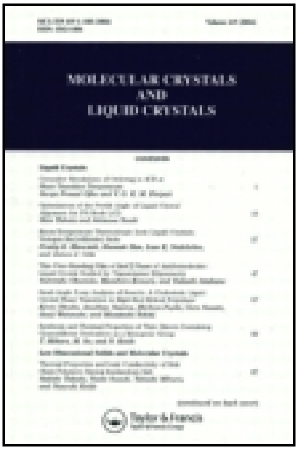

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Amphiphilic Character and Liquid Crystallinity

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To cite this article: A. Skoulios & D. Guillon (1988): Amphiphilic Character and Liquid Crystallinity, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 165:1, 317-332

To link to this article: http://dx.doi.org/10.1080/00268948808082205

Mol. Cryst. Liq. Cryst., 1988, Vol. 165, pp. 317–332
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Printed in the United States of America

Amphiphilic Character and Liquid Crystallinity

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(*Received December 18, 1987*)

The main families of compounds able to produce lyotropic or thermotropic smectic and columnar mesophases have been presented. Their molecules have been considered as being formed of two distinct parts, incompatible with one another, covalently bonded, but suitably separated in space. Their liquid crystalline structures have then been described in succession and analyzed in terms of microphase segregation. The common feature of the smectic and columnar ordering turns out to be the creation of fairly sharp interfaces between segregation microdomains. The amphiphilic character of the molecules seems, therefore, to play a predominant part in the establishment of both the smectic and columnar ordering.

INTRODUCTION

When examining the mesomorphic behavior of matter, one often considers that substances able to produce liquid crystals belong to one of two distinct classes of materials: the *amphiphilic* and the so-called *non-amphiphilic* mesogens. The first class includes soaps and soap-like materials leading to lyotropic, but also to thermotropic, mesophases.[1] The second includes rod-[2] and disk-like[3] mesogens giving rise only to thermotropic liquid crystals. Somewhat different in chemical structure, the two classes of mesogens have, traditionally, been studied independently by different groups of investigators, having different points of view and prompted by divergent considerations. Amphiphilic mesogens have been studied by scientists mainly interested in colloids,[4] surfactants, and biological membranes[5]; non-amphiphilic mesogens, on the other hand, have been investigated by chemists and physicists especially interested in the connections between chemical architecture and physical properties of liquid crystals, and also concerned with their technological applications (displays . . .). As a result, the amphiphilic character has, so far, been commonly associated only with the formation of lyotropic liquid crystals.

Regardless of whether mesogens are amphiphilic or non-amphiphilic, their observed optical properties pointed right from the outset to the existence of two types of liquid crystalline structures. In an attempt to systematically and critically analyze these two new states of matter, intermediate between the true three-dimensional crystal and the isotropic liquid, Friedel proposed two adjectives to distinguish them individually.[6] *Nematic* was meant to qualify the fluid and anisotropic state characterized by thread-like optical textures; *smectic* (σμῆγμα, soap) was suggested to describe the other, rather pasty, liquid crystalline state, initially obtained with soaps. With the present knowledge of liquid crystals, the term smectic may seem rather improper, since many smectic phases are in fact obtained with compounds which are far from being classical soaps. However, it carries a highly premonitory sense, in that it reveals what in our opinion is the basic property of the molecules able to produce smectic phases, namely the *amphiphilic character.*

In a recent and comprehensive account of the mesomorphic state,[7] aspects of the liquid crystalline behavior of both amphiphilic and non-amphiphilic mesogens were described together; but the amphiphilic character was systematically and exclusively used to explain the specific features of the amphiphilic mesogens alone. More recently, however, the amphiphilic character was considered to be an important and decisive factor that controls the smectic ordering of the non-amphiphilic materials as well.[8] In the present paper, the role of the amphiphilic character in the field of liquid crystals will be developed and analyzed to some extent, specifically in connection with the occurrence of the smectic ordering. It will also be used, however, to investigate and understand the formation of what is now defined to be the *columnar* ordering.

Before coming to the heart of the matter, it is useful to recall the classical meaning of amphiphilic character, its molecular origin, and its implications in the ordering and properties of condensed matter. The term amphipathy, synonymous with amphiphilic character, was long ago been proposed by Hartley[9] to explain the tendency for certain types of molecules to be adsorbed at interfaces or to form micelles in water solutions. Basically, it expresses the aptitude of these molecules to form homogeneous and thermodynamically stable solutions with water and polar solvents, as well as with oils and non-polar solvents.

