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Liquid Crystals

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Structural features of the hexagonal phase of phasmidic liquid crystals

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Eighteen compounds having the same molecular architecture, a rod-like aromatic core with four to six long aliphatic terminal groups, which all possess a hexagonal mesophase, have been studied by X-ray diffraction. From the lattice constants of these mesophases, we have deduced some information about the molecular organization. We discuss the curvature and the density of the interface between the aromatic and the paraffinic moieties, the orientational disorder and the packing of the rod-like central parts of the molecules. The occurrence of smectic, oblique or cubic mesophases in the same series underlines the similarities with lyotropic polymorphism and justifies a description of the molecular organization in terms of interfaces.

1. Introduction

Usually, the global shape of a mesogenic molecule is the predominant factor which determines the symmetry of the thermotropic mesophases. Thus, rod-like molecules form lamellar mesophases [1] and disc-like molecules columnar mesophases [2]; in addition the thickness of the lamellae and the section area of a column are nearly equal to the length of the rod or to the area of the disc, respectively. Liquid-crystalline phases in which arrays of parallel ribbons or columns of infinite length form a two-dimensional periodic network have been demonstrated in both cases [3, 4], but the section of a ribbon in the S_A or S_C phase contains at least ten rod-like molecules while the section of a column in a discotic mesophase consists of a unique molecule.

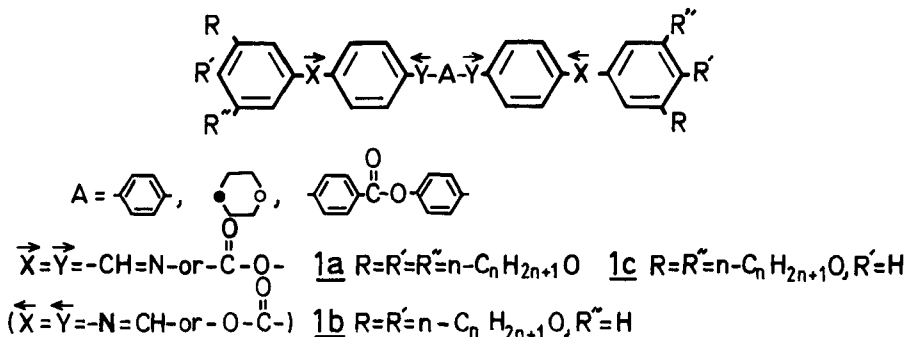
The recent discovery of a new class of mesogens, the *phasmids* [5], has filled the gap between rod-like and disc-like compounds. In the same series and sometimes for the same compound, both lamellar and columnar phases are found [6]. Nevertheless, the hexagonal columnar phase is seen in many of these compounds, and it is thus interesting to undertake a comparative study of the structural features of this mesophase for a great variety of compounds, in order to have a better understanding of the molecular organization.

We give a brief review of the chemical architecture and of the polymorphism of these compounds, and then discuss the hexagonal phase characteristics and give a comparison with mesophases of the same symmetry in disc-like mesogens. In the final section, we shall discuss the limits of the hexagonal domain.

2. Relationship between the chemical structure and phasmidic polymorphism

Strictly speaking, the term *phasmid* applies to mesogenic molecules with a rod-like aromatic core substituted at each end by three aliphatic chains because of their similarity of shape with a phasm [5]. In fact, if we vary the number of aliphatic chains between four and six on the same kind of core, we obtain similar mesophases, and here, we shall describe all these compounds with the same name.

