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Structural studies of columnar phases of some chiral disc-like molecules

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We have performed a structural study of the mesophases of some isomeric hexa-substituted phenanthrenes. Evidence for a new hexagonal columnar mesophase with three columns per unit cell was found in a chiral isomer. Moreover, a rectangular columnar phase with four columns per lattice, similar to the low temperature mesophase of a hexa-substituted rufigallol, was found in a different material. The relations between the structures and the electro-optical behaviour of the different mesophases are discussed.

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1. Introduction

Usually the extensive conformational disorder of mesogenic molecules enhances the symmetry of their global organization in the mesophases. Moreover, the electro-optical behaviour of these mesophases depends on their symmetry properties. For these reasons, liquid crystal displays based upon chiral molecules are especially interesting because of the low symmetry of the mesophases. The main example is found in the case of smectic C phases containing chiral species which have (under an applied electric field) ferroelectric properties [1].

After the discovery of columnar mesophases constituted of disc-shaped molecules [2] it was tempting to search for switchable columnar phases. The first attempt consisted in an extension of the successful model of ferroelectric smectics [3], and the first chiral disc-like mesogen was obtained [4]. In that case the structure of the two columnar phases was established: in the high temperature mesophase the molecules are tilted in each column, the columns form a rectangular lattice of symmetry $P2_1/a$‡, and it is potentially ferroelectric. The low temperature mesophase is of trigonal symmetry, and the unit cell contains four columns ($P321$ or $P312$) [5]. The molecular director is tilted with respect to the column axis and three columns have a two-fold symmetry, whereas the fourth column has a three-fold axis. No interesting electro-optical behaviour was established for these two mesophases.

Another attempt consisted in building columns with conical molecules such as triveratrylene so that the dipoles are parallel to the column axis [6]. However the molecule is flexible and the conical core can be inverted rather rapidly at high temperature [7]. In another case the molecule has a central polar NO_2 group, but the structure is hexagonal (four columns per lattice) and in fact, it appears that the dipoles are not parallel to the column axis [8]. Also, disc-like molecules can form columnar helical stacks, but this is not necessarily induced by the presence of asymmetric carbons in the molecules [9–11]. The pitch is of the order of a few nm, and the correlation range for this order extends from one pitch length to very long distances inducing, in some cases, a positional correlation between molecules stacked in different columns [10, 11].

Recently ferroelectric properties have been demonstrated in columnar phases of mesogenic molecules in which eight [12], five or six chiral chains [13] are grafted on a flat polyaromatic core of low symmetry. In fact, by varying the position of the grafted chains and

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‡Strictly speaking the glide mirror *a* is incompatible with the molecules symmetry, but the chiral chains are highly disordered and the electronic density map has the apparent $P2_1/a$ symmetry. Moreover, we have determined the direction of the binary axis by the analysis of X-ray diffraction patterns of a fan-shaped domain (unpublished results): the binary axis is along the shorter edge of the rectangular lattice.

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by changing the optical activity of binary mixtures of such molecules, it is possible to obtain samples with different electro-optical behaviour [14]. This behaviour is characterized by the number of different states which are observed on applying an a.c. field of convenient amplitude. A bistable behaviour means that the molecular dipoles are oriented parallel to the electric field and that the dipole direction switches rapidly as the field direction is reversed; this is a ferroelectric behaviour. If at zero field a third state is observed (tristable behaviour), the dipole array is probably different from that of ferroelectric samples. Therefore a structural study of various samples was undertaken in order to link, if possible, the electro-optical behaviour to the dipole organization.

2. Experimental

We have studied the X-ray diffraction patterns of four different compounds: a pure optically active (*R*)-1,2,3,6,7,8-hexa-substituted phenanthrene derivative (**1**) which shows a tristable switching behaviour under an electric field [14]; (**2**) an optically inactive mixture of different diastereoisomers of **1**, obtained by grafting racemic chains at the same positions; (**3**) a chiral (*S*)-2,3,6,7,8,9-hexa-substituted phenanthrene which shows no electro-optical effect and finally, a binary mixture of [85·3% (*S*)**1** + 14·7% (*S*) **3**] which we will call **M4** in the following discussion [14]. All these systems have one columnar phase. The (*S*)-diastereoisomers of **1** and **3** are represented in figure 1.