Surprising at first sight, this property is simply related to the chemical nature and architecture of the molecules. These are formed of two distinct parts, covalently bonded but suitably separated in space. One part is hydrophilic in character, that is soluble in water; the other is lipophilic, that is soluble in organic, non-polar solvents. Furthermore, the two parts are able to behave independently from one another to a large extent, without excessive mutual steric or interactional hindrances. A typical example of amphiphilic molecule is sodium hexadecylsulfate:

$$C_{16}H_{33}OSO_3^- \ Na^+$$

where the hexadecyl aliphatic chain is the lipophilic part, and the sodium sulfate ionic group is the hydrophilic one.

The most remarkable feature of amphiphilic molecules is the tendency of their constituent parts to segregate in space with creation of *interfaces*. The hydrophilic and hydrophobic moieties tend to separate from one another into distinct microdomains, alternately juxtaposed and mutually kept apart by rather well defined boundaries. Amphiphilic molecules generally concentrate themselves into aggregates so as to expose to the solvent their soluble moiety alone, their insoluble part being efficiently buried in the depth of the aggregate (Figure 1). Likewise, in the presence of an extraneous wall, amphi-

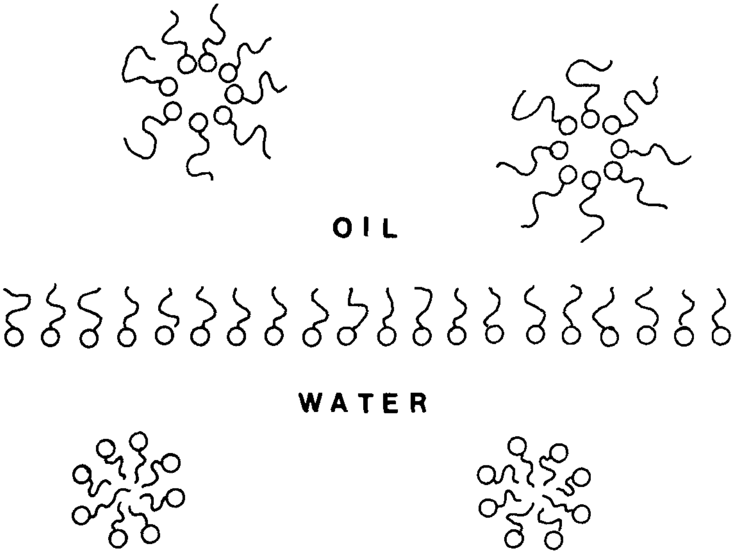


FIGURE 1 Schematic distribution of soap molecules in a oil-water two-phase system.

philic molecules are usually adsorbed onto that wall through their moiety which is compatible with it. Further illustrations of the local segregation of the molecules, along with examples of the autonomous behavior of the two molecular moieties, are to be given below.

SMECTIC ORDERING

Early visual[10] and optical[6] observations of liquid crystals suggested that the smectic ordering should consist of a stratified arrangement of molecules. Many experimental and theoretical studies have been carried out thereafter, aiming at a better understanding of the structure and physical properties of this type of liquid crystal.[11,12] It has now become a matter of common agreement to describe the smectic ordering as the stacking of layers formed of molecules (generally elongated in shape) arranged side by side, and oriented either perpendicularly or at an angle with respect to the layer normal. The thickness of the layers is generally of the order of a few nanometers, that is, comparable to the length of the molecules, and their lateral extension is indefinitely large. The positional correlation of the molecules inside the layers and the three-dimensional positional correlation of the superposed layers themselves depend on the polymorphic form of the smectic mesophase considered.[11]

Smectic, and more specifically smectic A, ordering is frequently encountered with soaps and amphiphiles. It has been observed at high temperatures with pure soaps, such as sodium or potassium alkanoates.[13] It has also been observed with a variety of ionic and non-ionic amphiphiles[1,14] in the presence of water,[15] hydrocarbons,[16] and water-soluble additives.[17] It corresponds to an alternate and periodic stacking of hydrophilic and lipophilic sublayers (Figure 2a). The hydrophilic sublayers are formed of the polar heads of the amphiphilic molecules, occasionally mixed with water and water-soluble substances. The lipophilic sublayers are formed of the aliphatic parts of the molecules and can also contain the lipophilic additives of the system. Both of them are liquid-like in character.