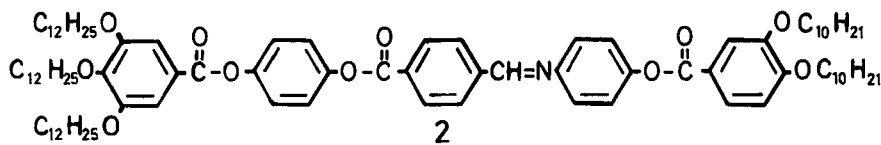
The rod-like central semi-rigid part of these molecules can be described by the general formula:



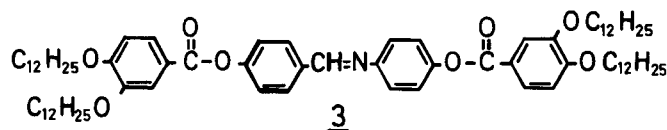
n-Alkoxy chains are linked on each terminal phenyl group in the 3,4,5,3',4',5'-positions in order to obtain symmetrical six (**1a**) or four-chain (**1b**, **1c**) compounds. Six-chain compounds possess in general a hexagonal phase and sometimes a rectangular or oblique phase (heptyloxy to tetradecyloxy substituted compounds have been studied). If the chain length of a four-chain compound is shorter than 10–11 carbon atoms, we obtain generally only lamellar (S_C) and nematic phases. The four-chain compound **1b**

($R = n-\text{C}_{11}\text{H}_{23}\text{O}-$, $A = \text{benzene}$, $\vec{X} = -\text{C}(=\text{O})-\text{O}-$, $\vec{Y} = -\text{CH}=\text{N}-$) has a polymorphism going from a low temperature smectic C phase to a high temperature hexagonal phase and with an intermediate oblique phase.

In addition, we have studied the five-chain compound **2**



with a unique hexagonal mesophase. The presence of columnar mesomorphism in three- and four-ring core molecules is still dubious; for example, no mesophases are found in some three- and four-ring core compounds substituted with four *n*-hexyloxy-chains [7], while the homologous *n*-dodecyloxy derivative **3**



exhibits a smectic C phase.

Finally, some phasmids have cubic phases and one compound, **1b** with $R = n-\text{C}_{11}\text{H}_{23}\text{O}-$, $A = \text{piperazine}$, $\vec{X} = \text{CH}=\text{N}-$, $\vec{Y} = -\text{C}(=\text{O})-\text{O}-$, has a hexagonal \rightarrow cubic




transition (the hexagonal phase is monotropic and obtained from the isotropic liquid on cooling). The hexagonal phase has a large lattice spacing [6] and will be considered separately in the following discussion.

3. Structural features of the hexagonal phase

We have detected characteristic textures of the hexagonal phase under the polarizing microscope. The birefringence decreases drastically when we go from a S_C to a hexagonal mesophase. Therefore, the orientational order parameter of the aromatic moiety is globally lower in the hexagonal phase than in the lamellar mesophase. A similar variation is observed at the hexagonal to lamellar transition in lyotropic systems [8].

In our X-ray diffraction experiments we have not obtained aligned samples except for compound **2**. In this case, a metastable phase is obtained by quenching a stretched sample at room temperature. One has a fibre pattern (cf. figure 1 (a)) corresponding to an imperfect two-dimensional crystalline structure with periodic columns. The periodicity along the column axis (parallel to the stretching direction) is 4.9 Å, with a slight modulation of a double periodicity. The mesophase is obtained by heating this sample and remains partially aligned. Nevertheless, the outer diffuse ring (cf. figure 1 (b)) is isotropic, and similar to the ring seen in X-ray patterns of the hexagonal phase of many disc-like compounds [4]. However, in the latter case we can also distinguish anisotropic diffuse spots originated in core-core interferences, whereas for the phasmidic hexagonal mesophase it is impossible to distinguish core-core interferences from interferences originating from the paraffinic medium. In consequence, we can only discuss the organization in terms of the lattice spacing of the two-dimensional network. Table 1 gives the lattice spacing of the hexagonal phases of all the phasmids studied.