X-ray diffraction experiments were performed in the absence of any applied electric field. We obtained powder patterns with a Guinier camera set-up using a monochromatic beam (CuK$_{\alpha_1}$); the temperature of the sample contained in a Lindemann glass tube was maintained within ± 1 K.

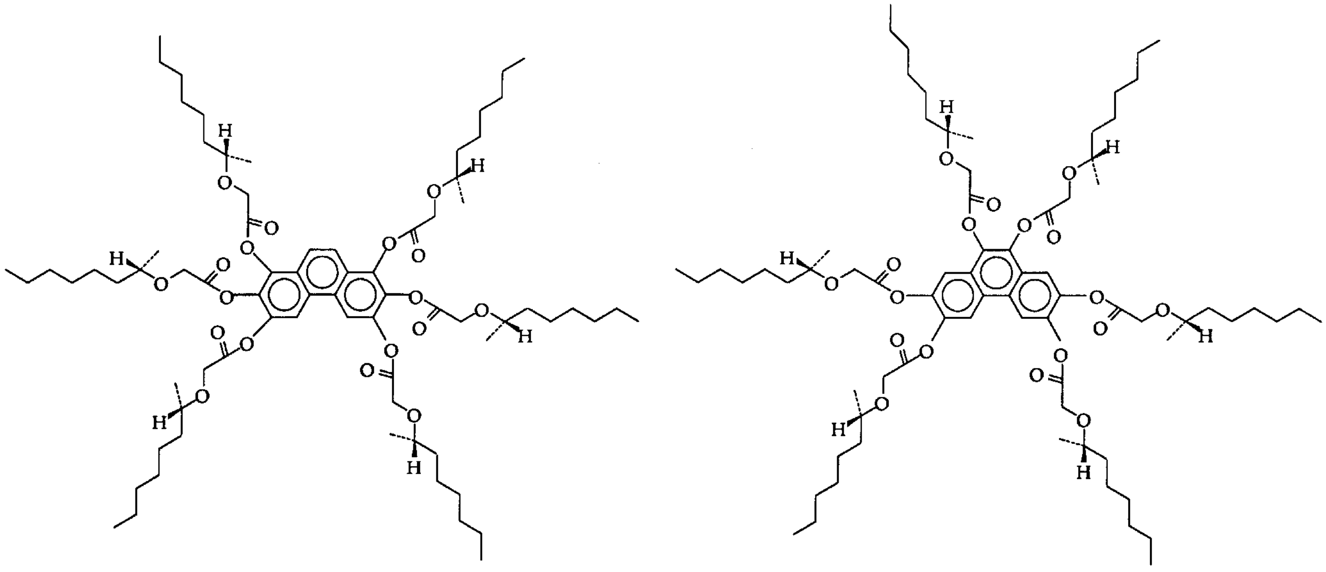
Aligned samples of columnar phases were obtained by stretching the pasty compounds on thin mica plates or by forming fibres if the compound was stiffer; they were illuminated with a point focusing CuK$_{\alpha}$ beam; the diffraction patterns were collected on flat photographic films, and the temperature of the sample was controlled within ±0·25 K.

3. Results and discussion

The diffraction patterns of **1** and **2** are characteristic of a columnar phase with a set of sharp rings at small angles and two outer diffuse rings characterizing the organization of the paraffinic chains and the intracolumnar organization of the molecular cores.

At a first glance, the pattern of compound **1** fits a hexagonal lattice ($a = 23 \cdot 3$ Å) as the most intense diffraction line corresponds to a lattice spacing of 20·3 Å. However, a weak line is visible at smaller angles and corresponds to a lattice spacing of $35 \cdot 05\,\text{Å} \cong 20 \cdot 3/3^{1/2}$ (figure 2 and table 1). The mean distance between molecules in each column is equal to 4 Å.

The non-optically active mixture **2** of isomers shows a similar pattern where, however, the weak inner line has disappeared. The lattice of the columnar phase of **2**



1

3

Figure 1. Chemical formulae of compounds (*S*)**1** and (*S*)**3**.

