraffinic chains in the lamellar phases which may be in a liquid-like or rigid state. Such as in the L_α phase, they give a diffuse scattering ring at a scattering vector equal to $2\pi/0.45\ \mathrm{nm}^{-1}$. Their conformational state is similar to that in the L_α phase. This is supported by the order parameter curves recorded by nuclear magnetic resonance on perdeuteriated chains of the same soap in both phases.[25] One could expect that, in the hexagonal phase, the disorder of the chains should increase with respect to that in the lamellar phase, as the mean area per polar group in the hexagonal phase increases significantly as well as the curvature. However, it has been shown that the chain behavior around its elongation axis is quasi independent of the shape of the investigated aggregate.[26]

Lyotropic systems consisting of one amphiphile species go from the hexagonal phase (homogeneous curvature with finite value) to the lamellar phase (homogeneous curvature with zero value), crossing one or more intermediate phases (depending on the chemical structure of the involved amphiphilic molecule) separated by biphasic domains. The structural phase transformations are function of the amphiphile concentration and the temperature. The hexagonal and lamellar phases generally extend over a wide concentration range, while the intermediate phases most often exist in narrow domains of the phase diagrams. Therefore, a careful exploration of the phase diagrams is needed in order to localize and identify these phases.

The earliest reported sequence of intermediate phases observed with increasing amphiphile concentration from the hexagonal to the lamellar phase in a variety of monovalent cation soaps and detergents involves three 2D phases (distorted hexagonal, rectangular, complex hexagonal) followed by a 3D periodically ordered cubic phase.[3] For instance, the whole sequence has been observed in the potassium palmitate/water system.[5]

It seems also worthwhile to mention the polymorphism observed in the phosphatidyl choline or egg lecithin/water system. Besides the hexagonal, H_α, and lamellar L_α, phases, the three dimensional phases, rhomboedral, R_α, and cubic, Q_α, have also been observed.[27] Recently, in the sodium dodecyl sulfate/water system, besides the already known two dimensional, H_α, and monoclinic (distorted hexagonal phase), M_α (P 2/m), phases, three, three dimensional rhomboedral, R_α, cubic, Q_α, and tetragonal, T_α, phases were identified.[28] The space groups of the 3D phases have not yet been identified.

It must be noted that the topology[29] of the 3D intermediate mesophases differs from that of the 2D cylindrical ones. For instance the cubic phase corresponds to a finite number of interwoven infinite media. Hence the above mentioned phase transformations imply changes in topology of the structures associated with changes of the amphiphile/water interfaces, *i.e.*, with the curvature of the interfaces. The driving force inducing changes in the shape of the interfaces has recently been analyzed in terms of stresses that can be released by a change in structure.[30]

Intermediate phases have also been observed in lyotropic systems made of two amphiphile species in the presence of water, and it seems that the polymorphism of some binary systems (one amphiphile species/water system) is enhanced when a second amphiphile species is added. For instance, 2D cylindrical mesophases have been identified in the sodium decyl sulfate (SdS)/1-decanol/water system.[31,32] Here we consider the mesophases that were identified following a particular line of the SdS/1-decanol/water phase diagram. Along this line, the water content (47.55 percent by weight H_2O) and temperature (23°C) are maintained constant and the SdS molecules are progressively replaced by decanol molecules. The sequence of phases when the decanol/soap molar ratio increases from zero to 2.63 is as follows: 2D Hexagonal phase ↔ 2D Rectangular phases with different symmetries ↔ 1D Lamellar phase, or: P 6/m 2/m 2/m ↔ C 2/m 2/m 2/m

↔ P 2_1/a 2_1/b 2/m ↔ Lamellar. We shall give an approach to the phase transformations based on, among other parameters, the chemical structure of the amphiphilic molecules. Both amphiphilic species have similar chain lengths, CH_3—$(CH_2)_9$—, but different polar heads. One is the ionic sulfate group: —OSO_3Na; the other is the non-ionic hydroxyl group: —OH.

We first deal with the 2D structures. The unit cell and symmetry elements characteristic of the 2D rectangular lattices are given in Figure 8 a and b. Following the above sequence, phase transformations take place when decanol molecules are added to binary SdS/water mixtures, although the water content and the temperature remain constant. Obviously, the non-ionic decanol molecules may be seen as the driving force for these transformations, and we shall give an insight of the mechanisms which are involved.

