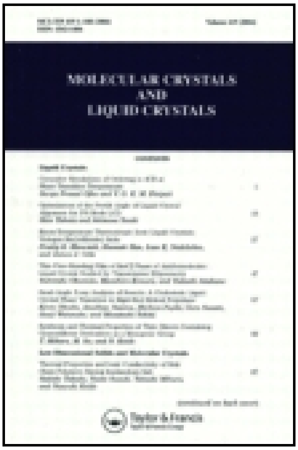

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POLAR COLUMNAR AND TETRAHEDRATIC PHASES

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1. INTRODUCTION

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 [1]. This study is driven by two key observations made for the still poorly understood B7 phase: a) freely suspended films decompose spontaneously into strands [2,3] and b) several of the textures observed for the B7 phase are reminiscent of textures observed for liquid crystalline columnar phases. Quite recently more experimental evidence was presented [4] in support of columnar features evident in the B7 phase.

One of the main results of our analysis [1] is that a chiral phase of C_1-symmetry results as soon as the macroscopic polarization is inclined with respect to the columnar axes and the 2D lattice directions. 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.

Recent experiments on the effect of an external electric field and of temperature variations have also revealed the occurrence of flow close to and in the isotropic phase near the B7 — isotropic phase transition [5]. Consequently, there is a need to look for models which can describe phases that are optically isotropic but not cubic and can show coupling effects between flow and electric fields and/or temperature gradients.

We discuss this [6] for the optically isotropic tetrahedratic phase characterized by a third rank tensor order parameter T_{ijk} [7]. We point out that an applied electric field or an applied temperature gradient will lead to flow. Reciprocally we predict that, for example, a shear flow applied to a tetrahedratic phase leads to an induced electric field and a temperature gradient.

It is unclear how the banana molecules are arranged in the columns or in the tetrahedratic phase. It can be expected that aggregates of those molecules are involved. Such structures are probably soft, in the sense that they can be distorted due to external fields, thus giving rise to additional physical effects. As a result, the effects of external electric field and flow on deformable tetrahedratic phases has been investigated, recently [8].

2. THE COLUMNAR BANANA PHASES

Columnar liquid crystal phases are 2-dimensional arrays of columns made of disk-like molecules [9,10]. The 2-dimensional lattice is either hexagonal or rectangular characterized by two directions, $\boldsymbol{l}_{1,2}$. The column axis will be called $\boldsymbol{k}$. Without a macroscopic polarization, $\boldsymbol{P}$, the planes built of $\boldsymbol{k}/\boldsymbol{l}_{1,2}$ and $\boldsymbol{l}_1/\boldsymbol{l}_2$ are mirror planes. The directions perpendicular to these planes are (at least 2-fold) symmetry axes (there can also be 4- and 6-fold axes). Thus these classical columnar phases, Col$_h$ and Col$_r$, are of D_{2h} (sometimes D_{4h} and D_{6h}) symmetry. We only consider structures without long-range positional order in the columns, i.e. 2D crystalline and 1D fluid behavior.

The symmetry of these phases is reduced when a macroscopic polarization $\boldsymbol{P}$ is present. What symmetry is left, depends on how the polarization is oriented with respect to the column axis $\boldsymbol{k}$ and the lattice axes $\boldsymbol{l}_{1,2}$. Since it is not clear a priori how the banana molecules are arranged in the columns, we discuss two principal possibilities for the orientation of the polarization $\boldsymbol{P}$, being either along the normal $\boldsymbol{n}$ of the "disks" that make up the columns or lying in the "disk" plane, (the oblique case would not give anything substantially new). In the former case the polarization is the only structural element of the "disks". If untilted, that means the polarization is parallel to the column axis, $\boldsymbol{P} \| \boldsymbol{k}$, this axis remains a 6-fold or 2-fold (or 4-fold) symmetry axis for a hexagonal or rectangular 2-D lattice, respectively. The plane perpendicular to $\boldsymbol{P}$ is no mirror plane anymore due to the polarity. Mirror planes always contain the polarization and one of the lattice directions $\boldsymbol{l}_{1,2}$. Thus a C_{6V} (Fig. 1a of [1]) or C_{2V} symmetric phase results, called Col$_{Ph}$ or Col$_{Pr}$, which is achiral and has a polar direction along the

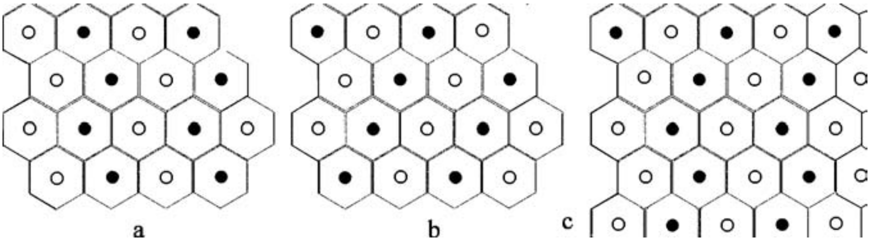

FIGURE 1 Hexagonal columnar phases with the polarization up (full circles) and down (open circles) the columnar axes. All horizontal rows are antiferroelectric, but different "stacks" lead additionally to a) 2 double-periodic antiferro-, b) 1 ferro- and 1 antiferro-, and c) 1 triple-periodic antiferro- and 1 ferri-electric (2 up and 1 down and vice versa) direction at $\pi/6$.

column axis. Quite similar phases can be expected from conical shaped entities (e.g. pyramidic [11] or buckyballs with feathers [12,13]).

