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Symmetries and physical properties of polar columnar phases in materials composed of achiral molecules

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Abstract. – Motivated by puzzling experimental observations made in compounds composed of banana-shaped molecules, we investigate the symmetries and the physical properties of liquid crystalline columnar phases with a macroscopic polarization in achiral materials. This study is driven by two key observations made for the still poorly understood B7 phase: a) freely suspended films decompose spontaneously into strands and b) several of the textures observed for the B7 phase are reminiscent of textures observed for liquid crystalline columnar phases. One of the main results of our analysis is that a chiral phase of C_1-symmetry results as soon as the macroscopic polarization includes an angle different from zero or 90° with the columnar axes. We argue that a chiral columnar phase composed of achiral molecules, not previously considered for classic columnar phases, is sufficient to account for many of the unusual physical properties of B7.

Introduction. – Liquid crystalline phases formed in compounds composed of achiral banana-shaped molecules have recently attracted considerable attention [1–13]. A still puzzling phenomena observed in this field is the phase transition from an optically isotropic liquid phase to the B7 phase [9,14]. Neither the symmetry nor the ground state of B7 are understood.

So far large B7 monodomains have not been successfully grown. Presumably it is not a typical smectic phase as it does not form stable freely suspended films. Rather, B7 films break-up into strands [14, 15]. X-ray investigations give rise to many diffraction peaks that cannot be indexed by a standard smectic or columnar phase known to form in other low molecular weight liquid crystalline compounds [14]. In the optical microscope, one observes many different patterns on cooling including: spirals of both hands growing into the isotropic phase, myelinic patterns and patterns showing spatial modulations, sometimes regular, in a second direction [9, 14].

Intrigued by the spontaneous break-up of freely suspended films into strands and the observation of textures that closely resemble those observed in discotic liquid crystals [16,17], we study the symmetries and physical properties of columnar phases that possess a macroscopic polarization even when composed of achiral molecules. While this study is a natural complement to our previous work on smectic and nematic phases with a macroscopic polarization in achiral systems [6, 11], it has uncovered a novel columnar structure not previously observed in classic discotics, a chiral columnar phase that does not require chiral molecules, that we present as a promising candidate for the structure of B7.

Symmetry considerations. – In classical columnar liquid crystals there are two main classes [16, 17] without a macroscopic polarization, **P**: hexagonal and rectangular columnar phases. They show in most cases D_{6h} (hexagonal) and D_{2h} (rectangular) symmetry. We note that square symmetry (D_{4h}) is a special case of rectangular symmetry and that parallelogram-shaped lattices also have D_{2h} symmetry. We consider structures that do not have long-range positional order in the columns, i.e. a 2D crystal and a 1D fluid.

In this section we consider hexagonal and rectangular columnar phases that have an additional macroscopic polarization **P**, which can have three different relevant orientations: a) *along* the columnar axes; b)*in the plane* of the 2D lattice (that is perpendicular to the columnar axes) and c) *oblique* (that is neither zero and 90°) with respect to the column axes (and the 2D lattice plane).

First we consider hexagonal columnar phases and we start with a polarization along the columnar axes: in this case the ground state has a six-fold axis and vertical mirror planes, which gives rise to C_{6v} symmetry. As will become clear in the following this is the highest symmetry compatible with columnar symmetry and the presence of a macroscopic polarization. This situation is shown in Fig.1a and we call this phase Col_{Ph}.