Among the eighteen compounds listed in table 1, we have a great variety of chemical structures. Nevertheless, for a large majority, the core length is similar (five rings) and among these compounds, the lattice spacing depends only on the length and on the number of paraffinic chains. In figure 2, we report the lattice spacing versus the chain length (n) for three series which each contains three different homologues; a comparison with the hexagonal mesophase of the hexa-alkoxy truxene derivatives is made [4]. The increment in the lattice spacing per methylene group is similar for three series among the four. The four-chain derivatives **1c** substituted in 3,5,3',5', with

$A =$ , $\vec{X} =$ , $\vec{Y} =$  clearly have a different behaviour

[9] (notice, in table 1, the large difference between the lattice spacing of the 3,5,3',5' and that of the 3,4,3',4' tetra- n -dodecyloxy derivative. This difference, due to the absence of para chains, implies that such molecules cannot enter in the general frame that we shall now discuss. For the other three series, the lattice spacing, for a given chain length, is considerably higher for the phasmidic compounds than for disc-like compounds, and higher for a four-chain than for a six-chain derivative. Assuming that we have one column per unit cell, the diameter of the column is always smaller than the largest size of the molecule. It is clear, if we wish to progress with our comparison, that we have to compare the size of the cell to the molecular weight. Therefore, we define the specific area of a column [4], i.e. the area of the hexagonal lattice divided by the molecular weight. These values are reported on table 1, and also, for fourteen compounds (which enter in our general frame) in figure 3 (a).

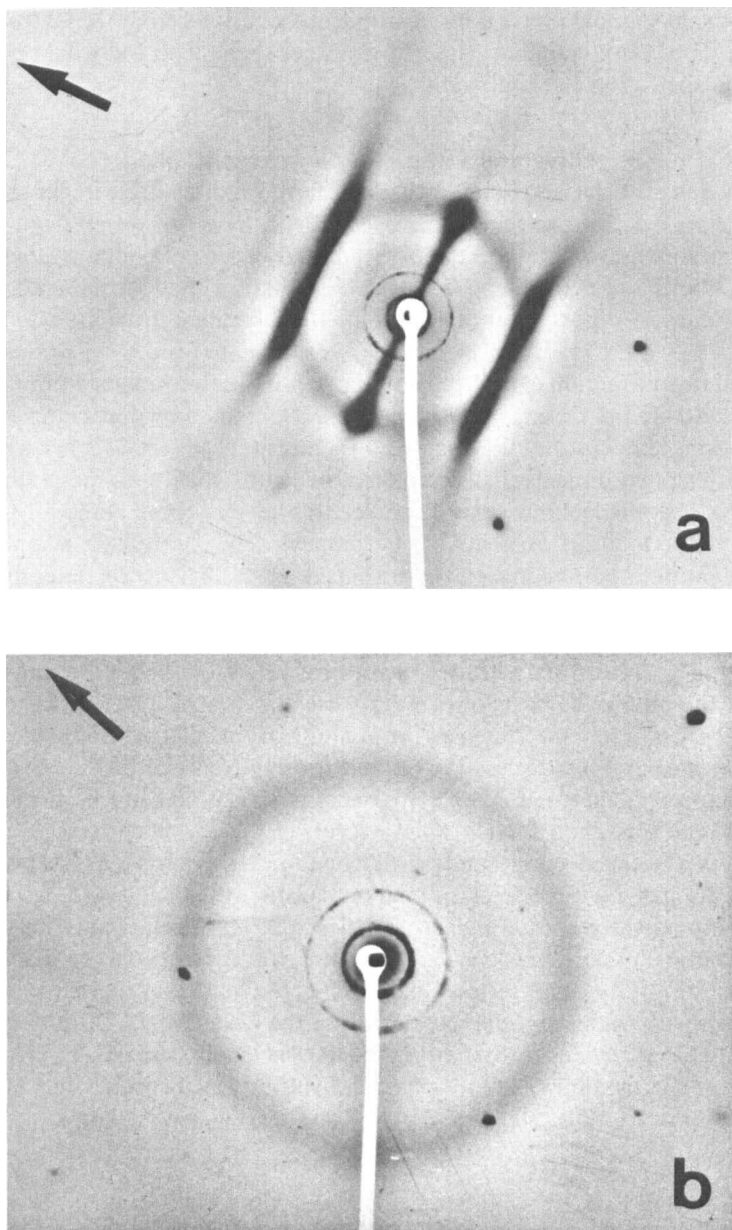



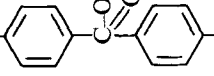










Figure 1. X-ray diffraction patterns of aligned samples of **2** stretched in the direction of the arrows on a mica plate. A few Bragg spots of the mica crystal and two powder rings at small angles coming from impurities are seen on the two patterns which in fact do not correspond to the same scaling factor (the scale is given by the size of the diffraction rings from the impurities) (a) The sample is quenched at room temperature, (b) $T = 120^{\circ}\text{C}$ in the mesophase. A diffraction crescent corresponding to hexagonal ordering is seen inside the two diffraction rings from the impurities. A diffuse ring is seen for a scattering vector of the order of $(2\pi/4.5) \text{ \AA}^{-1}$.