The shape of the cylinders through the whole sequence has been determined by X-ray and neutron diffraction studies.[31-34] In a SdS/water mixture, the cylinders have a circular section, and, when the amount of decanol is increased, the section becomes more anisotropic along with the decanol concentration. This anisotropy is associated with inhomogeneous distribution of both amphiphilic molecules. Such inhomogeneous distribution implies the relative concentrations of the non-ionic hydroxyl and ionic sulfate groups are modulated along the interface, hence the mean area per polar head at the interface, and

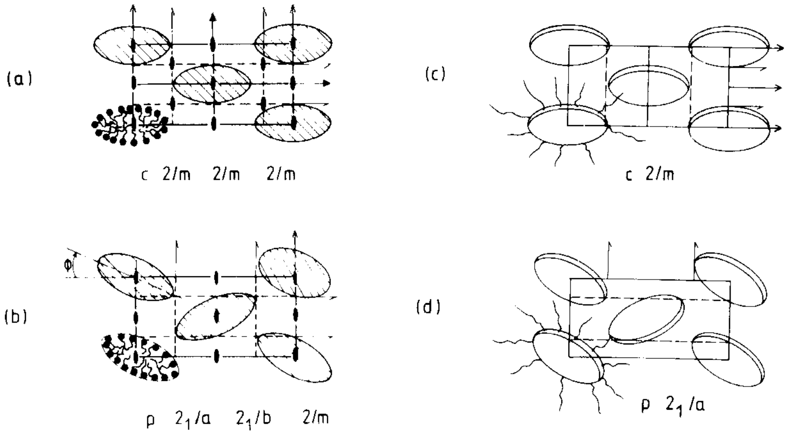


FIGURE 8 Molecular organization and symmetry elements in the rectangular phases of a lyotropic system and a thermotropic one. (a) centered rectangular phase in a lyotropic ternary system; (b) rectangular herring-bone structure in the same system; (c) centered rectangular phase; and (d) herring-bone structure in disk-like mesogens.

therefore the shape of the amphiphile/water interface changes, *i.e.* the normal section of the cylinders deviates from that of a circle. Fluctuations of the relative concentrations of both amphiphiles promote the coexistence of interfaces with different curvature.[33,35]

However, in spite of changes of the interface which is the more pronounced with increasing the decanol content, the symmetry of the hexagonal lattice is preserved until the decanol/SdS molar ratio is 0.15. At this stage only the intra-aggregates properties are affected. The aggregates are still parallel and equidistant. Their non-circular sections must be orientationally disordered along their long axis with at least a six-fold symmetry. When the decanol/SdS molar ratio is 0.15, the deformation of the section of the infinite amphiphilic rods becomes too large and they lose the mean six-fold symmetry imposed by the hexagonal lattice: the latter transforms into a 2D centered rectangular lattice, C 2/m 2/m 2/m. Both intra- and inter-aggregate properties are affected. The aggregates cannot be but infinite ribbons. Their normal section may be schematized as a piece of amphiphile bilayer limited on both sides by hemispherical caps. The anisotropy of the section is 1.5.[32] The non-uniform distribution of both ionic and non-ionic polar heads induces a modulation of the surface charge density at the interface. The surface charge density is lower in the domains of the interface where the relative concentration of the alcohol groups is high, *i.e.*, where the curvature of the interface approaches that of a flat one. Due to their anisotropic section, the aggregates behave like quadrupoles. This may account for the transformation of the C 2/m 2/m 2/m phase into the P 2_1/a 2_1/b 2/m one. The packing of the aggregates is governed by interactions between aggregates which contain an electrostatic repulsive term. The longitudinal long axis of the ribbons are parallel to each other in both lattices, but, with increasing decanol content, one may expect the quadrupolar component of the electrostatic repulsive interactions becomes rapidly strong enough to promote the herring bone structure of the P 2_1/a 2_1/b 2/m space group.[33]

The occurrence of the lamellar phase for a still higher decanol/soap ratio is less obvious. The cylindrical and lamellar phases are separated by a polyphasic domain. The structure of the lamellar phase near the boundary of the polyphasic domain deviates from that usually proposed. In the first section of this paper it has been evoked that the X-ray pattern shows diffuse scatterings in addition to the Bragg reflections characteristic of 1D structure. The diffuse scatterings which characterize intra layer modulations of density have been interpreted as resulting from water pores or channels piercing the amphiphilic bilayers.[21] These water regions must be associated with highly curved interfacial amphiphile boundaries within the lamellae, and the existence of water channels would suggest that the lamellae are made of parallel cylinders without any long range correlation between adjacent layers.

The 2D rectangular phases lie also in the vicinity of the nematic phases. When water is added to the first ones, a uniaxial nematic phase occurs whose aggregates probably result from the fragmentation of infinite ribbons. This is supported by the fact that the aggregates of a nematic phase of the same type in a similar ternary system are finite rods whose normal section (perpendicular to their major symmetry axis) is not circular.[36] When this uniaxial phase is diluted, it transforms into the uniaxial phase of the other type, crossing the biaxial one, and the aggregates are disc-like, with a flattened core surrounded by a hemi spherical rim. The relation between the shapes of the aggregates of the nematic phases and their ordering has been put forward by X-ray[37] and light scattering studies.[38]

A rich polymorphism has been put forward in the above ternary system. It results from the difference in chemical composition of the two amphiphilic molecules or, more precisely, from the difference between their polar heads that promotes modulations of the interfacial curvature therefore allowing changes in the shape of the aggregates. Moreover, the interactions between anisotropic aggregates can give rise to changes of the symmetry of the mesophases. Although it is not the most general, such a sequence can be put in parallel with sequences observed with thermotropic mesogens, and this will be outlined in the following section.