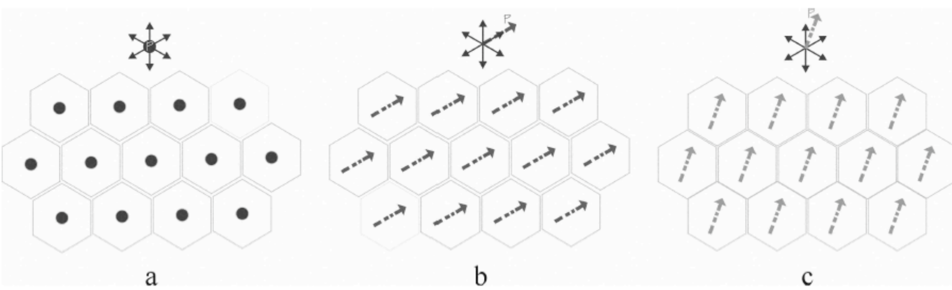

Fig. 1 – *The case of hexagonal columnar phases with three different orientations of the macroscopic polarization* **P**. *a)* **P** *is along the columnar axes:* C_{6v}*; b)* **P** *is in the plane and parallel to one of the sides of the hexagons:* C_{2v}*, and c)* **P** *is in the plane but neither parallel nor perpendicular to one of the sides of the hexagons:* C_{1h}*.*

We note for completeness that there was an effort to produce a liquid crystalline phase isomorphic to the Col_{Ph} phase a number of years ago using pyramidic shaped compounds [18]. But since they turned out to be almost solids, their electrical and electro-optic properties are still not known.

For a hexagonal lattice with a polarization in the plane that is parallel or perpendicular to one of the sides of the hexagons, we have left over as symmetry elements a vertical mirror plane and a two fold axis within this mirror plane resulting in a C_{2v} symmetry. We denote this phase depicted in Fig.1b as Col_{Ph2}. The overall symmetry of this phase is the same as that of the smectic C_P phase suggested and characterized by the present authors earlier [1, 6] and found experimentally very recently in compounds composed of banana-shaped molecules [19].

TABLE I – *This table shows the symmetries and the physical properties of the classical columnar phases without a macroscopic polarization as well as these of the novel phases discussed here.*

class	**symmetry**	**polarization**	**2D lattice**	first-rank tensor
$\mathrm{Col}_{\boldsymbol{h}}$	D_{6h}	**none**	**hex**	none
$\mathrm{Col}_{\boldsymbol{r}}$	D_{2h}	**none**	**rect**	none
$\mathrm{Col}_{\boldsymbol{Ph}}$	C_{6v}	**along columns**	**hex**	1D along polarization
$\mathrm{Col}_{\boldsymbol{Ph1}}$	C_{1h}	**in the lattice plane oblique to hex directions**	**hex**	2D in the lattice plane
$\mathrm{Col}_{\boldsymbol{Ph2}}$	C_{2v}	**in the lattice plane along hex directions**	**hex**	1D along polarization
$\mathrm{Col}_{\boldsymbol{Pr}}$	C_{2v}	**along columns**	**rect**	1D along polarization
$\mathrm{Col}_{\boldsymbol{Pr1}}$	C_{1h}	**in the lattice plane oblique to rect directions**	**rect**	2D in the lattice plane
$\mathrm{Col}_{\boldsymbol{Pr2}}$	C_{2v}	**in the lattice plane along rect directions**	**rect**	1D along polarization
$\mathrm{Col}_{\boldsymbol{Pi}}$	C_1	**oblique to columns and to lattice plane**	**any**	3D any orientation

If we take a hexagonal lattice and a polarization in the plane that is neither parallel nor perpendicular to the sides of the hexagons we have C_{1h}-symmetry. There is no n-fold axis with $n > 1$ left, but horizontal mirror planes: along the columnar axes everything looks the same. The symmetry of this phase (Fig.1c), Col_{Ph1}, is the same as that of the C_{B1} phase discussed for smectic phases which could be formed by banana-shaped molecules [6,10]. There appears to be no experimental observation of such a phase as yet, neither for smectic nor for columnar phases (compare also Table 1).

Next we discuss rectangular symmetry for the columnar lattice plus a macroscopic polarization and we start with a polarization along the column axis. In this case we have C_{2v} symmetry since the polarization distinguishes between head and tail and there are no horizontal mirror planes left - thus the symmetry of this phase, which we call Col_{Pr}, is again the same as that of the C_P phase mentioned above as well as that of the Col_{Ph2} phase. When we start with rectangular symmetry for the columnar lattice and a polarization parallel to one of the sides of the rectangle, we have again C_{2v}-symmetry but in this case the polarization lies in the plane perpendicular to the columnar axes: Col_{Pr2}.