For a long time, the interfaces between lipophilic and hydrophilic microdomains in soap/water systems were considered to be infinitely sharp, suggesting perfect segregation. With this picture in mind, the thickness of the sublayers and the molecular area (typically, 40 Å^2) of the amphiphilic molecules could be deduced from the smectic period measured by X-ray diffraction. The only parameters needed to perform this calculation were the chemical composition of the

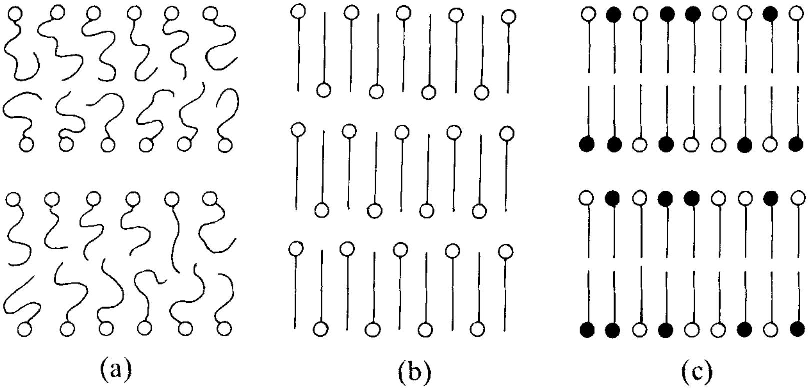


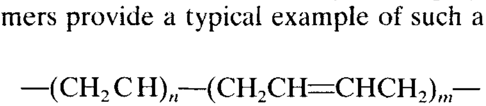
FIGURE 2 Schematic view of the lyotropic smectic layering of amphiphiles: a, double-layered disordered smectic; b, single-layered ordered smectic; c, double-layered ordered smectic. Empty circles represent the hydrophilic moieties of the soap molecules, filled circles stand for the hydroxy endgroups of the alcohol molecules, and lines for the hydrophobic chains. The soap and soap/alcohol sublayers are separated from one another by the water molecules in the system.

mixture and the partial specific volumes of the lipophilic and hydrophilic species in the system.[14-17] Recent nuclear magnetic resonance studies[18] showed that, in fact, interfaces are not infinitely sharp. Of the order of a few tenths of a nanometer, their thickness is, however, still very small compared to the smectic period, indicating that the microphase separation due to the amphiphilic character is indeed clear.

Microphase separation turns out to be so efficient in soaps that the two constituent parts of the molecules behave quite independently from one another as illustrated by the two smectic modifications to be described now. The first modification was observed with aqueous lyotropic smectic phases of potassium, rubidium, and cesium soaps. In these systems, the aliphatic chains "crystallize" upon cooling, without any other change of the smectic structure.[19] At low temperature, these adopt a fully extended conformation and arrange themselves in single layers as shown in Figure 2b. Depending upon thet temperature, they are laterally packed either according to a two-dimensional hexagonal crystal lattice, producing what can be defined as a smectic B lyotropic mesophase, or according to a centered-rectangular crystal lattice, producing a smectic E lyotropic mesophase. For a given soap, the transition between the two structures takes place at a temperature which is independent of the water content of the system: the aliphatic chains within the lipophilic sublayers are fairly free to undergo structural transitions as if they were engaged in a thermodynamic phase of their own.

The second smectic modification provides, this time, evidence for the freedom of the polar heads. In the single-layered ordered smectic phases just described (Figure 2b), the molecular area of the polar heads has values ($\cong 40$ Å^2) comparable to those generally observed with soap/water smectic phases at high temperature when the aliphatic chains are "melted." It corresponds exactly to twice the molecular area of the "crystallized" aliphatic chains.[19] When half of the soap molecules are replaced by linear alcohol molecules of the same length, the ordered smectic phases observed contain double-layered, instead of single-layered, lipophilic sublayers (Figure 2c). The stretched aliphatic chains are still arranged laterally according to a hexagonal or a centered-rectangular two-dimensional crystal lattice depending on temperature, and the molecular area of the polar heads is still equal to twice that of the "crystallized" aliphatic chains.[19] Molecules are, therefore, arranged either in single or double layers, depending on whether soap molecules in the layers are alone or interdigitated with alcohol molecules, but, most significantly, the molecular area of the polar heads is kept constant as required by their specific electric interactions.