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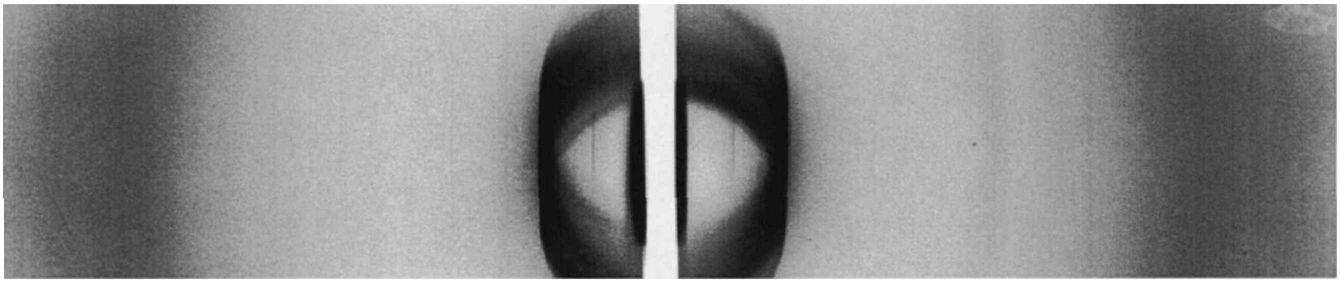

Figure 2. Powder diffraction pattern of the mesophase of **1**.

Table 1. Comparison of measured and calculated lattice spacings (in Å) for the hexagonal lattice (a=40·42 Å) of the mesophase of **1**. In brackets: co-ordinates of the reciprocal points in the fundamental hexagonal lattice a=23·3 Å. Note that there is only one measurable diffraction peak specific to the superlattice.

Lattice spacings		
Measured	Calculated	Indices (*hk*)
35·05	35·00	1 0 (1/3 1/3)
20·3	20·21	1 1 (1 0)
11·7	11·67	3 0 (1 1)
—	10·10	2 2 (2 0)
7·57	7·64	4 1 (2 1)

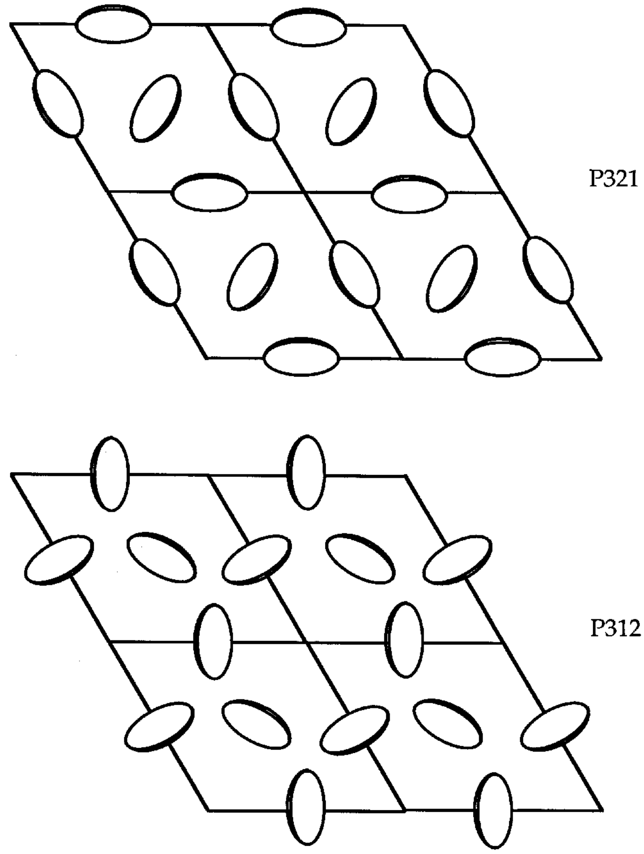

Figure 3. Schematic representation of the columnar organization in the mesophase of **1**.