In case we take a rectangular columnar lattice plus a polarization in the plane perpendicular to the columns at an oblique angle to the sides of the rectangle, there is C_{1h} symmetry as there is no n-fold axis, but again there are horizontal mirror planes. Since the basic lattice is rectangular instead of hexagonal as above for the Col_{Ph1} phase, we call this phase Col_{Pr1}.

We note that all ferroelectric arrangements with the polarization along the column axes or in the planes considered up to now have mirror planes. This implies that none of these phases is chiral. Thus they are unlike C_{B2} and C_G considered [6, 10] for smectic phases formed by banana-shaped molecules.

This situation is different when we go to the most general case, the Col_{Pi} phase with C_1 symmetry: The polarization, $\mathbf{P}$, is inclined relative to the column axis and its projection onto the 2D lattice plane is also inclined to the preferred symmetry axes (Fig.2).

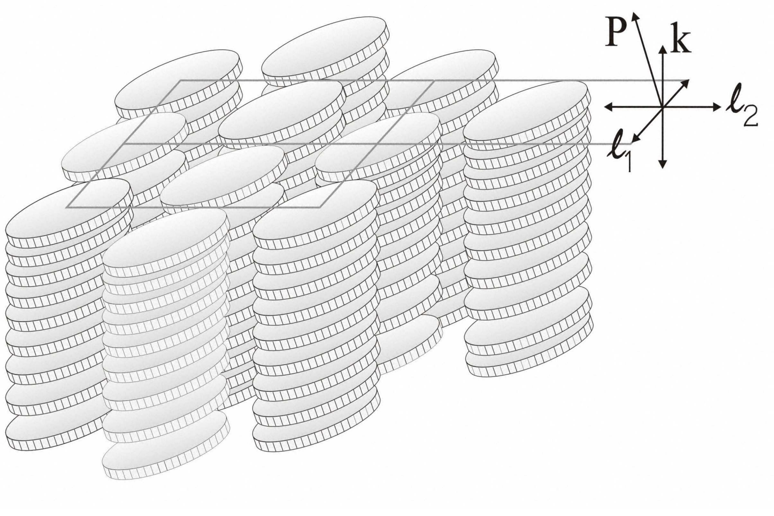

Fig. 2 – *The local structure of the* Col_{Pi} *phase for disk-shaped objects with* $\mathbf{k}$ *the column axis,* $\mathbf{P}$ *the macroscopic polarization and* $\mathbf{l_{1,2}}$ *the non-polar symmetry directions in the planes of 2D positional order.* $\mathbf{P}$ *is inclined to all of the planes* $\mathbf{k}/\mathbf{l_1}$, $\mathbf{k}/\mathbf{l_2}$ *and* $\mathbf{l_1}/\mathbf{l_2}$. *The* Col_{Pi} *phase has no mirror plane and is, therefore, chiral.*

This is realized as soon as we tilt e.g. disk-shaped objects in the columns about a suitable axis (Fig. 2). It has the same symmetry as the C_G phase possible for layered phases formed by banana-shaped molecules arranged in layers [6]. We note one important difference in this respect between smectic and columnar phases. For columnar phases, tilting the disk-shaped objects once is sufficient to reach the lowest symmetry level, while in the smectic C_G phase, banana-shaped molecules are tilted twice, i.e. about two different orthogonal axes.