3.2. The cylindrical phases with thermotropic mesogens

New mesophases, built with mesogens having other molecular shapes than those described so far were discovered at the same time in several places. All these molecules have a flat core surrounded by six long paraffinic chains. The molecules can pile up to form cylinders and the cylinders form a regular two-dimensional array. The first example was reported in 1978 by S. Chandrasekhar *et al.*[39] Furthermore, it appears that the lattice could be either hexagonal or rectangular, but the coordination of a cylinder is always six.[40]

It is clear that the column is built with the same constraints as the lamellae in a smectic: the cores are parallel, a segregation between chains and cores takes place, and the paraffins are in a melted state which insures the decorrelation between adjacent columns. It is therefore obvious that many points of the comparison between lyotropic and thermotropic lamellar mesophases can also be underlined in the case of the columnar mesophases. Nevertheless, some specific properties of the columnar mesophases allow one to draw a better parallel between the two kinds of mesophases. First, the contribution of the paraffinic chains to the molecular weight is large and therefore many physical properties are mainly governed by the behavior of the chains. Second, the ordering of the cores inside each column has a smaller impact upon the global behavior of the system. Not only is the screening of the chains more efficient, but, in addition, a periodical 1D ordering inside the columns is in theory unexpected.[41] Consequently, even if the linear positional correlation function between cores can change from one sample to another, the phase is qualitatively always the same. In other words, the identity of the physical properties can be found assuming a suitable change of the length scale.

It appears that the correspondence between the structure of the lyotropic and thermotropic columnar phases is more obvious than for lamellar phases. A phase sequence similar to the one described above can be found in some truxene derivatives, which we would now like to present. Among all the possible mesogenic flat cores, the truxene series,[42] shown in Figure 9, bring interesting insight upon the disc-like polymorphism. They all undergo several columnar mesophases for a chain length between 6 and 14 carbon atoms. For X =

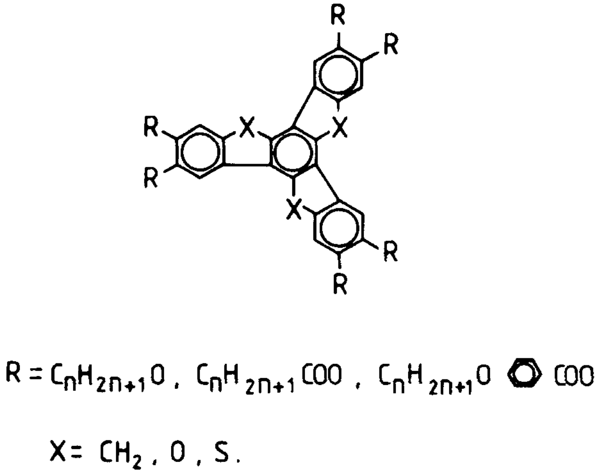


FIGURE 9 The truxene derivatives.

S, R = CH_3—$(CH_2)_n$—O—, one can have three columnar mesophases. The sequence is, with increasing temperature[43]:

Crystal ↔ Nematic ↔ P 2_1/a ↔ C 2/m ↔

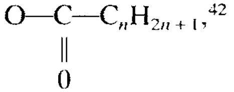
P 6/m 2/m 2/m ↔ Isotropic liquid.

The unit cell and symmetry elements of the rectangular phases are given in Figure 8 c and d. This sequence is very similar to that which describes for the ternary SdS/1-decanol/water system: P6/m 2/m 2/m ↔ C2/m 2/m 2/m ↔ P 2_1/a 2_1/b 2/m. The difference between the orthorhombic groups for the lyotropic system and the monoclinic groups for the thermotropic is due to the fact that the director in the thermotropic columnar rectangular mesophases is not parallel to the columnar long axis.

Let us look at the molecular organization in the sequence, P2_1/a ↔ C2/m ↔ P6/m 2/m 2/m. Inside each column, all the heteroaromatic cores are parallel and the plane of the cores makes an angle of about 50° with the column axis. The chains are in a melted state, and they fill the space between two columns. We will discuss in the following section the problem of their specific volume. There are various experiments (NMR,[44] X-ray diffraction) which show that the chains lie on average in a plane perpendicular to the column axis. The anisotropy of a column section is mainly localized in the core region and at the interface between chains and core, which contains the carboxylic linkages. Therefore we can consider that the interface between the paraffinic chains and the second medium bears a quadrupole. The shape of the columns and the interactions between adjacent columns are similar in this case as well as for the lyotropic, SdS/1-decanol/water, ribbon phases. Let us remark however that the anisotropy of the section of a column is constant and on the order of 1.15 for a chain length of 9 carbon atoms while it varies between 1 and ~1.5 in the case of a cylinder of the lyotropic system.

