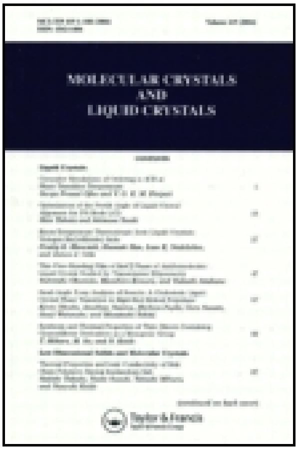

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Columnar Mesomorphic Order in Thermotropic Liquid Crystals

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COLUMNAR MESOMORPHIC ORDER IN THERMOTROPIC LIQUID CRYSTALS

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The first examples of thermotropic mesomorphism with discotic molecules were observed by S. Chandrasekhar in the hexa-alkanoyloxy benzenes. Since then, the columnar mesomorphic order has been deeply investigated thanks to the synthesis of many types of disk-shaped molecules. In such mesophases, the molecules are packed one upon another to form columns. These latter then organize according to a two-dimensional lattice. These last years, appeared a variety of compounds with quite different molecular architectures, exhibiting also columnar mesophases. Some significant results of the most recent systems are presented. They concern pseudo-polymeric chains of metal soaps and polycatenar molecules. These typical examples of new columnar structures are described with emphasis given on the relationships between the columnar structure and the molecular architecture, along with the specific interactions responsible for the establishment of this type of supramolecular organization.

Keywords: columnar; polycatenar; mesomorphic structure; metallomesogens

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INTRODUCTION

Columnar mesophases generally present a pronounced order, since they result from the self-assembly of columns of indefinite length on a two-dimensional lattice [1]. The symmetry of the latter is found to be hexagonal, rectangular or oblique (Fig. 1) [2]. The formation of the columns can result from different molecular or macromolecular species and/or from different types of interactions. In all cases however, one column has, in general, a central, usually rigid core surrounded by a flexible part directly attached to it (for example aliphatic chains) or free to move around it (organic solvent). This ensures the movement of columns with respect to one another, and thus the liquid-crystal nature of the two-dimensional phases encountered. One typical example is the case of thermotropic columnar mesophases obtained from pure metal soaps [3]. The molecules of these materials associate into indefinite columns through their polar heads which are assembled laterally according to different two-dimensional lattices. In these structures, the aliphatic chains are quite disorganized being in a quasi liquid

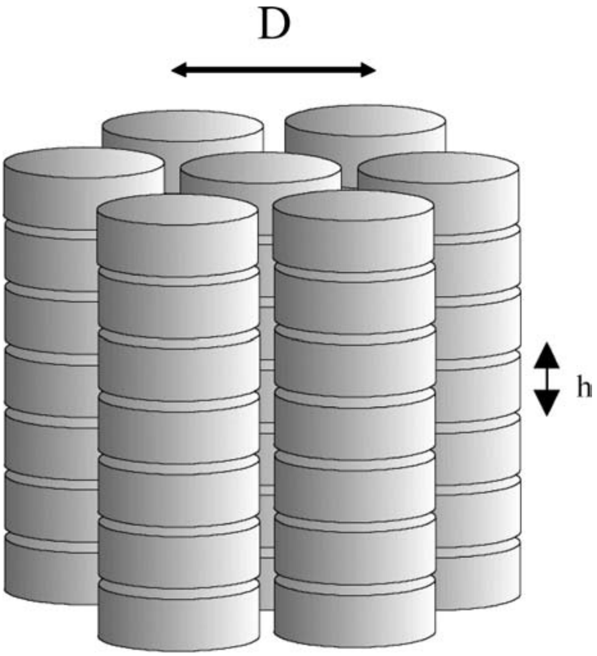


FIGURE 1 Schematic of a two-dimensional hexagonal arrangement of columns where *D* is the intercolumnar distance and *h* the stacking period along the columnar axis.