Up to this point, the amphiphilic character has only been applied to soap and soap-like materials whose molecules are usually formed of a water-soluble and a water-insoluble part. The structural behavior of block copolymers to be considered now clearly shows that the amphiphilic character can easily be extended and applied also to systems which are not classical soaps. Sure enough, block copolymers resemble soaps from the standpoint of their chemical architecture, as their molecules are formed of two types of linear polymer chains (the *blocks*) covalently united end on. Polystyrene/polybutadiene two-block copolymers provide a typical example of such a system:



$$-(CH_2\underset{\Phi}{\underset{|}{C}}H)_n-(CH_2CH{=}CHCH_2)_m-$$

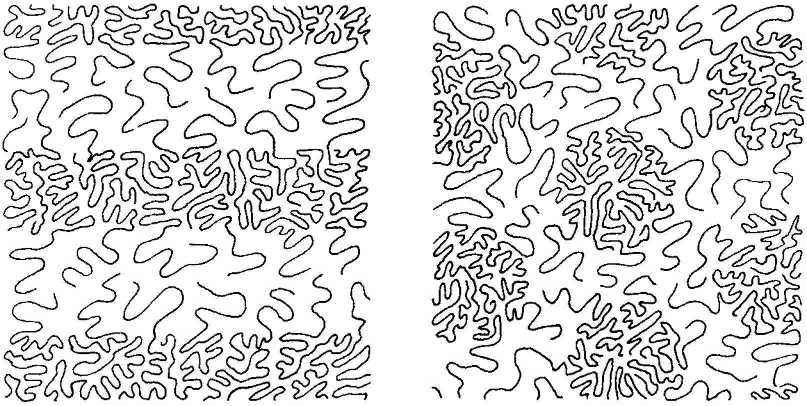
However, contrary to soaps, block copolymers usually behave differently with regard to water and hydrocarbons. The two constituent parts of their molecules are indeed incompatible with one another, but their incompatibility is not related to water solubility and water insolubility. Incompatibility, here, is in fact related simply to van der Waals repulsions due to different polarisabilities.[20]

X-ray diffraction and electron-microscopy have established that, like soaps, block copolymers can produce well developed liquid crystalline phases.[21] Among these, the smectic phases (Figure 3a) consist of two types of sublayers periodically and alternately superposed, each sublayer being formed of blocks of the same chemical nature. As the molecular dimensions of the blocks are usually large, the thickness of the smectic layers is also large, having values of the order of a few tens of nanometers. Depending upon the case, blocks can either crystallize or remain in the amorphous state,[22] acting in the latter case as a glass or a mobile fluid.[23] They can also swell differently in various solvents according to their specific affinity towards them.[24] As for the thickness of the interfacial regions between sublayers, elaborate X-ray analyses have given evidence that this is actually of only a few nanometers, that is almost negligible compared to the overall layer spacing[25]: once again, the high degree of incompatibility of the blocks and the important role played by the amphiphilic character in the occurrence of smectic mesophases are perfectly clear.

Finally, a great variety of smectic phases has been found with calamitic mesogens. These are formed of one rod-like, generally aromatic part, and one or two aliphatic chains attached directly to the rigid core.[26] Typical examples are:

$$CH_3{-}(CH_2)_n{-}\Phi{-}CH{=}N{-}\Phi{-}N{=}CH{-}\Phi{-}(CH_2)_n{-}CH_3$$

$$CH_3{-}(CH_2)_n{-}\Phi{-}\Phi{-}C{\equiv}N$$



(a) (b)

FIGURE 3 Schematic representation of the smectic (a) and the columnar (b) structure of block copolymers.