The herring-bone structure is the most ordered one in both systems. With increasing temperature, the amplitude of vibration of a column along its long axis increases. The two columns of the rectangular lattice become equivalent (the azimutal direction for the tilt is the same), and the lattice is centered rectangular. In fact, the C 2/m phase exists only for four derivatives of the series: $n = 9$, 12, 14 and 15. For the other derivatives one goes directly to the true hexagonal lattice that, in fact, corresponds to a uniaxial disorder of the tilt director. The stability domain of the C 2/m is small and recalls the narrow domain of the equivalently described lyotropic phase. Evidence that the cores are still tilted in the hexagonal phase can be found in the lattice spacing measurements that show no important variation through the three columnar phases. This has been confirmed by birefringence measurements in the hexagonal phase of a triphenylene ester that also presents a columnar phase of symmetry $P2_1/a$.[45]

Another surprising feature is the occurrence of a low temperature nematic phase. In fact, the existence of this phase is characteristic of the truxene cores. Besides in this series, the occurrence of a nematic phase is rare and only seen when alkoxy benzoyloxy chains are grafted on a triphenylene or truxene core. In the last case, the sequence, $P\,2_1/a \leftrightarrow N \leftrightarrow C2/m \leftrightarrow N$, has been observed.[46]

Looking at the series: $X = CH_2$, $R =$  $\text{O—}\underset{\underset{\displaystyle 0}{\|}}{\text{C}}\text{—}C_nH_{2n+1}$,[42] three features help to understand the sequence: $\text{Crystal} \leftrightarrow N \leftrightarrow P\,2_1/a \leftrightarrow P\,6/m\,2/m\,2/m$:

i) As we increase the temperature the correlation length for the stacking of the cores along a column increases.

ii) The specific gravity in the nematic phase is higher than in the $P2_1/a$ phase.

iii) The diffraction pattern of the nematic phase oriented in a magnetic field indicates some pretransitional columnar ordering.

It is somewhat paradoxical that the apparent correlation length for the stacking of the cores increases as the temperature increases. Moreover, the increment of the molar specific volume at the transition from the nematic to the $P2_1/a$ columnar phase is independent of the length of the grafted chains and therefore corresponds to an increment of 2% of the core specific volume. Let us assume that the configuration of the molecules inside a column does not change with temperature. As we decrease the temperature going from the hexagonal phase, the mean distance between two cores tends to decrease. But, as the configuration remains unchanged, the chain packing is submitted to a distorsion force inducing a splay deformation.

In a first step, the response of the system can be a modulation of the core–core distance as predicted by de Gennes.[47] Nevertheless, it is possible to release the distorsion forces by putting randomly spaced defects inside the columns. Consequently, the correlation length for this ordering can decrease even as the temperature is decreased. On a second step, the constraint is sufficiently high, breaking the column and inducing a nematic having short range columnar ordering. However, simultaneous changes in the molecular conformation can occur and, at low temperature, new columnar phases can follow the nematic.

A priori, the molecular architecture of a disc-like mesogenic molecule is completely different from that of a lipid. Nevertheless, if we consider the column or the ribbon as the elementary aggregate, the similarities between both can be easily underlined. On one hand, the unidimensional character of the aggregate enhances the properties of universality. On the other, the occurrence of lyotropic ternary systems in which two kinds of lipids can be inhomogeneously shared in the aggregate has raised the question of the influence of interactions between aggregates upon the mesophase symmetry, while this problem was previously restricted to thermotropic mesophases. Moreover, under the action of the temperature (mesogenic aggregates) or of the amount of water (amphiphilic aggregates), the cylinders can be broken into finite aggregates forming a nematic mesophase in both cases.

However, the same amphiphilic molecule can undergo both the lamellar and the columnar phase by simple variation of the water content. The two kinds of mesogens, smectogens and discogens, give distinct mesophases of different symmetry and are immiscible even in the nematic phase. The ability of a lyotropic system to form a wide variety of mesophases has been reproduced for hybridous thermotropic mesogens. This will be the subject of our last section.

4. THERMOTROPIC LIQUID CRYSTALS: TRANSITION FROM THE SMECTIC TO THE COLUMNAR PHASES

In the previous section we have shown how the discovery of thermotropic disc-like molecules have brought new elements into the comparison between thermotropic and lyotropic liquid crystals. Nevertheless, the major difference between them originates in the fact that the first result from organizations of individual molecules while the second result from organizations of molecular aggregates. In the first case, the shape of the interface between aromatic and paraffinic moieties is determined by the core structure, and only weak changes of the structural elements (column, lamella) can occur. In the second case, the elasticity or flexibility of the paraffinic/polar interface allows different shapes for the aggregates and therefore ensures a rich polymorphism that involves 1D, 2D and 3D periodical structures, while the conformational state of the molecules is nearly constant.

However cubic mesophases have also recently been observed with some thermotropic mesogens.[48] Moreover, the existence of a transient hexagonal phase has been reported for one compound that forms a cubic phase and several smectic phases.[49] Such a hexagonal phase may have a structure similar to that of the thermotropic hexagonal mesophase of anhydrous divalent cation soaps.[24] The occurrence of ribbon phases with polar rod like molecules is another example which illustrates precursor effects toward a change in the topology of the mesophases.