Table 1. Relation between the structural features of the hexagonal mesophase and the chemical architecture of the mesogenic molecules.

Chemical structure			Chains C _n H _{2n+1} O		Hexagonal phase		
\bar{X}	\bar{Y}	A	Positions	n	Temperature/°C	Lattice spacing/Å	Specific area × 10 ⁷ /cm ² g ⁻¹
C-O 	CH=N		3,4,5,3',4',5'	7	81-82	39.4	6.70
				12	81.5-92	45.0	6.53
C-O 	CH=N		3,4,3',4'	11	170-187	46.9	9.52
				9	110-114	43.8	8.26
				10	7-116	46.1	8.75
				12	68-116	49.6	9.31
			3,4,3',4'	12	196-233	54.0	11.05
CH=N 			3,4,3',4'	10	161-169	45.9	9.57
				11	155.5-173	46.4	9.31
				14	144-169	50.3	9.61
CH=N 			3,4,3',4'	11	(158-147)	135	78.7
				14	monotropic 141-164	50.3	9.59
C-O 			3,4,5,3',4',5'	11	83-92.5	43.75	6.32
				12	88-94	43.9	6.05
				13	90-93.5	45.9	6.29
C-O 			3,4,3',4'	13	134-156	49.7	9.51
				14	121-152	50.3	9.45
	2		3,4,5,3',4'	11.2	75-132	46.9	8.15

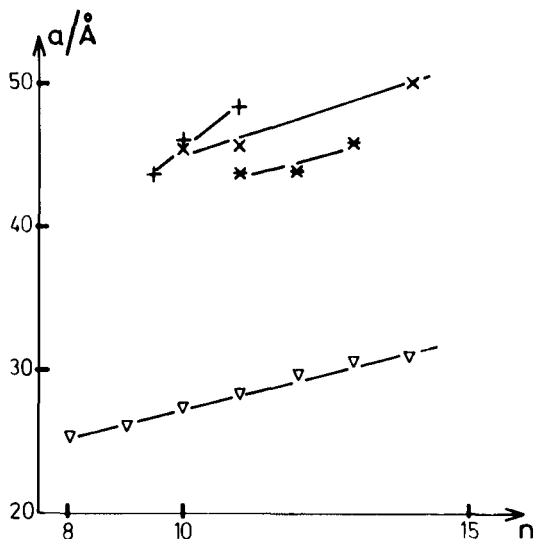


Figure 2. Lattice spacing of the hexagonal phase for four homologous series. Δ , hexaalkoxyl truxene; *, six chains (3,4,5,3',4',5') phasimdic derivatives with $\bar{X} = \text{COO}$, $\bar{Y} = \text{CH}=\text{N}$, $A = \text{C}_6\text{H}_4$; x, four chains 3,4,4',5' derivatives $\bar{X} = \text{CH}=\text{N}$, $\bar{Y} = \text{COO}$, $A = \text{C}_6\text{H}_4$; +, four chains substituted in 3,5,3',5' derivatives $\bar{X} = \text{COO}$, $\bar{Y} = \text{CH}=\text{N}$, $A = \text{C}_6\text{H}_4\text{-COO-C}_6\text{H}_4$.