As already stated, their smectic structure is described in terms of stratified arrangements of rods, with various possible packings within the layers. Depending upon the chemical nature of the mesogen and the polymorphic form in consideration, rods are upright, with their centers either irregularly (smectic A) or periodically (smectic B, E) distributed in each layer; or else, tilted at an angle in relation to the layer normal, with their centers again either irregularly (smectic C) or periodically (smectic G, H . . .) located in each layer.[11]

Although very suggestive, this purely geometrical and static picture of the smectic ordering considers that molecules are simple rods and does not specify the position of the aromatic cores with respect to the aliphatic chains. It furthermore neglects thermal agitation and possible diffusion of molecules through the material, especially across the layers. It amounts, therefore, to saying that the lateral register of the molecules along their elongational axis is perfect. To take into account the dynamical aspect of the molecular arrangement, theories analyze the smectic layering in terms of what is defined to be a smectic order parameter.[27] They invoke the presence of a pair potential taking into account a short range lateral (Maier-Saupe type) interaction between neighbouring molecules. These are no longer assumed to stand on well defined and infinitely sharp parallel surfaces, but are supposed to be periodically distributed in space following a sinusoidal law. The order parameter measures then the amplitude of the sinusoidal distribution of molecules along the layer normal and expresses their tendency to arrange in lateral register.

Following this interpretation, it is generally believed that the sinusoidal distribution of molecules has a rather weak amplitude. As a result, the smectic A to nematic transition as a function of temperature should be very weakly first order, if not second order at all. In addition, X-ray diffraction patterns should contain only the first Bragg harmonic of the smectic layering; and the thermal diffusion of molecules, in particular across the layers, should be rather easy. In reality, smectic A to nematic transitions, and more significantly phase transitions involving an ordered smectic mesophase, are commonly first order[28]; moreover, higher smectic Bragg harmonics are quite often present in the X-ray patterns[29]; and also, the amplitude of the thermal agitation of the molecules across the layers is of the order of only a few tenths of a nanometer.[29] In addition to these observations, systematic volume measurements with homologous series of calamitic smectogens show that the aromatic core and the aliphatic chains of the molecules have distinct volume behaviors, indicative of thorough phase segregation.[30] Finally, and more conclusively, a phase diagram drawn with a binary mixture of the aromatic core of a given smec-

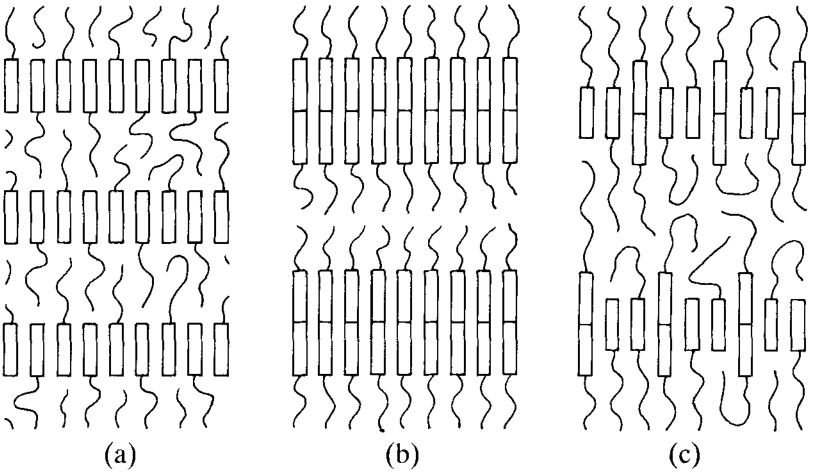


FIGURE 4 Schematic view of the smectic layering of calamitic mesogens: a, monolayer; b, bilayer; c, partial bilayer. Rectangles represent the aromatic cores of the molecules, and curved lines the aliphatic chains.

togen, on one hand, and its aliphatic chain, on the other, displays an important miscibility gap up to temperatures largely above the clearing temperature of the smectic phase.[31] It seems, therefore, that a good description of the smectic structure of calamitic molecules involves fair segregation between the two constituent parts of the molecules, similar to that observed with amphiphiles or block copolymers. The smectic structure results from the alternate stacking of aromatic and aliphatic sublayers, separated by interfacial regions which are thin when compared with the total smectic period (Figure 4a,b).

It is of interest to report here the case of highly polar cyano-ended dissymetric smectogens whose structure is partially bilayered.[32] Due to the strong dipole interactions of the cyano endgroups, some of the molecules are head-to-head associated in pairs[8] as illustrated in Figures 4c. Quite obviously, the interfacial regions between aromatic and aliphatic sublayers is here substantially diffuse, the amphiphilic interactions being opposed by the dipolar ones. However, the amphiphilic character keeps playing an important part in the lateral register of the aromatic cores, regardless of whether or not these are partially associated in pairs.