Since the shape of the molecule seems to be the first factor which governs the organization of the molecules in a thermotropic mesophase, variations of core shape or position and number of grafted chains have been undertaken by chemical scientists. It appears that cone[50] and ring[51] shaped cores form columnar mesophases when the number of grafted chains is sufficient to ensure good compactness at the aromatic/paraffinic or core/chain interface. Oppositely, changing the number of grafted chains at each end of a rod-like core does not disturb the smectogenic character, if the number of chains is not too high.[52] An intermediate shape between a rod-like core and a disc-like one can be ensured by the synthesis of lath-shaped molecules.[53] With such molecules, only smectic C and nematic phases have been observed.

Another interesting example is found in charge transfer complexes or ionic radical salts.[54] Let us look at the molecular organization in the mesophase of a complex 1/1; the donor belongs to a thioaryl-pyranilidene series with four grafted alkyl chains and the acceptor is the small TCNQ molecule. The neutral donor does not undergo any liquid crystalline phase. Upon complexation with TCNQ (and not with I_3^- or ClO_4^-) a lamellar mesophase appears around T = 120°C. Nevertheless, stacks of donor molecules with a core–core distance of 3.4 Å are still present in the mesophase. The layer thickness is rather small compared to the molecular size and the mean area per chain in each lamella is 0.36 nm^2, which is larger than the usual value in a smectic phase.

It has recently been shown that several flat cores with electronic donor properties induce mesogenic properties when associated with counter ions. Depending on the core size and on the number of grafted chains, the mesophase can be either a lamellar or a columnar phase[55] based on the global symmetry of the organic partner. In fact, due to the ionic character of the two components which form this mesophase, the discrimination between the thermotropic and lyotropic character is not obvious. Moreover, the role of the smallest ionic species (generally BF_4^- or ClO_4^-) has not yet been put clearly into evidence. The strong interaction between the organic electron donors favors local columnar order with a short core–core distance of 0.34 nm. This strong intramolecular interaction is specific of a thermotropic liquid crystal.

During the last three years a new class of mesogenic molecules, the phasmidic compounds,[56] have been synthesized. Owing to their chemical structure, they may behave either as rod-like or/and as disc-like shaped molecules. Therefore, the phasmidic compounds are the best candidates to form mesophases similar to lyotropic mesophases. Their aromatic part is a long rod-like core made of at least five phenyl (or cyclohexane) rings linked by Shiff bases or carboxylic groups; two or three *n*-alkoxy long chains are grafted in ortho and para positions on each terminal phenyl group. Many of these compounds show a hexagonal columnar mesophase. Rod-like cores with four grafted chains (two at each end), also known as biforked mesogens,[57] show a N and a Sm C phase for short chain lengths ($<C_{10}$) and a hexagonal phase for longer chain lengths. Compounds with intermediate chain length may present a polymorphism where both Sm C and columnar phases exist. Moreover, in the same range of chain length, a transition from a hexagonal mesophase into a cubic one is also observed.

The molecular organization of the biforked mesogens in the Sm C phase is the usual one: the tilt angle is about 50° and the layer thickness is compatible with the idea of parallel assembly of molecules in their extended conformation. Moreover, total miscibility is found with the Sm C and N phases of rod-like compounds.[58]

Despite the low symmetry of the phasmidic molecules (six chains and four chains or biforked compounds), the most frequently observed mesophase is hexagonal. This phase is encountered if the semi-flexible rod core is sufficiently long (five or six phenyl rings) and if the paraffinic mass exceeds the aromatic one. Cores and chains are in a liquid state with a mean core–core or chain–chain distance of 0.45 nm. The lattice spacing of the hexagonal network and the value of the specific molecular volume support the concept of cylindrical aggregates similar to those of a lyotropic inverted hexagonal mesophase. A slice of a column 0.45 nm thick, contains at least three molecules. The number of chains in the same slice, for a given core length, does not depend on the chemical structure of the core nor on the number of chains grafted on each core.[59] Therefore, a column is made of a central region which contains the aromatic core surrounded by an external region of paraffinic chains. These regions look the same for all the compounds, and the chain area at the interface between core and chains is 0.25–0.30 nm.[2]

The knowledge of the molecular organization in phasmidic hexagonal mesophases help us to understand the polymorphism of this new class of molecules.

For a low paraffinic content (4 short chains) the mesomorphic state is driven by the core–core interaction. Because of the long rod-like core, smectic and nematic phases are observed (the core specific volume is probably higher than in a normal smectic phase). By increasing the chain length one can obtain a sequence where the Smectic C phase is followed at higher temperature by two dimensional oblique and hexagonal phases. As the temperature is increased the conformational disorder of the chains destroys the parallel core ordering and therefore favors a curvature of the interface between the aromatic and the paraffinic moities.