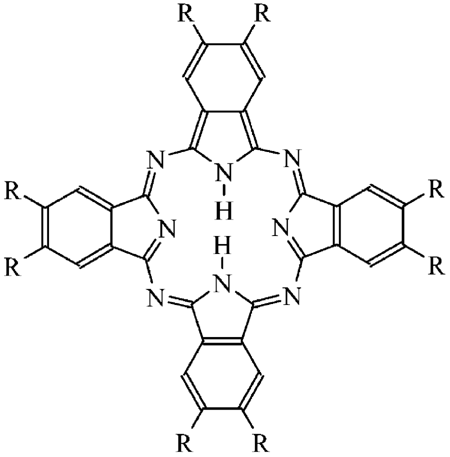


FIGURE 2 Chemical structure of substituted phthalocyanine molecules.

state, and fill uniformly the space available between the polar heads forming the core of the columns. Another typical example is the case of polypeptides [4]. Here, the columns are constituted by individual molecules. Taking into account their helical conformation stabilized by intramolecular hydrogen bonding, the polypeptide molecules have indeed the shape of long rods with a diameter of 20 Å and a relatively strong rigidity corresponding to a persistence length of about 300 Å. In the presence of an appropriate solvent, and in concentrated solutions, these columns keep away from each other and organize themselves into a lyotropic columnar mesophase with hexagonal symmetry. The same type of lyotropic mesophase is encountered in concentrated solutions of nucleid acids (such as DNA) which have a double helix conformation within a rigid, rod-like shape [5].

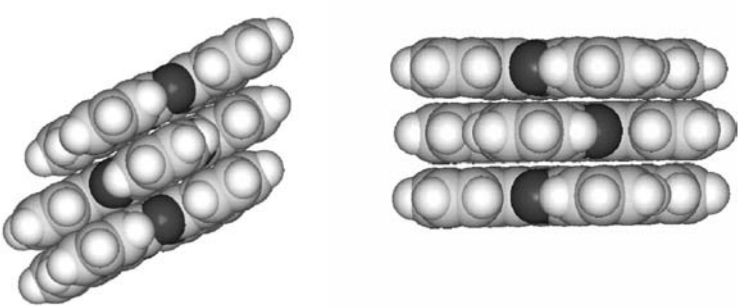


FIGURE 3 Tilted and upright stacking arrangement of the phthalocyanine cores with respect to the columnar axis in the mesophase. (See Color Plate XIII).

In this paper, we will describe how columnar mesophases can be obtained from various systems and how they can be analysed from a structural point of view. These systems are not limited to the well known disk-shaped molecules [6] and similar to the first ones reported in liquid crystals by S. Chandrasekhar *et al.* [7] and Billard et al. [8]. Depending upon the molecular structure and the intermolecular interactions involved, they can be side-chain polymers without a mesogenic moiety, dendrimers, pseudo-polymeric chains of metal soaps, polycatenar molecules, or other systems driven by specific interactions such as hydrogen bonding or dipolar interactions.

STRUCTURAL PARAMETERS OF THE COLUMNAR MESOPHASES

From a geometrical point of view, the columnar structure is characterized mainly by two parameters: the cross-sectional area of the column, S, and the periodicity along the columnar axis, h (see Fig. 1).

As a rule, the two-dimensional ordering of the columns is present over large distances and hence, is easily to be determined experimentally by small-angle X-ray diffraction. On the other hand, the internal structure of the columns can be more difficult to handle, and this is especially true for tilted, intracolumnar arrangements, and for non-oriented samples because of the high viscosity of columnar mesophases in general. The periodicity, h, can be deduced from the value of the specific volume, V, which can be measured by dilatometry [9], and from the cross-sectional area of the columns, S, as determined by small-angle X-ray diffraction through the relationship : $Sh = VM/N_A$ in which M is the molecular weight of the repeat unit and N_A is Avogadro's number [10].

DISCOTIC MOLECULES

Among the large variety of flat, discotic molecules which have been synthesized these last years, substituted phthalocyanine molecules represent one large class of materials designed for obtaining self-assembled, supramolecular wires [11]. Substituted with eight rather long peripheral chains, phthalocyanines are well known to form mesophases with columnar organisation [12]. Upon heating, the alkyl chains become disordered at the transition from the crystal to the liquid-crystalline state, and the system adopts a structure corresponding to the stacking of the aromatic cores in columns which in most cases are assembled into a two-dimensional, hexagonal lattice. The interest in phthalocyanine molecules lies in several characteristic features. Firstly, their flat aromatic core is quite large and offers the possibility for extended π-electron delocalisation; secondly, strong van der Waals' interactions between the flat cores enhance the thermal stability of the mesophases; finally, there is the possibility to include a variety of metal atoms in the central cavity of the molecules, in an attempt to produce one-dimensional metallic systems with potentially interesting conducting properties.