COLUMNAR ORDERING

Discussions of the columnar ordering were initiated in 1977 when Chandrasekhar first reported the occurrence of liquid crystals with flat, discotic organic molecules.[33] Actually, columnar mesophases had already been obtained with rod-like polymers of biological interest, such as desoxyribonucleic acids[34] or polypeptides[35] in concentrated solution, or with soaps[13] and block copolymers.[21] Whatever the chemical nature and architecture of the substances leading to the formation of columnar liquid crystals, the columnar ordering may be described as the packing of indefinitely long columns of molecules according to various two-dimensional crystal lattices, with significant positional disorder along their axis. Columns in general are formed by the association of a great number of molecules with various types of geometrical arrangements inside each column. (Mesophases obtained from nucleic acids and polypeptides constitute a special class of columnar liquid crystals, for they involve columns formed of non-associated single molecular species; they will not be further analyzed in the following.) The lateral size of the columns is of the order of a few nanometers and is comparable to the molecular dimensions. In the case of block copolymers, the lateral size of columns is, however, significantly larger, and reach values of the order of a few tens of nanometers.

Columnar ordering with molecular association has been observed with a large variety of ionic and non ionic amphiphiles in the presence of water.[1,14,15] It corresponds to cylindrical columns formed of amphiphile (or water) molecules, arranged according to a two-dimensional hexagonal lattice, and embedded in a continuous matrix of water (or hydrophobic chains) as shown in Figure 5. Both water and hydrophobic chains are liquid-like in character. The polar heads of the amphiphilic molecules are located at the interfaces between the hydrophilic and lipophilic micordomains. Similar hexagonal mesophases have also been obtained with block copolymers (Figure 3b).[21,24] As reported above for the smectic lyotropic structures of soaps, the thickness of the interfacial region is small compared to the diameter of the cylinders. Once again, the role of the amphiphilic character bringing about the microphase separation is perfectly clear. In contrast, however, to the smectic mesophases, the interfaces here are no longer planar, but cylindrical in shape.

Columnar mesophases have also been observed with pure metal soaps at high temperature. Incompatible with the aliphatic moieties, the polar metal carboxylate endgroups segregate in space to form columns of various geometrical shapes (ribbons,[13] "rods" [36] . . .), surrounded by the paraffin chains in disordered conformations. Depending upon their symmetry, columns are laterally arranged according to centered-rectangular (sodium soaps[13]), oblique (potassium

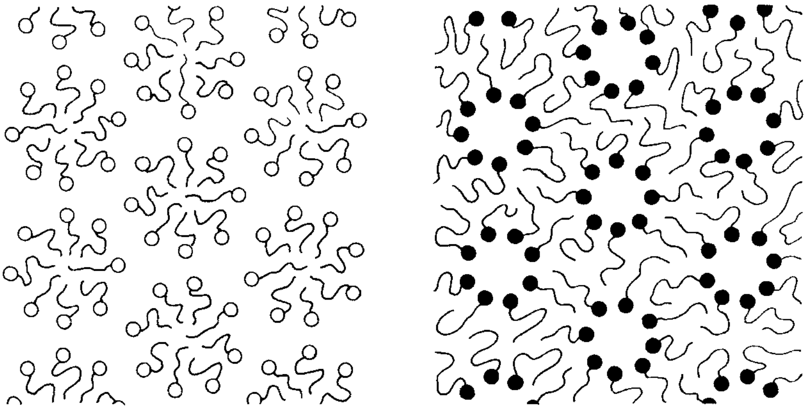


FIGURE 5 Schematic view of the cylindrical structure of the lyotropic columnar mesophases of soaps: a, columns formed of soap molecules are embedded in a water matrix; b, columns formed of water molecules are embedded in a paraffinic matrix. Circles stand for the polar heads of the soap molecules and lines for the disordered aliphatic chains.

soaps[13]), or hexagonal (magnesium or cadmium soaps for example[36]) two-dimensional crystal lattices (Figure 6). The lateral distance between columns is of the order of magnitude of the molecular dimensions. Systematic X-ray diffraction studies of homologous series of metal soaps as a function of temperature and chain length have shown that the polar heads of the molecules within the columns are assembled in a compact way, presumably as regular as in a crystal. Extended x-ray absorption fine structure spectroscopy (EXAFS) performed on copper (II) alkanoates, which also display columnar mesophases,[37] has confirmed this point, and led also to a description of the geometry of coordination of the polar endgroups.[38]