Let us remark that with some biforked mesogens, cubic phases also occur. Only one case has been studied by X-ray diffraction. The sequence is:

$$\begin{tikzcd}
\text{Crystal} \arrow[r, leftrightarrow] & (\text{Sm C}) \arrow[r, leftrightarrow] & \text{Cubic} \arrow[rr] & & \text{I} \arrow[dl] \\
& & & \text{Hex} \arrow[ul] &
\end{tikzcd}$$

The Smectic C phase is metastable and has not been studied; the cubic phase has a body centered cubic structure with a lattice spacing of 16.2 nm; the hexagonal phase has a large lattice spacing of 13.5 nm. It is obvious that the cubic phase and this new hexagonal phase with large lattice size are mesophases where the curvature of the interface between the aromatic and the aliphatic region is weak and inhomogeneous. If the cubic phase is not yet understood, the hexagonal phase has a structure similar to that of a lyotropic complex hexagonal phase. It can be described as follows: the central part of each column, similar to the columns of hexagonal mesophases generally observed in phasmidic compounds, is surrounded by a second molecular layer whose curvature is weak (Figure 10). Increasing the chain length in the same series, hexagonal phases with lattice spacing between 4 and 5 nm occur and therefore correspond to the ones generally encountered.

The similarities between the polymorphism of the lyotropic mesophases and that of the phasmids appears clearly. In the first ones, the transformation of the lamellar into the hexagonal phase is managed by the lipid (amphipatic)/water interfacial curvature; in the latter, by the interfacial curvature between two amphipatic media. Intermediate steps involve phases whose structure elements exhibit inhomogeneous interfacial curvatures.

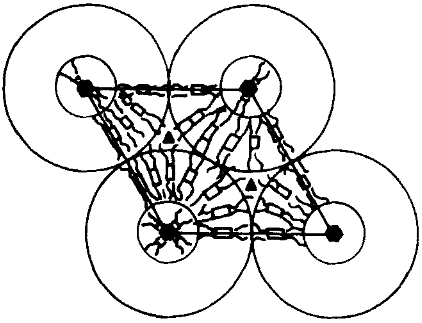


FIGURE 10 Molecular organization in a thermotropic complex hexagonal structure.

It must be pointed out that, up to now, no Sm A has been put into evidence with phasmidic compounds. Much of work remains to be done in the search of new pure thermotropic mesogenic compounds and in the study of binary mixtures of phasmidic molecules with other mesogenic and specially rod-like molecules.

5. CONCLUSION

Liquid crystals were discovered one hundred years ago. An important contribution in this field is that of G. Friedel who demonstrated that many thermotropic and lyotropic mesophases were both organized in periodic stacks of liquid layers. In that way, he has pointed out an essential simularity relating thermotropic and lyotropic layered phases. Since then, the two classes of mesophases, thermotropic and lyotropic, were described according to their own specificities.

Layered thermotropic mesophases result from the organization of individual mesogens with a rigid rod-like core, and therefore the important physical parameter is the orientational order. Layered lyotropic mesophases result from the organization of aggregates of amphiphilic molecules, and therefore the apolar/polar interfaces are important. The aggregates of layered lyotropic structures are lamellae, à priori similar to the smectic thermotropic layers. Nevertheless, the smectic organization is driven by the core ordering of rod-like mesogens, while the mean area per polar head, which depends on the chemical structure of the amphiphilic molecules, is the main feature of the lamellar lyotropic organization.

After the discovery of disc-like mesogens, the structures of the thermotropic columnar mesophases were described in analogous terms to those of smectics, while a unique description also holds for the lyotropic mesophases of various symmetries. Disc-like mesogens are able to form thermotropic columnar phases, while a large number of lyotropic systems give rise to organizations of cylindrical aggregates. The area of the section of a column is defined by one disc-like mesogen, while that of a cylinder is defined by a large number of amphiphilic molecules. The organization of the molecules of one amphiphilic species in lyotropic cylindrical mesophases may be affected by the chemical properties of the system which induce changes in the molecular interactions and consequently impose a peculiar shape to the liquid/liquid interface, *i.e.*, to the shape of the cylinders of the mesophase. Moreover, the interactions between the cylindrical aggregates are then affected, and the resulting structures can be compared to those of arrays of stacks of disc-like mesogens. These stacks can also have an anisotropic section, due to the molecular shape or induced by the core orientation. Nevertheless, the interface between cores and chains is homogeneous along the columnar axis. Similarities of the properties of interfaces (paraffinic/aqueous or core media) induce similar interactions between cylinders, and therefore the structures have nearly the same symmetry.

Owing to their chemical structure, both thermotropic (aromatic core/aliphatic chains) and lyotropic (aliphatic chains/polar groups) molecules form molecular organizations which divide the space into sub-spaces or into media with different properties. This particularity confers a double character to the liquid crystals: they may be considered at one and the same time as the homogeneous bulk matter of a single species or as a unique entity composed of two distinct media. The concept of homogeneous matter has been enhanced, and therefore thermotropic liquid crystals were compared to molecular crystals, until the discovery of phasmidic compounds. The phasmidic mesogens show that their core interactions may be less important compared to the chemical segregation between their aromatic and paraffinic parts. The concept that thermotropic mesophases may result from the packing of aggregates becomes more and more obvious since the synthesis of the phasmids. Indeed, these mesogens form mesophases whose structure elements are no longer individual molecules but stacks of molecules whose shape depends on the interface between the semi-rigid core and the liquid aliphatic chains. Therefore, different mesophases are formed and the polymorphism obtained with phasmidic mesogens is comparable to the rich polymorphism of lyotropic mesophases. It now appears that the same physical concepts apply to the organization of the molecules in both kinds of mesophases.