The nature and the length of the peripheral aliphatic chains play an important role in the intra- as well as in the inter-columnar ordering of these phthalocyanine derivatives. The stacking period of the molecules along the columnar axis was calculated from the variation of S as a function of the length of the terminal chains. It was found to be equal to 3.5 Å for the alkoxy and 4.9 Å for the alkyl and methylenoxyalkyl derivatives. This is interpreted in terms of two stacking modes: in the alkoxy series the molecules are oriented perpendicular to the columnar axis, while in the alkyl and methylenoxyalkyl series the molecules are tilted at an angle of 46° to the columnar direction. In both cases, the aromatic cores were found to be in close contact with each other. The distinction between the two arrangements is in agreement with observations of aromatic compounds showing that oxygen atoms attached directly to a planar aromatic system exert significant effect in promoting a tilted rather than a perpendicular arrangement through weak hydrogen bonding [13]; steric effects may also be important here. Indeed, the presence of an oxygen atom attached directly to the core acts as a joint allowing the peripheral chains to point in different directions in space, in order to adapt their conformations to accommodate neighbouring chains. In contrast, when the chains are attached directly to the core, they are much more constrained and the cores have to tilt in order for the chains to find enough spatial freedom.

Regarding the lateral arrangement of the columns, which is described by a two-dimensional lattice, three packing modes were found related to the shape of the columnar cores and their azimuthal orientation about their unique axis. With alkoxy peripheral chains, the projection of the aromatic cores onto the column is quite circular and therefore in agreement with a pure, two-dimensional hexagonal lattice (case B in Fig. 4). However, with methylenoxyalkyl and alkyl peripheral chains, the aromatic columnar cores give an elliptical projection (due to the tilt with respect to the columnar axis) and their orientation with respect to the hexagonal lattice becomes a matter of great importance. Thus, for short side chains, the cross-sectional anisotropy of the columns is relatively pronounced, their azimuthal orientational ordering is well developed, and their packing results in a herringbone configuration (case A in Fig. 4). For long side chains, the cross-sectional anisotropy of the columns is reduced strongly and their hexagonal packing is achieved with complete rotational disorder about the columnar axis. Finally, for intermediate chain lengths, the columnar packing develops a herringbone configuration at low temperatures and a rotationally disordered configuration at high temperatures.