is a simple hexagonal one with one column per lattice, whereas the chiral material has a new structure with a triangular lattice of threefold symmetry, and three columns per unit cell. This new structure can be considered as a superstructure lattice ($\times 3^{1/2}$) of the usual hexagonal columnar phase. In **1**, each column has a two-fold axis, the space group is *P*321 or *P*312 and the symmetry is consistent with a tilt of the director with respect to the column axis. However, taking into account the core symmetry, the tilt is not a consequence of the lattice symmetry and it only emerges from optical observations [14]. The electric dipole of each column is parallel to the two-fold column axis, i.e. perpendicular to the director and to the column axis. As a result of the three-fold symmetry the total dipole moment is zero. The dipole is either parallel to the [10·0]—space group *P*321—or to [11·0]—space group *P*312 axes (figure 3). This new phase can be considered as an antiferroelectric phase [15] which transforms into a ferroelectric phase when the applied electric field is above a threshold value. The zero field antiferroelectric organization is the origin of the tristate switching behaviour. A $\times 3^{1/2}$ superstructure involving a helical array was demonstrated for the first time by Heiney *et al.* in a thio-ester of triphenylene [11]. This is in fact a different structure, as the columns have a circular section and form a three-dimensional lattice where the three columns are differentiated only by the origin of the helix in a direction parallel to the column axis. Therefore, this new columnar phase reminds one of the previous reported chiral or dipolar columnar phase of the same space group, but with four columns per lattice [5], where three columns have orientations similar to those described here, and the fourth, located on a three-fold axis, is orientationally disordered.

Compound **3** can be easily aligned in fibres. The diffraction patterns show many sharp diffraction arcs located in the equatorial plane (figure 4). When the

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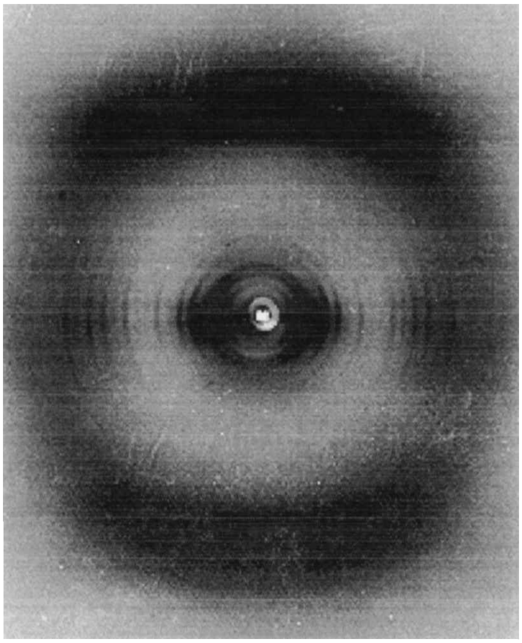

Figure 4. Diffraction pattern of a fibre of **3**.

fibres are perfectly aligned, we can distinguish about 20 sharp arcs corresponding to reticular distances between 4 and 30 Å. They can be assigned to a rectangular lattice ($a=36{\cdot}8$ Å, $b=42{\cdot}4$ Å) of symmetry $P2_12_12$ as the $h0$ and $k0$ reflections are forbidden for odd values of h (k). Table 2 gives the assignment of the diffraction pattern for reticular distances >7 Å. (Below this value, given the high density of reciprocal lengths in the lattice, and the limited resolution of the experimental pattern, a comparison between experimental and calculated values is no longer significant.)

Along the column axis there is a meridional reflection which corresponds to a mean distance between molecules in a column of $c=4{\cdot}65$ Å, so that the number of molecules in the unit cell is $Z=4$. We propose an orthorhombic space group $P2_12_12$ according to the symmetry of the molecule and to the extinction rules of the diffraction pattern. The rectangular lattice can be considered as the association of two rectangles ($a\times b/2$) with $2a/b=1{\cdot}736\cong 3^{1/2}$. Therefore the four columns per rectangular planar unit cell are probably in a slightly distorted hexagonal array. The orthorhombic symmetry implies that the molecular director is parallel to the column axis. The diffraction pattern also fits with an apparent $P2_1/a$ monoclinic symmetry (tilted columnar phase) if one assumes that a pseudo-mirror symmetry is allowed by a significant conformational disorder of the paraffinic medium. However, the large number of visible reflections, the high Z value and the absence of an electro-optical effect support the concept of a highly ordered organization and we propose a model (figure 5) based upon the orthorhombic symmetry. Furthermore, another disc-like molecule, the 2,3,4,7,8,9-hexa-*n*-octanoate of rufigallol has a monotropic mesophase with a rectangular lattice and four columns per lattice [16]. In fact, taking into account the similarities in the diffraction patterns, we can assume that the molecular organization in these two mesophases is much the same, the differences originating in the core and chains symmetry properties.