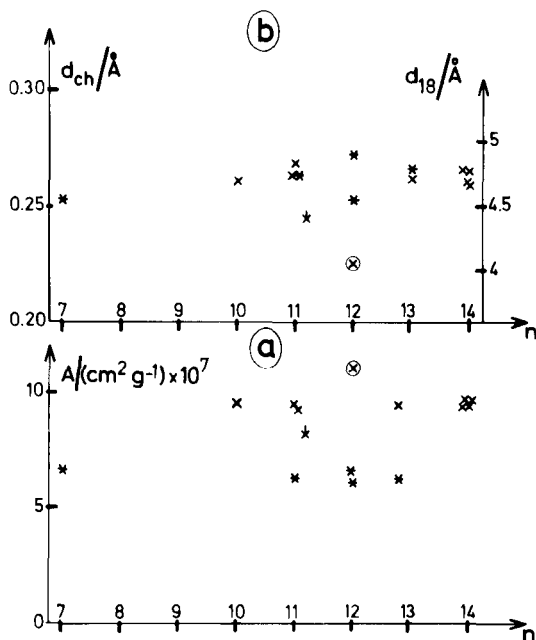


Figure 3. (a) A plot of the specific area versus the chain length. (b) A plot of the mean axial distance between two chains versus the chain length (the right vertical scale is enlarged by a factor of 18) *, six chain derivatives; ★, five chain derivatives; x, four chain derivatives. The circle indicates the unique derivative of a six ring rod-like core.

A physical meaning of this ratio can be derived from the relation which links the specific gravity ρ , the number of molecules included in a slice of a column of unit length, $1/d$, (d is the mean distance between two molecules along the column axis) and the specific area A . Thus

$$\rho = \frac{1}{dA}$$

with

$$A = \frac{1}{2}\sqrt{3} \frac{a_n^2}{M_n},$$

where a_n is the lattice spacing, and M_n is the molecular weight of the derivative of chain length n . The specific area is independent of the chain length. If we assume that all the mesophases studied have the same specific gravity, the linear molecular density is higher for four-chain than for six-chain phasmids. Moreover, the linear molecular density along the column axis of all the compounds of the same core length varies as the inverse of the number of chains n_{ch} grafted on to the core. As a consequence, *all the hexagonal phases of phasmidic molecules corresponding to the same core length form columns with the same axial chain density*. Assuming a specific gravity of 1 g cm^{-3} , (the specific gravity of one six-chains phasmid has been measured [10] and its value is 0.964 g cm^{-3}) the mean distance, $d_{\text{ch}} = (d/n_{\text{ch}})$, between two chains is equal to 0.26 \AA (cf. figure 3(b)). The only exception shown in figure 3 corresponds to the largest core length compound (six phenyl rings) for which $d_{\text{ch}} = 0.225 \text{ \AA}$. It is evident that these low values of the axial interchain distances are not in relation with the true minimum distance between two paraffinic chains which is of the order of 4.5 \AA . In fact, we can consider that we have a crown of about eighteen paraffinic chains located in the same section of a column; such a crown will correspond to three six-chain phasmidic molecules according to the previous suggestion [5, 10] with an equivalent of 3.6 five-chain molecules and 4.5 four-chain molecules. On the right-hand side of figure 3(b), we have shown a distance scale which is enlarged by a factor of eighteen. The mean value $4.7 \mp 0.2 \text{ \AA}$ corresponds to a realistic core-core distance in parallel packing. An exception is made for the longest core since 21 chains or 5.2 molecules correspond to the same core-core interspace.

Since we have established that the molecular organization, measured by the axial chain density, is independent of the chain length, the specific volumes of the aromatic cores and of the paraffinic moiety can be derived from the variation of the lattice constant versus the chain length. The volume of one methylene group is $V_{\text{CH}_2} = (\frac{1}{2}\sqrt{3}d_{\text{ch}})(d/dn)(a_n^2)$.