It is time now to discuss the class of the so-called discotic molecules which are at the origin of the present developments in the field of the columnar mesomorphic state.[3,39] Substances belonging to this class are characterized by disk-shaped molecules formed of a flat central aromatic core surrounded by several peripheral aliphatic chains (Figure 7). In general, these substances are purely organic in character; but sometimes, as in the case of alkylated phthallocyanines,[40] they may also be organometallic, their molecules including metal atoms in the central aromatic core. In the columnar state, discotic molecules are described as piling up over one another with their aromatic moieties in register, so as to form indefinitely long columns

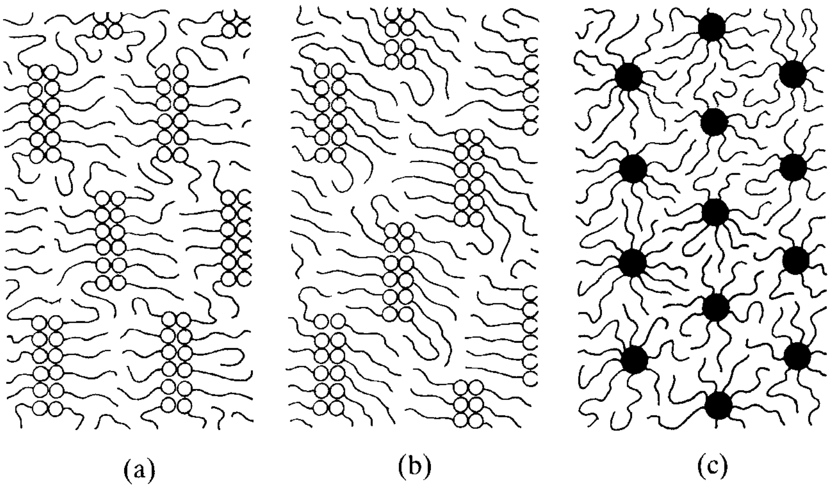


FIGURE 6 Schematic representation of the columnar mesophases of pure soaps: a and b, the ribbons of the polar heads are packed according to a centered-rectangular and an oblique two-dimensional crystal lattice, respectively; c, the "cylindrical rods" formed by the polar heads of the molecules are packed according to a hexagonal two-dimensional crystal lattice.

embedded in a liquid-like aliphatic continuous matrix. Discs may orient themselves either perpendicularly or at an angle with respect to the columnar axis, and be stacked atop one another either regularly or in a liquid-like manner.

Whatever the stacking of molecules inside the columns and whatever the way columns are laterally packed in space, the main feature

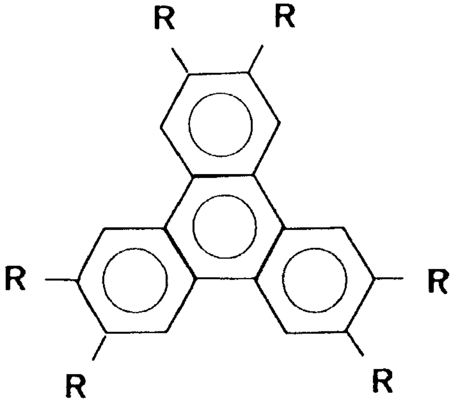


FIGURE 7 Hexa-alkanoate [R = CH_3—$(CH_2)_{n-2}$COO—] of triphenylene: an example of discotic molecule.[39]

of the columnar ordering lies in that the aromatic cores of the molecules are in register with one another and that the disordered peripheral aliphatic chains are rejected out of the aromatic microdomains, inside the continuous matrix between the cores of the columns. As for the smectic mesophases, an interface can be defined to separate the aromatic from the aliphatic microdomains, and a molecular area can be calculated for the aliphatic peripheral chains attached to the interface. Of the order of 25 Å^2 for the phthalocyanine columnar phases,[41] the molecular areas found are in good agreement with the known bulkiness of the aliphatic chains.[42] The analogy between columnar mesophases obtained with discotic mesogens and smectic mesophases obtained with calamitic molecules is corroborated by the occurrence in both cases of a nematic mesophase upon heating (or cooling). The transition to a nematic from a smectic or a columnar mesophase is related to the loss of register between the aromatic cores of the molecules,[3] presumably due to the thermally induced miscibility of the two otherwise incompatible parts of the molecules. While the lateral register of the aromatic cores is one-dimensional for the smectic phases, it is two-dimensional for the columnar ones.