Until now, the emphasis was put upon the existence of interfaces between two media as a consequence of the amphipatic character of the molecules. Questions are now arising on the mechanisms of the variation of their curvature and modifications of the topology which induce phase transformations. One goes progressively from a structural description of the different organizations toward an attempt to understand the mechanisms associated with the phase transformations, through the evolution of the shape or curvature of the interfaces.

Note

In this paper we have presented some particular features of thermotropic and lyotropic LC, and therefore it is not a complete compilation of all the known structures and systems. More exhaustive reviews have already been written. Examples of such reviews can be found in the first issue of the Journal de Chimie Physique, Paris, **80**, 1983, and in Advances in Liquid Crystals, Volume 1, edited by G. H. Brown.

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References

1. G. Friedel, *Annales de Physique* (*France*), **18**, 273 (1922).
2. V. Luzzati, in biological membranes, edited by D. Chapman (Academic Press) London, p. 71 (1968).
3. V. Luzzati, H. Mustacchi, A. Skoulios and F. Husson, *Acta Cryst.*, **13**, 660 (1960).
4. See for example G. W. Gray, Molecular Structure and the Properties of Liquid Crystals, Academic Press, New York (1962).
5. F. Husson, H. Mustacchi and V. Luzzati, *Acta Cryst.*, **13**, 668 (1960).
6. B. Gallot, in Liquid Crystalline Order in Polymers, edited by A. Blumstein (Academic Press) p. 192 (1978).
7. F. Hardouin, A. M. Levelut, M. F. Achard and G. Sigaud, *Journal de Chimie Physique* (*Paris*), **80**, 53 (1983).
8. P. G. de Gennes, The Physics of Liquid Crystals, Clarendon Oxford (1974).
9. J. Charvolin and A. Tardieu, *Solid State Phys.*, Suppl. 14, edited by F. Seitz and D. Turnbull, Academic Press, (1978).
10. A. Leadbetter and P. G. Wrighton, *J. Physique*, **40**, C3, 234 (1979).
11. P. Seurin, D. Guillon and A. Skoulios, *Mol. Cryst. Liq. Cryst.*, **71**, 51 (1981).
12. a) B. Deloche and J. Charvolin, *J. Physique*, **37**, 1497 (1976); b) B. Deloche, Thesis, Université Paris-Sud, Orsay (1978).
13. B. Mély and J. Charvolin, Physicochimie des composés amphiphiles (Editions du Centre National de la Recherche Scientifique, Paris) (1979).
14. R. J. Meyer and W. L. Mac Millan, *Physical Review A*, **9**, 899 (1974).
15. R. B. Meyer, L. Liébert, L. Strzelecki and P. Keller, *Journal de Physique Lettres*, **36** L, 69 (1975).