Table 2. Comparison of measured ($\geqslant 7$ Å) and calculated lattice spacings (in Å) for the rectangular lattice ($a=36{\cdot}8$ Å, $b=42{\cdot}4$ Å) of the mesophase of **3**.

Lattice spacings		
Measured	Calculated	Indices (h k)
27·60	27·80	1 1
21·31	21·22	0 2
18·46	18·40	2 0
	18·38	1 2
—	16·88	2 1
13·92	13·90	2 2
—	13·20	1 3
11·78	11·78	3 1
—	11·21	2 3
10·63	10·62	3 2
	10·61	0 4
9·23	9·27	3 3
	9·20	4 0
	9·19	1 4
—	8·99	4 1
8·39	8·44	4 2
	8·27	1 5
—	8·02	3 4
7·73	7·71	4 3, 2 5
—	7·25	5 1
7·07	7·07	0 6
	6·98	3 5

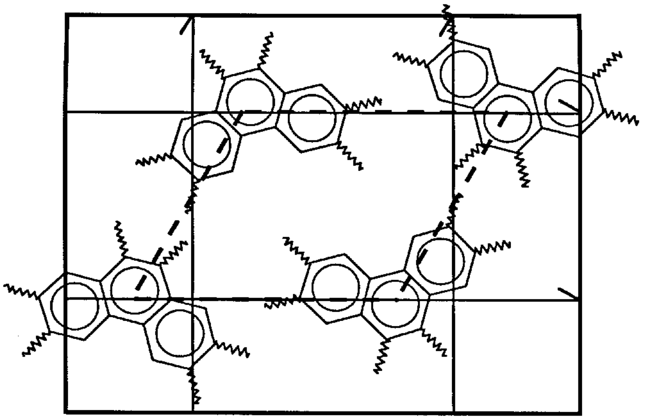

Figure 5. Schematic representation of the columnar organization in the mesophase of **3**. The columns form a slightly distorted hexagonal array (dashed lines) and the phenanthrene aromatic cores have four different orientations.

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The powder pattern of mixture **4** evolves progressively from room temperature until 65–70°C. At room temperature the low angle part of the pattern is consistent with the superposition of two different lattices: a rectangular lattice $46{\cdot}3\times34{\cdot}3$ Å^2 and a hexagonal lattice $a=23{\cdot}22$ Å. As the temperature is increased the rectangular lattice rings decrease in intensity, while the intensity of the unique hexagonal ring increases. In the wide angle part of the pattern one sees a broad ring superimposed over a series of sharp reflections. All the sharp reflections but one ($d_0=20$ Å) disappear above $T\approx65$°C, so that the hexagonal lattice is characterized by only one ring. The corresponding column diameter is 23·09 Å, and, moreover, we have no evidence of any superstructure. Therefore at room temperature we have a coexistence of two phases: one is isomorphic with the rectangular mesophase of **3** and the second is likely to be columnar hexagonal. As the temperature increases, the first mesophase disappears and the stable phase is hexagonal ($a=23{\cdot}6$ Å). In fact, the diffraction pattern of this mesophase shows a unique sharp ring and neither outer rings at $d_0/3^{1/2}$ and $d_0/2$ nor an inner ring as in pure **1** is visible. The absence of outer rings is likely to be a consequence of the fluctuations in column diameter resulting from the mixture of two molecules. Therefore the space group symmetry is $P622$, with one column per unit cell.