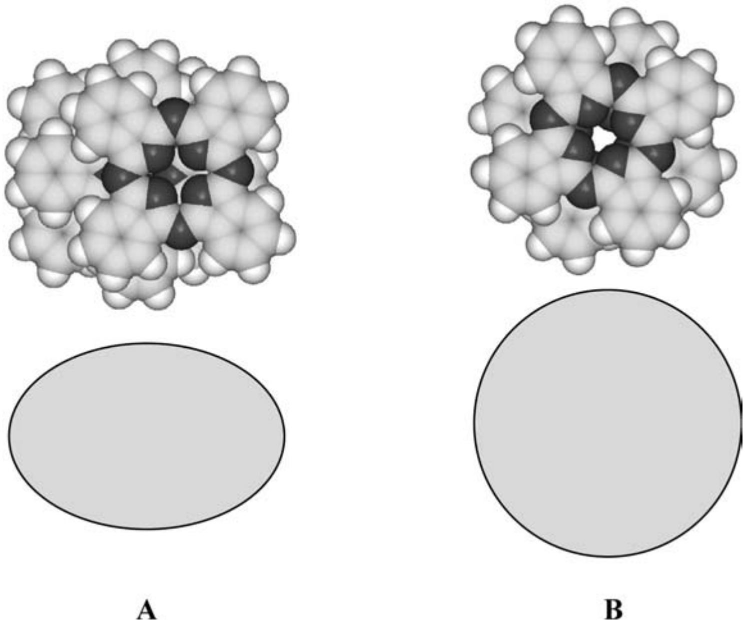


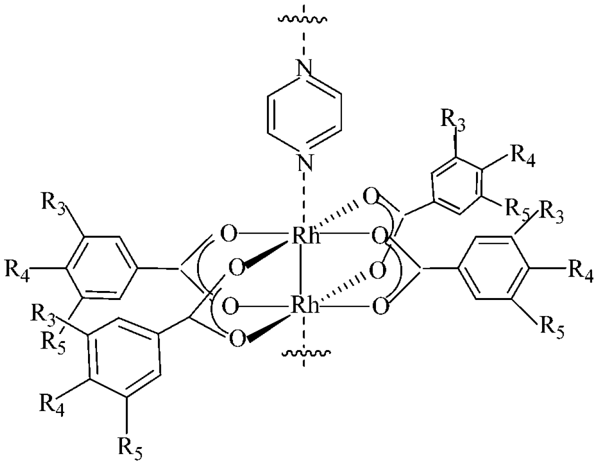
FIGURE 4 Cross-sections of the internal columnar cores corresponding to tilted and upright arrangement of the phthalocyanine cores with respect to the columnar axis in the mesophase. (See Color Plate XIV).

POLYMERIC CHAINS OF METALLOMESOGENS

Liquid-crystalline coordination polymers form a class of materials expected to present both the properties of coordination polymers (complexes in which the metallic centres are bridged by appropriate ligands giving extended structures), and metallomesogens (metal-containing liquid crystals) [14]. The interest in such compounds arises mainly from the possibility of combining the properties of one- or two-dimensionally organized metal centers – polymeric systems in which the monomers communicate electronically to give rise to new collective properties – with the fluidity and anisotropy of liquid-crystalline phases and the processability of polymers.

Columnar mesophases have already been reported for "pseudo-polymeric systems" in which the metal atoms are bound by weak intermolecular coordination between "discrete" molecular units, as in some vanadyl β-diketonates [15] or some bimetallic carboxylates [16]. In the last case, the supramolecular structure found in the crystalline phase for the unsolvated copper [17] and rhodium [18] alkanoates – where the axial positions are occupied by oxygen atoms of neighbouring molecules – remains in the LC phase, giving rise to a 2-D hexagonal arrangement of columns. These electron-rich, bimetallic carboxylates with a "lantern structure" are powerful building blocks for 1-D coordination polymers, since long-chain divalent copper, rhodium, ruthenium, molybdenum and chromium carboxylates (without axial ligands) present thermotropic columnar mesophases [16].

A suitable ligand often used to "connect" metallic centers is pyrazine (pz) and, indeed, many efforts have been directed towards the synthesis of such $[M_2(O_2CR)_4pz]_\infty$ 1-D polymers. Unfortunately, none of the compounds obtained, namely $[Cu_2(O_2C_nH_{2n-1})_4pz]$ (n = 10, 16) [19], $[Ru_2(O_2C_{12}H_{23})_4pz]$ [20] and $[Rh_2(O_2C\text{-}C_6H_4\text{-}OC_8H_{17})_4pz]$ [21] showed any mesomorphic behaviour. The absence of mesomorphism in these compounds was explained on the basis of space filling requirements. Thus, the intercalation of pyrazine between the binuclear units creates a void which needs to be filled to obtain a stable, condensed phase. When the benzoates bear only one chain, the interdimeric space is likely to be filled by the aliphatic chains belonging to a different polymeric chain, giving rise to a crossed-supramolecular structure which prevents the formation of a columnar mesophase (which needs a parallel arrangement of columns). However, liquid-crystalline behaviour was induced in the case of mixed-valence diruthenium(II,III) benzoates complexed with bulky equatorial ligands bearing two or three aliphatic chains; with such ligands, it was possible to fill the interdimeric space correctly and thus to induce a thermotropic columnar mesophase [22]. Using the same strategy, pyrazine-polymerized divalent rhodium benzoates have been obtained recently [23] (see Scheme 1 below).



Contrary to all previously reported pyrazine-bridged, bimetallic carboxylates, the benzoate homologues with $R_1 = R_2 = R_3 = OC_nH_{2n+1}$ (n = 10, 14 and 18) exhibit a thermotropic mesophase. The transition from the crystalline to the LC phase is detected by polarized optical microscopy (see the texture on Fig. 5 that show defects similar to broken fans), DSC and X-ray diffraction. This mesophase has been identified as a columnar hexagonal phase with long range, intracolumnar order: the broad peak detected in most of the diffraction patterns at 8.7–8.9 Å correspond to the intracolumnar periodicity. The use of the Scherrer expression, which correlates the position of the Bragg peak and its width at half height with the domain size, allowed a rough estimation of the correlation length, which has been evaluated to be 75 Å, a distance corresponding to 8–9 repeat units.