In fact, we do not have a great range in chain length, especially for four-chain compounds because of their polymorphism; the hexagonal phase is not always stable and we can only give a rough approximation

$$V_{\text{CH}_2} \simeq 21 \text{ \AA}^3 \text{ for the six-chain phasmids,}$$

$$V_{\text{CH}_2} \simeq 24 \text{ \AA}^3 \text{ for the four-chain compounds.}$$

In smectic phases, the specific volume of a methylene is of about $27\text{--}30 \text{ \AA}^3$ and reaches $27\text{--}28 \text{ \AA}^3$ for a disc-like columnar phase [11]. The corresponding specific volumes are $0.92 \text{ cm}^3 \text{ g}^{-1}$ in the hexagonal phase of six-chain phasmids and $1.02 \text{ cm}^3 \text{ g}^{-1}$ in the same phase of four-chain phasmids. Finally, we can deduce the

Table 2. Mean methylene volume, paraffinic and core specific volume; a comparison between the phasmids and the hexa-alkoxy truxene derivatives.

	Six-chain compounds	Four-chain compounds	Disk-like compounds†
$V_{\text{CH}_2}/\text{\AA}^3$	21	24	27.4
Specific volume chains/ $\text{cm}^3 \text{g}^{-1}$	0.92	1.02	1.18†
Specific volume core/ $\text{cm}^3 \text{g}^{-1}$	1.30	0.98	1.49

†The core-core axial distance for the hexagonal mesophase of the hexa-alkoxytruxene derivative is about 3.6 Å as measured from X-ray diffraction pattern.

core specific volume; we find $1.20 \text{ cm}^3 \text{g}^{-1}$ for a six-chain phasmid and $0.98 \text{ cm}^3 \text{g}^{-1}$ for a four-chain phasmid (cf. table 2). In fact, it is not obvious that the density modulations are so different when varying the number of substituted chains; the X-ray diffraction rings of the hexagonal lattice are nearly of the same intensity (compared to the large angle diffuse ring). This fact underlines the inaccuracy of our evaluation taking into account only two levels of density. Moreover, the chain specific volume appears to be underestimated for the six-chain phasmids. In fact, changes in core packing can occur as the chain length increases.

Until now, we have only considered the dependence of the lattice spacing upon the molecular structure, with a unique assumption of a constant specific gravity. If we want to know which kind of forces drive the phasmidic polymorphism, we must also discuss some geometrical parameters such as the disorientation between neighbouring cores, and the shape of the aromatic-paraffinic interface. It is important to emphasize a few points before we proceed:

The hexagonal phase is obtained only for molecules in which the paraffinic chains contribution to the molecular weight is at least half.

The hexagonal phase is always the high temperature mesophase and is obtained directly from the isotropic liquid.

The area of a section perpendicular to the long axis of a molecule in the aromatic zone is nearly equal to the section of one extended aliphatic chain.

Taking into account these three points we find that a hexagonal phase in which the paraffinic moieties occupy the external crown of each column will allow a suitable packing for the two antagonist parts of the molecule, but it will imply a high orientational disorder of the cores that could only exist for a high proportion of paraffinic chains and a high temperature. Let us consider first the problem of packing.

Assuming that the cores occupy the zone of each column which on average is axially cylindrical the transverse area for a core is $(\pi l_c^2 n_{\text{ch}} d_{\text{ch}})/4l_c$ where l_c is the core length, equal to the diameter of the axial zone and $n_{\text{ch}} d_{\text{ch}} = d$, the mean distance between two molecules along the column axis. The chain area measured at the interface is $\pi l_c d_{\text{ch}}$. Therefore if we have $n_{\text{ch}} = 4$, the chain area at the interface is equal to the core transverse area and the columnar configuration ensures a good packing of both the aromatic and the paraffinic parts of the molecule. If we vary the length of the core with the same number of substituted chains, the mean distance between two chains must decrease in order to keep the same density and as we have seen for a derivative of a six ring core with four chains grafted on to the 3,4,3',4'-positions,

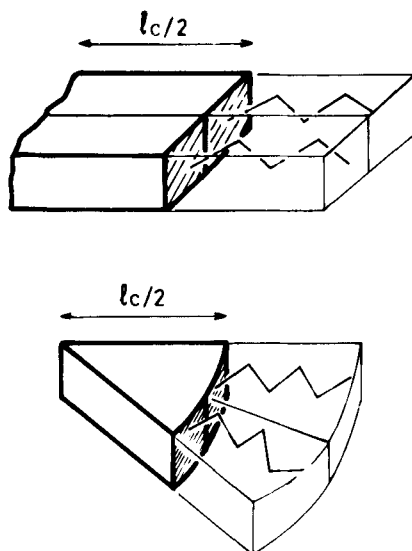


Figure 4. Schematic representation of the molecular packing; in the smectic A phase (upper part), in the hexagonal mesophase (lower part), l_c is the core length, heavy lines indicate the core volume and the light line the paraffinic chain volume.