The Col_{Pi} phase is chiral as is manifest by the existence of a pseudoscalar: $\tilde{q} = [\hat{\mathbf{p}} \cdot (\mathbf{k} \times \mathbf{l_1})][\hat{\mathbf{p}} \cdot (\mathbf{k} \times \mathbf{l_2})][\hat{\mathbf{p}} \cdot (\mathbf{l_1} \times \mathbf{l_2})]$ with $\mathbf{P} = P_0\hat{\mathbf{p}}$, where P_0 is the magnitude and $\hat{\mathbf{p}}$ the direction of the polarization. For $\mathbf{P} \to -\mathbf{P}$ the chirality changes from, say, right- to left-handed. The chirality can, but need not, show up in helical structures which would be right- as well as left-handed (ambidextrous chirality), since the structure is made of achiral molecules.

Thus it emerges that tilted columnar phases with a polarization and C_1 symmetry are a natural candidate for B7. It is a columnar structure whose symmetry cannot be further lowered when anti-ferroelectric aspects are included.

There are many ways to generate antiferroelectric or similar arrangements. Three examples are shown in Fig.3.

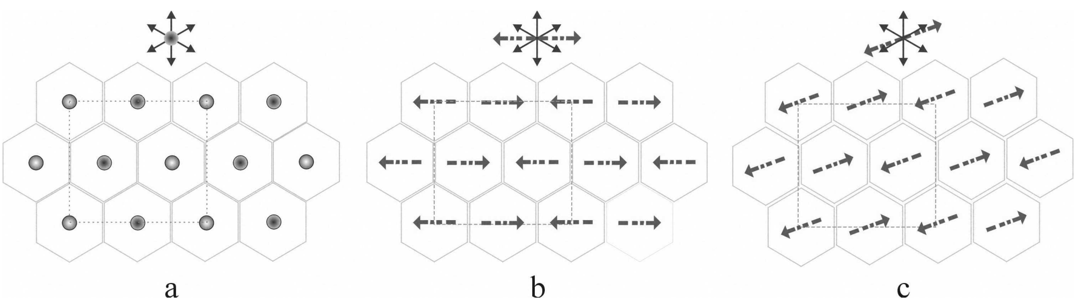

Fig. 3 – *Three examples of regular antiferroelectric arrangements: a) shows a configuration with alternating macroscopic polarization* $\mathbf{P}$ *along the columnar axes; in b) and c) the alternating polarization is in the lattice plane and either parallel or at an angle different from* 0 *and* 90° *to one of the sides of the dashed rectangular structure, respectively.*

The structure shown in Fig.3a has a horizontal mirror plane spanned by the columnar direction and the horizontal dashed line, through the midpoints of the hexagons. It repeats for every row of hexagons. In addition there is a 2-fold rotation axis in the direction of the columns, through any midpoints of the border lines between two hexagons of the same polarity. There are additional symmetry elements, which are not as obvious: if the structure is reflected at the lattice plane, all up and down polarizations are interchanged. However, this is a structure completely equivalent to the original one - only shifted by one hexagon to the left (or right), which is irrelevant for an infinite bulk system. Thus this structure has globally D_{2h} symmetry.

In Fig.3c the polarization lies in the lattice planes, which are the mirror planes. There is also a 2-fold symmetry axis perpendicular to the mirror planes through the middle of the sides of the hexagons separating areas of antiparallel orientations that are not horizontally adjacent. Since these are all symmetry elements, the structure has C_{2h} symmetry. In addition Fig.3b has horizontal mirror planes like those in Fig.3a and is thus also of D_{2h} symmetry.

We stress that there are many other possible antiferroelectric, frustrated and disordered states leading to even lower symmetry for both the polarization along the column axes and in the planes, and for hexagonal as well as for rectangular arrangements.