The measured stacking distance of 8.9–9 Å is slightly shorter than that expected for the repeat unit of the polymeric chain (Rh_2-pz) in a completely extended conformation, which has been evaluated as 9.6–9.7 Å by the addition of crystallographic interatomic distances. This probably points to a slightly bent conformation in the Rh-Rh-N and Rh-N-N angles (smaller than 180°), as already found in some Ru_2-phenazine compounds [24].

Thus, the application of a strategy designed to fill the intermolecular space in "ionic" polymeric diruthenium carboxylates in an intracolumnar fashion was successful also in the present case ("neutral" coordination polymers). Indeed, the use of bulky, equatorial carboxylates allowed the preservation of the mesomorphic character of pyrrazine-polymerized dirhodium carboxylates. These results show that it is possible to obtain polymeric columnar metallomesogens in which the electron-rich metal

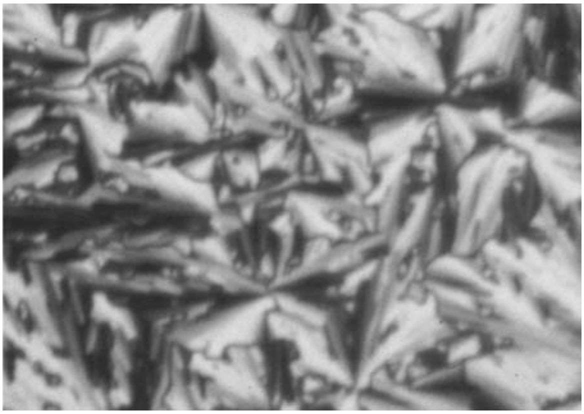


FIGURE 5 Optical texture characteristic of the pyrazine-bridged dirhodium carboxylates in the hexagonal mesophase.

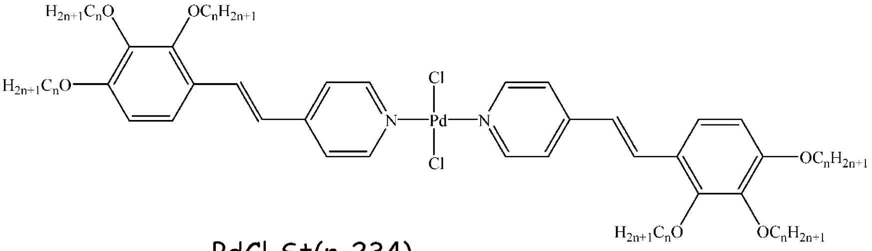
centres are connected by communicating ligands, giving rise to structures which may act as molecular wires. In order to make improvements in this direction, different aspects have to be optimized, namely the possibility of obtaining long-range polymeric structures along the columnar axis and macroscopically oriented samples, the increase in the interdimeric interactions, and the use of metals having a more suitable electronic structure.

POLYCATENAR MOLECULES

If it is straightforward to understand why columnar mesophases are easily obtained with disk-like molecules (the columns are formed by the stacking of the flat cores of the molecules, the molten aliphatic chains filling the space between the columnar cores), it may appear rather surprising, at first sight, to observe columnar mesophases with polycatenar molecules. These mesogens are composed of long, rigid aromatic cores (containing four to six aromatic rings) with two or three paraffinic chains at each end [25–28]. They are one of the several examples of liquid-crystalline compounds with molecular shapes deviating from the usual rod or disc-like motif. Tetracatenar molecules (two chains at both ends) give rise to a very interesting polymorphism which may include nematic, smectic, cubic and columnar liquid-crystalline phases.

The general description of the molecular packing within the columnar mesophase formed by polycatenar molecules is based on a model proposed previously for a hexacatenar compound [29]. This model considers the transverse section of the columns to be constituted by several rigid cores, disposed side by side, and surrounded by the corresponding disorganized terminal aliphatic chains. The number of molecules in a slice of a column depends upon the number and the length of the terminal chains.