$d_{ch} = 0.225 \text{ \AA} \simeq \frac{5}{6}(0.26) \text{ \AA}$. However, we can reduce the size of the core zone if n_{ch} decreases and if the curvature of the interface increases. In fact, for cores with chains on 3,5,3',5', the absence of para alkoxy chains favours an interface of high curvature but implies distorted cores. The existence of a highly curved interface is shown by the values of n_{ch} found for the unique series of this kind which we have studied: $0.26 \text{ \AA} < n_{ch} < 0.30 \text{ \AA}$ compared to 0.225 for the same core substituted in 3,4,3',4'. Moreover, only monotropic mesophases are seen for shorter cores substituted in 3,5,3',5' [9] probably because the high distortion imposed to the core is not very stable. The case of four-chain compounds appears to correspond to a good molecular packing in the hexagonal mesophase. Let us now see what would be the situation if the number of chains decreases: from one to three chains until now only nematic and smectic phases are seen [12]. An interesting case is the limit $n_{ch} = \frac{1}{2}$ which corresponds to a partially bilayer smectic A phase of polar molecules [3]. Undulations of layers appear as precursors of interfaces negatively curved in the opposite direction (i.e. with the chain in the inner side). In contrast increasing the number of chains above four will decrease the core packing for the same chain packing (see table 2). If we assume a circular shape for the columns, the core transverse area will exceed the chain area, respectively 36 \AA^2 and 23.6 \AA^2 , for a six-chain plasmid. However, a decrease of the symmetry of the central part will diminish the ratio of the internal volume to the interface area (at constant diameter). With a triangular section of the central part, there are equal areas for the transverse sections of cores and chains ($\approx 30 \text{ \AA}^2$). Moreover, for the shortest chains, the paraffinic and aromatic masses become nearly equal and the hexagonal phase can be built with triangular prisms alternatively filled with paraffinic and aromatic medium as proposed previously [5]. Nevertheless, we must emphasize that the interface has no rigid form since the statistical disorder of the cores is important. The shapes which we have discussed are only *mean shapes*.

Let us now try to estimate the orientational disorder of the rod-like cores in such hexagonal mesophases. X-ray diffraction patterns do not provide any evidence of the existence of a long period modulation parallel to the column axis, twist or splay periodic deformation as suggested by de Gennes [13]. Therefore, the uniaxial symmetry of the column exists even on a short scale. Two models are nearly equivalent: in the first, we consider a stack of equivalent slices of thickness 4.7 \AA , each slice having uniaxial symmetry. In the second model each slice is made of parallel cores and the uniaxial symmetry is established within three slices of thickness 4.7 \AA [10]. In addition, we assume that the rod-like cores are rigid and packed with a six-fold coordinance. With these assumptions the mean disorientation between two adjacent cores is proportional to the inverse of the axial core density. This angle varies from 26° if there are 5.2 molecules in a slice of 4.7 \AA thickness to 40° for only three molecules in the same slice. In fact, for a disorientation of 40° , it is unrealistic to assume that the cores are rod-like and rigid. Therefore, it appears that the flexibility of the cores can favour the formation of hexagonal phases and the higher the flexibility the lower can the axial core density be. In contrast, rigid cores favour smectic mesomorphism in which the neighbouring cores are parallel to each other. In some cases, phases of intermediate curvature are found between the hexagonal and the smectic phases: we shall now discuss this point briefly.

4. Mesophases of intermediate curvature

In a series of four chains compounds, smectic C and nematic phases are seen for short chain length. When the chain length increases, the curvature becomes more pronounced, and the layer structure can be broken into ribbons; an oblique phase is obtained, in which the width of a ribbon is of the order of 30 \AA [6] (i.e. about six chains). Similar rectangular or oblique phases can also be found for six-chain derivatives [5].