Physical properties of columnar phases with a macroscopic polarization. – In this section we summarize some of the physical properties characteristic of columnar phases with a macroscopic polarization. Due to the nature of the macroscopic polarization, all these phases are ferroelectric (compare also Table 1). Because Col_{Ph} - Col_{Pi} possess a polar vector, they have interesting macroscopic electric and electromechanical properties. For the relevant part of the generalized energy we get to lowest order

$$\Phi = \int d\tau [\epsilon_{ij}^E E_i E_j + P_i E_i + E_i(\zeta_i^T \delta T + \zeta_i^p \delta p + \zeta_i^c \delta c) + d_{ijk} E_i \nabla_j u_k] \quad (1)$$

The contribution $\sim \epsilon_{ij}^E$ is the usual dielectric term with six, four, and three independent coefficients for triclinic (C_1), monoclinic (C_{1h}), orthorhombic (C_{2v}) symmetry, respectively and 2 coefficients for tetragonal (C_{4v}) and hexagonal (C_{6v}) symmetry [20]. The next term is characteristic of all ferroelectric materials. The terms $\sim \zeta_i^T, \zeta_i^p$ and ζ_i^c relate to pyroelectric effects, pressure electric effects and to an electric response resulting from a concentration change in mixtures. The 'dimension' (i.e. the number of independent components) and the direction (relative to the columnar structure) of the first rank tensors are listed in Table 1. The last term in eq.(1) is related to piezoelectric effects coupling the electric field to gradients of the displacement vector in the planes of the positional order. Since we have a columnar structure, which is fluid in the columns, only first order gradients $\nabla_j u_k$ contribute, where k, j can be x and y, when the columnar axis is denoted by z. This results in 9, 6, 2 and 1 independent piezoelectric constants for C_1, C_{1h}, C_{2v} and C_{nv} (n=4,6) symmetry.

In addition to these linear electric and electromechanical effects, the symmetry of Col$_{Ph}$ - Col$_{Pi}$ also allows for second harmonic generation. The corresponding contribution Φ_{SHG} reads

$$\Phi_{SHG} = \int d\tau \chi_{ijk}^{(2)} E_i E_j E_k \quad (2)$$

where $\chi_{ijk}^{(2)}$ contributes 10, 6, and 3 independent coefficients for C_1, C_{1h}, and C_{nv} (n=2,4,6) symmetry.

One can also set up the macroscopic dynamics for Col$_{Ph}$ - Col$_{Pi}$, including dissipative and reversible parts, using the usual procedure [21–23]. It turns out, that in particular the dissipative contributions bring along a host of coefficients due to the low symmetry of the columnar phases discussed here. These rather detailed aspects will be discussed elsewhere [24].

The two phases that are purely dielectric are the classical columnar phases listed in the first two lines of table 1.

The only type of columnar phase that is chiral in spite of being composed of achiral molecules is the phase we call Col$_{Pi}$. One can expect, however, that this phase is rather frequent for columnar phases with a macroscopic polarization, since it occurs for columnar as well as for hexagonal lattices and since it requires the "molecules" to tilt only once.

This phase is distinguished from the columnar phases formed from chiral molecules, whose electric-optic response has been investigated a few years ago [25, 26].

Conclusions and perspective. – We have analyzed the influence of a macroscopic polarization on the symmetry of various columnar phases. We find that many of the new columnar phases discussed here, Col$_{Ph}$ - Col$_{Pr1}$, for which the polarization is along the columnar axes or in the planes with positional order, have interesting electro-mechanical properties, but are not chiral when composed of achiral molecules. Only when the polarization includes an angle different from 0° or 90° with the column axes, a Col$_{Pi}$-phase (C_1-symmetry), which is chiral appears. For the columnar case only one tilt is necessary to achieve this ground state, while for the C_G phase in smectic liquid crystals it is necessary to tilt the molecules twice [6]. Among all phases composed of banana-shaped molecules observed so far, the B7 phase obtained for molecules with a central nitro group [9, 14] looks like the most promising candidate for the novel Col$_{Pi}$ phase suggested here.

Note added in Proof After this manuscript was submitted, A. Jakli and D. Walba reported at the '8th International Conference on Ferroelectric Liquid Crystals' in Washington (D.C.)

the observation of a phase with C_1 symmetry in banana-shaped molecules. At this same conference, H. Pleiner pointed out that these observations are also compatible with the Col_{Pi} phase discussed here.

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