Here let us consider the case of palladium complexes designed in order to reduce the transition temperatures often observed in metallomesogens [30]. This has been achieved through the addition of several aliphatic chains to the main polarizable part:



$PdCl_2St(n\text{-}234)_2$

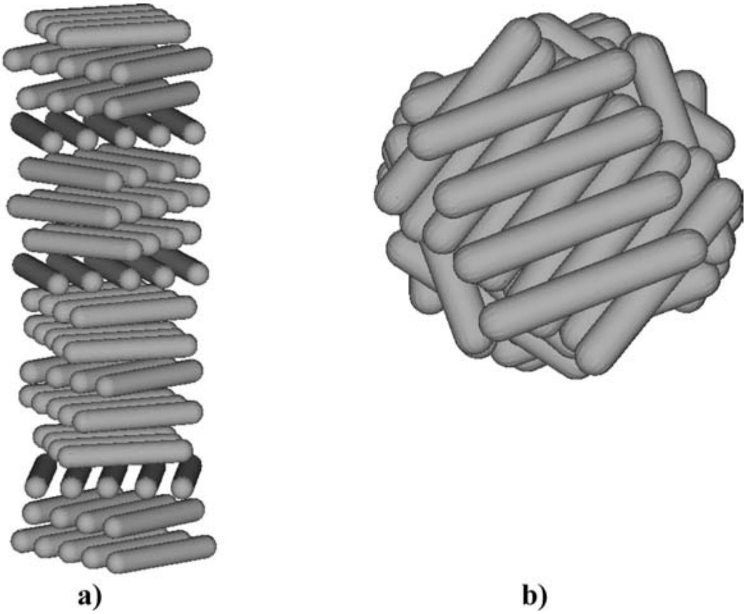


FIGURE 6 Side view (a) and top view (b) of one columnar core formed by the stacking of clusters of polycatenar molecules. (See Color Plate XV).

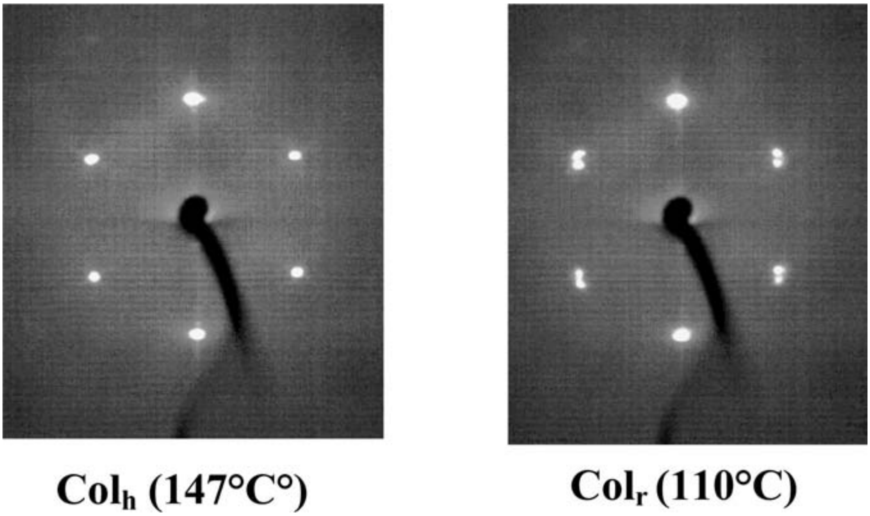


FIGURE 7 X-ray diffraction patterns of $[PdCl_2St(10\text{-}2,3,4)_2]$ registered in the hexagonal and rectangular columnar mesophases. (See Color Plate XVI).

This type of hexacatenar complex exhibits two columnar mesophases for the same homologue. On heating, the crystals melt to give a rectangular mesophase which transforms at higher temperature into a hexagonal columnar mesophase, as in the following example:

$$\mathbf{PdCl_2St(10-234)_2}$$

$$\text{Crys.} \xrightarrow[61^\circ\text{C}]{} \text{Rec.} \xrightarrow[124^\circ\text{C}]{} \text{Hex.} \xrightarrow[149^\circ\text{C}]{} \text{I}$$

The X-ray diffraction patterns are shown in the next figure for both mesophases and confirm the structural nature of the phases encountered as observed by optical microscopy.