Finally, it is worth mentioning the special case of columnar mesophases obtained with phasmids[43] which, in fact, are calamitic molecules with three aliphatic chains attached to each end of the central rod-like aromatic core. The columnar structure of phasmids may be described as the stacking of disk-like groups of molecules associated three by three with their aromatic cores packed parallel to one another and their aliphatic chains spreading outwards from the columnar axis in a fan-shaped disordered conformation (Figure 8).[44] This arrangement is similar to the ribbon-like arrangement of pure alkali metal soaps in the columnar state, described above. Here again, the microphase segregation due to the amphiphilic character of the molecules is perfectly visible. Basically rod-like in shape, phasmidic molecules have a tendency to pack parallel to one another in layers, but these immediately break up into short disk-like clusters owing to the important bulkiness of the aliphatic chains.

CONCLUSION

From the structural models reported above, it is clear that the positional ordering observed in both smectic and columnar mesophases is closely related to the amphiphilic character of molecules. These are, indeed, formed of two distinct parts which are insoluble in one

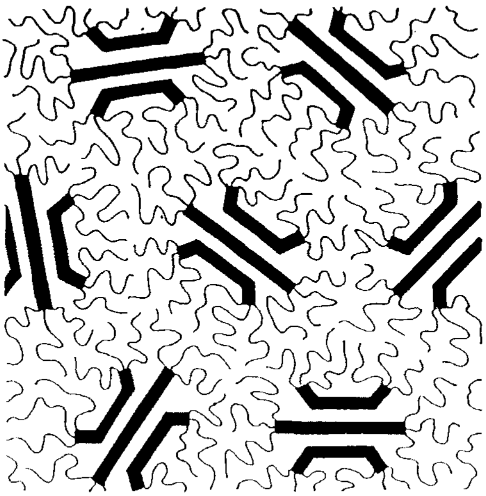


FIGURE 8 Schematic representation of the columnar structure obtained with phasmidic molecules: thick lines represent the aromatic cores of the molecules, and wavy thin lines the aliphatic chains.

another; as a consequence, they have a strong tendency to segregate in space. Segregation is achieved simply through positioning of the covalent junctions of the constituent moieties of the molecules on rather well defined surfaces and through bringing together the like moieties on the same side of these surfaces. Such a description is equivalent to saying that the like parts of the molecules are in lateral register. It is important to point out that, owing to thermal agitation, the interfaces are not infinitely sharp; instead, they have a nonvanishing thickness dependent on the intensity of the amphiphilic character. The diffuseness of the interfaces is generally small in comparison with the molecular dimensions and may thus be neglected for most purposes. In some instances however, especially when the amphiphilic character is weak, the interfacial thickness may increase with temperature, leading to the fading out of the interfaces and, eventually, to the formation of nematic phases.

Interfaces are typically planar for the smectic and cylindrically curved for the columnar mesophases. For the discotic molecules, the curvature is imposed on the system in a natural way due to the circular shape of the rigid central core of the flat molecules. For the other mesogenic molecules, curvature depends on the bulkiness and the specific interactions of the molecular moieties on each side of the interfaces. With block copolymers for instance, interfaces between microdomains are planar when the lateral space around the layer normal needed for the blocks to adopt their random conformation is of comparable importance; otherwise, interfaces are curved, the bulkier blocks sitting on the convex side of the interfaces.[21] With soaps, on the other hand, the bulkiness and the repulsive interactions of the polar heads as compared to the bulkiness of the aliphatic chains of the molecules constitute a factor which determines the shape of the interfaces (planar or curved) and the nature of the moieties that are located on the convex side of the interfaces when these are curved (see R-theory,[7] for example).

The calamitic molecules deserve the following specific comments. Because of the rigidity of their rod-like aromatic core, the bending of the interfaces observed is, generally, highly hindered, for it involves large splay elastic energies. As a result, when the bulkiness of the aliphatic moieties of the molecules becomes important, the interfaces, and hence the smectic layers themselves, are broken down into ribbons,[8] giving rise to what is described[45] as modulated smectic phases. A particularly clear illustration of this phenomenon is provided by the occurrence of columnar mesophases with phasmids.[44]

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