16. G. Barbero and G. Durand, 7th Liquid Crystal conference of Socialist countries, Pardubice, Czechoslovaquia (1987). See also G. Barbero, I. Dozov, J. F. Palierne and G. Durand, *Phys. Rev. Lett.*, **56**, 2056 (1986).
17. J. J. Benattar, F. Moussa and M. Lambert, *Journal de Chimie Physique* (*Paris*), **80**, 99 (1983).
18. J. M. Vincent and A. Skoulios, *Acta Cryst.* **20**, 432, 441, 447 (1966).
19. J. Charvolin, *Journal de chimie physique* (*Paris*), **80**, 15 (1983).
20. A. M. Levelut, N. Guyen Huu Tinh, *Journal de Phy te*, **48**, 847 (1987).
21. M. C. Holmes and J. Charvolin, *The J. of Phys. Chem.*, **88**, 810 (1984).
22. a) P. Kékicheff, B. Cabane and M. Rawiso, *J. Phys. Lett.* (*Paris*), **45**, 813 (1984); b) Y. Hendrikx, J. Charvolin, P. Kékicheff and M. Roth, *Liquid Cryst.*, **2**, 677 (1987).
23. The use of conventional 3D space groups for the description of the 2D networks formed by an assembly of parallel rods of infinite length is discussed in Ref. 40.
24. P. Spegt and A. Skoulios, *C. R. Acad. Sci.* (*Paris*), **251**, 2199 (1960) ib. **254**, 4316 (1962).
25. B. Mély, J. Charvolin and P. Keller, *Chem. and Phys. of Lipids*, **15**, 161 (1975).
26. J. Charvolin and Y. Hendrikx, in *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J. M. Emsley, 449 (1985).
27. V. Luzzati, J. Gulik-Krzywicki and A. Tardieu, *Nature*, **218**, 1031 (1968).
28. P. Kékicheff and B. Cabane, *J. Physique*, **48**, 1571 (1987).
29. J. Charvolin, to be published in Progress in Microemulsions, edited by D. Senatra, Ettore Majorama Series (Plenum Press).
30. a) J. F. Sadoc and J. Charvolin, *J. Physique*, **47**, 683 (1986); b) J. Charvolin and J. F. Sadoc, *J. Physique*, **48**, 1559 (1987).
31. Y. Hendrikx and J. Charvolin, *J. Physique*, **42**, 1427 (1981).
32. S. Alpérine, Thesis, Université Paris-Sud, Orsay (1985).
33. Y. Hendrikx and J. Charvolin, *Liquid Cryst.*, **3**, 265 (1988).
34. Y. Hendrikx, J. Charvolin and M. Rawiso, *J. Coll. Interface Sci.*, **100**, 557 (1984).
35. S. Alpérine, Y. Hendrikx and J. Charvolin, *J. Phys. Lett. Paris*, **46**, 27 (1985).
36. Y. Hendrikx, J. Charvolin and M. Rawiso, *Physical Review B*, **33**, 3534 (1986).
37. A. M. Figueiredo-Neto, Y. Galerne, A. M. Levelut and L. Liébert, *J. Phys. Lett.* (*Paris*), **46**, L 499 (1985).
38. M. B. Lacerda-Santos, Y. Galerne and G. Durand, *Phys. Rev. Lett.*, **53**, 757 (1984).
39. S. Chandrasekhar, B. K. Shadashiva and R. A. Suresh, Pramana **9**, 471 (1977).
40. A. M. Levelut, *Journal de Chimie Physique* (*Paris*), **80**, 149 (1983).
41. L. D. Landau, in Collected Papers of L. D. Landau, ed. D. ter Haar, p. 209, Gordon Breach, New York, (1965).
42. P. Foucher, C. Destrade, N Guyen Huu Tinh, J. Malthête and A. M. Levelut, *Mol. Cryst. Liq. Cryst.*, **108**, 219 (1984).
43. R. Cayuela, Thesis, Université de Bordeaux I (1986).
44. C. Destrade, H. Gasparoux, P. Foucher, Nguyen Huu Tinh, J. Malthête and J. Jacques, *J. Chimie Physique*, **80**, 137 (1983).
45. A. M. Levelut, P. Oswald, A. Ghanem and J. Malthête, *J. Physique*, **45**, 745 (1984).
46. D. Goldfarb, Z. Luz and H. Zimmerman, *J. de Phys.*, **42**, 1303- (1981).
47. P. G. de Gennes, *J. Physique Lettres*, **44**, L 657 (1983).
48. J. Billard, *C. R. Acad. Sci. Paris, Série II*, **305**, 843 (1987).
49. a) D. Demus, D. Marzotko, N. K. Sharma and A. Wiegelben, *Kristall und Technik*, **15**, 331 (1980); b) J. E. Lyndon, *Mol. Cryst. Liq. Cryst. Letters*, **72**, 79 (1981).
50. a) J. Malthête and A. Collet, *Nouveau Journal Chimie*, **9**, 151 (1985); b) H. Zimmermann, R. Poupko, Z. Luz and J. Billard, *Z. Naturforsh. Teil*, **A 40**, 149 (1985).
51. J. M. Lehn, J. Malthête and A. M. Levelut, *J. Chem. Soc. Chem. Com.*, 1794 (1985).

52. a) J. Malthête, J. Conceill, J. Gabard and J. Jacques, *Tetrahedron*, **37**, 2823 (1981); b) W. Weissflog and D. Demus, *Mol. Cryst. Liq. Cryst.*, **129**, 235 (1985).
53. a) J. Malthête, J. Billard and J. Jacques, *C. R. Acad. Sci. (Paris)*, **C 281**, 333 (1975); b) J. Malthête, *C. R. Acad. Sci. Paris Serie II*, **296**, 435 (1983).
54. P. Davidson, A. M. Levelut, H. Strzelecka and V. Gionis, *Journal de Physique Lettres*, **44**, L 823 (1983).
55. a) V. Gionis, R. Fugnitto, H. Strzelecka and P. Le Barny, *Mol. Cryst. Liq. Cryst.*, **95**, 351 (1983); b) P. Davidson, C. Jallabert, A. M. Levelut, H. Strzelecka and M. Veber, *Liquid Crystals*, to be published; c) H. Strzelecka, C. Jallabert, M. Veber, P. Davidson, A. M. Levelut, J. Malthête, G. Sigaud, A. Skoulios and P. Weber, *Mol. Cryst. Liq. Cryst.* Proceeding of I.C.O.S.S. Lyon 6–10 Jul. (1987).
56. J. Malthête, A. M. Levelut, N. Guyen Huu Tinh, *Journal de Physique Lettres*, **46**, L 875 (1985).
57. N Guyen Huu Tinh, C. Destrade, A. M. Levelut and J. Malthête, *Journal de Physique*, **47**, 555 (1986).
58. Y. Fang, A. M. Levelut and C. Destrade, to be published.
59. A. M. Levelut, J. Malthête, C. Destrade and Nguyen Huu Tinh, *Liquid Crystals*, **2**, 877 (1987).