In addition to the signals detected at low angles of diffraction, two diffuse halos are present at wide angle, corresponding to periodicities of 4.5 and 9–10 Å. The first one is obviously related to the average distance between aliphatic terminal chains as usual, while the second relates to a periodicity along the columnar axis. The values of the rectangular lattice parameters, a and b, are about 53–55 Å, and 28–29 Å respectively. It is interesting to note the regular variation of the a/b ratio as a function of increasing temperature, changing from about 2 in the rectangular mesophase at low temperature, to $\sqrt{3}$ at the transition into the columnar mesophase. This clearly indicates that the transition between the two columnar mesophases occurs continuously with, in particular no discontinuity in the variation of the columnar section, indicating no lateral expansion or contraction. Moreover the repeat distance along the columnar

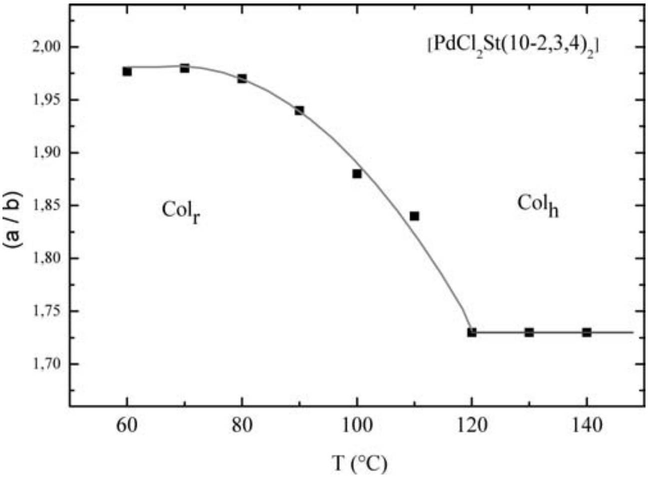


FIGURE 8 Variation of the ratio (a/b) of the lattice parameters of the rectangular mesophase as a function of temperature. (See Color Plate XVII).

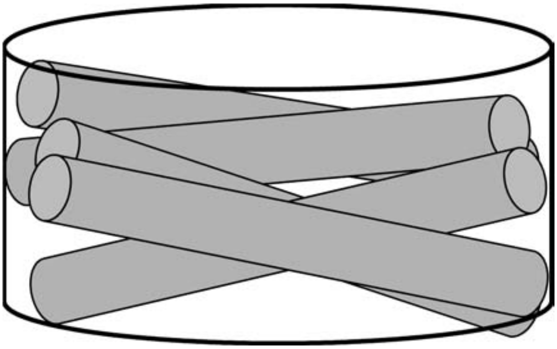


FIGURE 9 Schematics of the possible arrangement of $[PdCl_2St(10\text{-}2,3,4)_2]$ in the columnar mesophases. (See Color Plate XVIII).

axis does not vary significantly, being about 10 Å in both mesophases. This behaviour is a strong indication of more isotropic distribution of the aliphatic chains around the central columnar core and also of an increasing disorder within this columnar core when the temperature increases.

To go further into the description of the molecular organisation of these molecules within the columnar mesophases, let us calculate the number of molecules every 10 Å along the columnar axis. This can be deduced directly from the relationship : $N = (hS)/V_{mol}$ where S is the area occupied by one column in the plane of the two-dimensional lattice, and V_{mol} the molecular volume. It turns out that there are 3 molecules every 10 Å. Moreover, the diameter of the internal core, which can be deduced from S and the volume fraction of the rigid aromatic part of the molecules, is found to be close to 14 Å, much smaller than the molecular length of the same rigid part which is about 25 Å. This clearly suggests a tilt of the molecules with respect to the columnar axis. Such a tilt is in agreement with the presence of a rectangular mesophase, since the columnar core cross-section is thus elliptical. The hexagonal mesophase is then obtained through the isotropic spreading of the aliphatic crown around the columnar core and presumably also through a pronounced disorder within the core as represented schematically in the next figure.

CONCLUSION

From the different systems reported in this paper, it is seen that columnar mesophases can be obtained with different types of molecules through particular supramolecular organisation of the constituent molecules. This involves specific molecular architectures and/or specific intermolecular forces. There are now enough molecular and theoretical tools to control the organization of these systems better, and further steps are conceivable to tune finely the properties of these materials, in order to develop novel molecular devices.

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