Other phases of intermediate curvature, such as cubic phases [6], are seen. At this time knowledge of the structure of these phases remains sparse but interesting information can be obtained for the hexagonal monotropic mesophase with a large lattice constant [6]. In this case, the lattice spacing of 135 \AA is about twice the largest size of the molecules. Therefore, we have to assume that each column contains at least two shells of paraffinic or aromatic regions with an intermediate zone of the other kind.

If we assume (cf. figure 5(a)) that the molecules are aligned along the radii of a circular column, we obtain a very dense paraffinic central part and an external paraffinic zone of very low density. Such an organization seems unlikely. In contrast, a structure in which the axial zone of the column is similar to that of the other phasidic columnar phases, would imply a reasonable packing of the two regions. A second shell of lower curvature surrounds the axial zone. Assuming a uniform density, we estimate that about 37 molecules lie in a slice of 4.7 \AA of a column with only 4.5 molecules in the axial zone. The mean angle between two adjacent molecules is about 6.5° ; the general curvature is thus very low. This hexagonal phase can also be considered as a layer structure with a regular array of disclination lines $+1$ on six-fold axes and $-\frac{1}{2}$ on three-fold axes. Such a structure is also compatible with the fact that the most intense diffraction rings correspond to a lattice spacing of about 40 \AA .

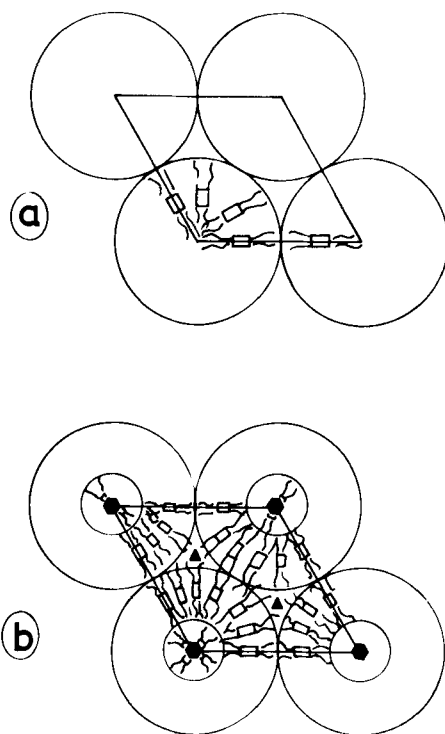


Figure 5. Two possible models for the complex hexagonal phase. (a) Radial distribution of molecules in each column. (b) Layered column structure with a regular array of disclination lines $+1$ on the six-fold axis and $-\frac{1}{2}$ on the three-fold axis.

5. Conclusion

The hexagonal mesophase of phasmidic molecules is very similar to the hexagonal phases of lyotropic systems [14]. The mean area per paraffinic chain is larger than the corresponding area in a lamellar structure. The interface between the aromatic cores and the paraffinic moiety is curved since the total area for the paraffin is at least equal to twice the transverse core area. Nevertheless, the nature of the linkage between the aromatic and paraffinic moieties, the length and the rigidity of the core induce specific limitations to the existence of a hexagonal mesophase. It seems that the ideal architecture is a five-ring rod-like core with two or three paraffinic chains at each end, but the absence of long chains in the para positions can diminish the mesogenic tendency. Moreover, as in lyotropic polymorphism [14], two dimensional oblique or rectangular lattices or three dimensional cubic phases are inserted between the lamellar and the hexagonal phases. At last, we have demonstrated a metastable precursor of the cubic phase. The organization in this phase which has a two dimensional lattice with a large period can be described as a closed-packed array of parallel disclination lines in a lamellar phase.

Further investigations on binary mixtures and studies of the order parameter on a local scale would bring a better insight into the microstructure of the phasmidic mesophases. These new classes of mesogens offer the opportunity of a better understanding of the mechanisms which transform lamellar to hexagonal phases.

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