The bistable switching behaviour of mixture **M4** can be explained easily by its structural properties: the molecular director is tilted with respect to the column axis, but in the absence of any applied electric field the projection of the director on the plane perpendicular is orientationally disordered (probably fluctuating from column to neighbouring column), in order to keep the global hexagonal symmetry. Under an external applied field, all the dipoles of individual columns become parallel and the final structure is likely to be centred rectangular [17] (figure 6). Note that the high temperature mesophase of rectangular symmetry seen in a chiral hexa-alkanoyloxytriphenylene [5] is polar despite the fact that the dipoles of individual columns are not parallel to one another. One may ask whether this symmetry can be induced by an applied electric field of intermediate strength. Moreover the relation between the two mesophases described in reference [5] and the antiferroelectric structure is an interesting question. Following reference [17], there is another phase of hexagonal or oblique symmetry which has not yet been evidenced experimentally. This phase is an intermediate step between the antiferroelectric phase (three columns per lattice) and either the hexagonal phase of same space group (but with four columns per lattice) or the rectangular phase symmetry $P2_1/a$ (two columns per lattice). The mean number of columns per unit cell is non-integral and the dipole orientation is modulated with a period

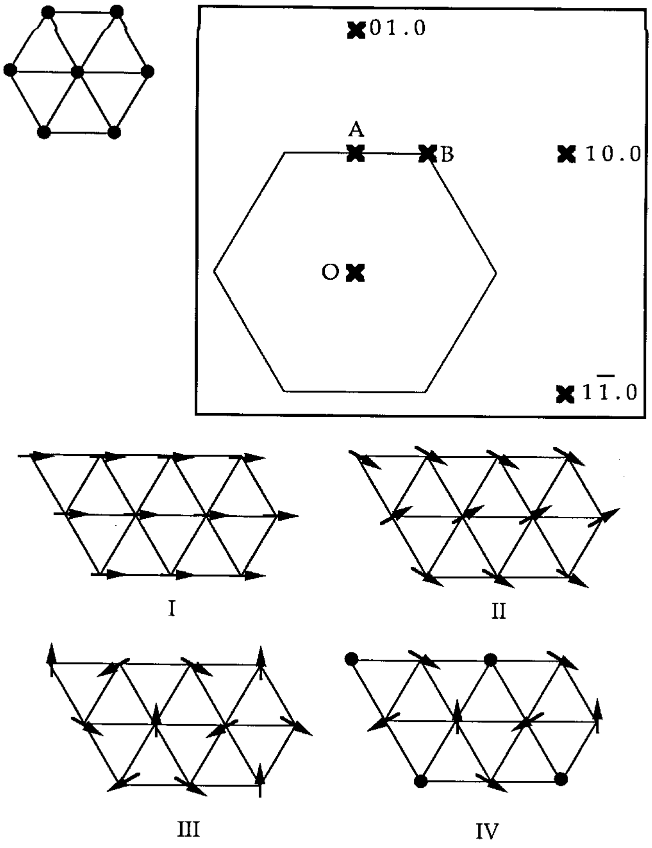

Figure 6. The different dipole organizations discussed in reference [17]. The upper part of the figure shows the disordered hexagonal columnar mesophase and its reciprocal space (in the inset). The ferroelectric phase (I) corresponds to a homogeneous orientation (one column per unit cell); the hexagonal symmetry is broken and the reciprocal lattice is built with two of the three basic vectors of the primitive hexagonal reciprocal unit cell, thus, forming a centred rectangular lattice. By changing the control parameters of the free energy, new reciprocal nodes, located on the Brillouin zone boundary of the primitive lattice, appear, building a superlattice in which the dipoles of different columns have different orientations. Note that lattices of different symmetry might be built with the same reciprocal vectors, which means that they are stable for the same values of the control parameters. As an example, starting from A (0, 1/2, ., 0), it is possible to build a rectangular lattice (II); the two reciprocal basic vectors join the origin to the points 1,—1/2, ., 0 and 0, 1/2, ., 0. However, a hexagonal superlattice symmetry with four columns per unit cell (IV) is built if three points, equivalent to A, are taken into account. Starting from point B (1/3, 1/3, ., 0), the hexagonal symmetry is preserved and the unit cell (III) contains three columns per unit cell (antiferroelectric array of dipoles). For any other point of the Brillouin zone boundary between A and B, the lattice is either oblique or hexagonal with an incommensurate modulation of the dipole orientation.

which is incommensurate with the distance between neighbouring columns.

4. Conclusion

In conclusion, a comparative structural study of four different samples has allowed us to discuss the electro-optical behaviour of these samples on the basis of structural features. One can link this behaviour to the different orientational ordering possibilities in a triangular lattice of columns described theoretically by Carton *et al.* [17].

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