With a hexagonal lattice an arrangement that is antiferroelectric in all 3 lattice directions is not possible. Figure 1 shows some examples of the essential frustration.

If the polarization is tilted away from the column axis in the direction of one of the lattice axes (say $\boldsymbol{l_1}$), then this $\boldsymbol{k}/\boldsymbol{P}/\boldsymbol{l_1}$ mirror plane is the only symmetry element left. This phase, called Col_{Ph1} or Col_{Pr1} in [1] has C_{1h} symmetry and the polar direction can lie anywhere in the mirror plane. They are of the same symmetry as the C_{B1} smectic banana phase [14,15]. If the tilt direction of $\boldsymbol{P}$ is oblique to the 2-D lattice axes, no symmetry is left (C_1 symmetry). The phase (called inclined polar or Col_{Pi}) is chiral and can have the polar direction anywhere (Fig. 2 of [1]). It has the same symmetry as the C_G phase possible for smectic phases formed by banana-shaped molecules [14]. The Col_{Pi} phase is chiral as is manifest by the existence of a pseudoscalar: with the polarization $\boldsymbol{P}=\boldsymbol{P_0}\hat{\boldsymbol{p}}$ (P_0 is the magnitude and $\hat{\boldsymbol{p}}$ the direction of the polarization) the scalar $\tilde{q}=[\hat{\boldsymbol{p}}\cdot(\boldsymbol{k}\times\boldsymbol{l_1})]\ [\hat{\boldsymbol{p}}\cdot(\boldsymbol{k}\times\boldsymbol{l_2})]\ [\hat{\boldsymbol{p}}\cdot(\boldsymbol{l_1}\times\boldsymbol{l_2})]$ changes sign under spatial inversion. For $\hat{\boldsymbol{p}}\to-\hat{\boldsymbol{p}}$ 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.

If the polarization $\boldsymbol{P}$ is perpendicular to the (non-polar) "disk" axis $\boldsymbol{n}$, the objects that form columns are biaxial. In the untilted case, $\boldsymbol{n}$ along the column axis $\boldsymbol{k}$, the polarization is in the 2D-lattice plane. If $\boldsymbol{P}$ is parallel to one of the lattice axes $\boldsymbol{l_{1,2}}$ this axis is a 2-fold rotation axis and the plane $\boldsymbol{k}/\boldsymbol{P}$ is a mirror plane. The phase has C_{2V} symmetry and is called Col_{Ph2} or Col_{Pr2} (Fig. 1b of [1]). If $\boldsymbol{P}$ is oblique to both, $\boldsymbol{l}_1$ and $\boldsymbol{l}_2$, the mirror plane $\boldsymbol{l_1}/\boldsymbol{l_2}$

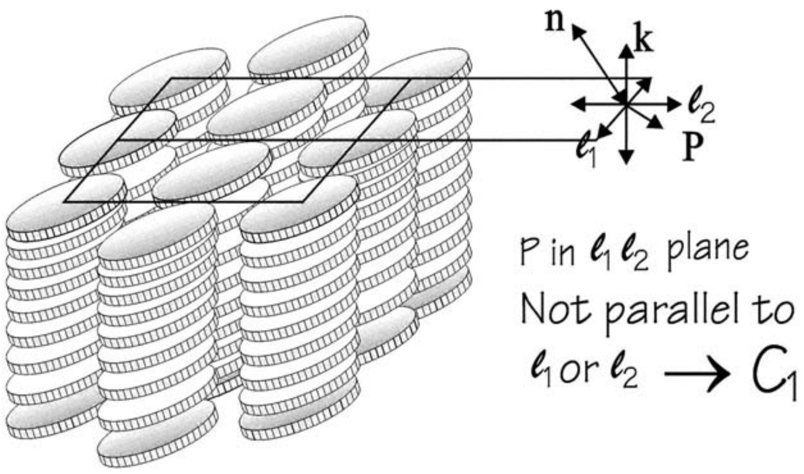

FIGURE 2 The local structure of the Col$_{Pi}$ phase for disk-shaped objects with $\boldsymbol{k}$ the column axis, $\boldsymbol{P}$ the macroscopic polarization perpendicular to the disk axis $\boldsymbol{n}$, and $\boldsymbol{l}_{\mathbf{1,2}}$ the non-polar symmetry directions in the planes of 2D positional order. $\boldsymbol{P}$ is not parallel to $\boldsymbol{l}_{\mathbf{1}}$ or $\boldsymbol{l}_{\mathbf{2}}$.

is the only symmetry element left and again a C_{1h}-symmetric phase is obtained (Col$_{Ph1}$, Figure 1c of [1] or Col$_{Pr1}$). Fully antiferromagnetic ordering is not possible in the hexagonal case and may result in a frustrated configuration as discussed above, or in a rearranging of the columns into a rectangular lattice. In the tilted case, $\boldsymbol{n}$ not parallel to the column axis $\boldsymbol{k}$, generally a C_1-symmetric Col$_{Pi}$ phase results (with no symmetry element left and with ambidextrous chirality as discussed above) – except for the special case that the tilt of $\boldsymbol{n}$ is such that $\boldsymbol{P}$ is along one of the lattice directions $\boldsymbol{l}_{1,2}$. In this latter case $\boldsymbol{P}$ is a 2-fold symmetry axis and the phase has C_2 symmetry (Col$_{Pi2}$), similar to the C$_{B2}$ smectic banana phases. Here $\boldsymbol{P}$ is the 2-fold axis and $\tilde{q} = [\hat{\boldsymbol{p}}\cdot(\boldsymbol{k} \times \boldsymbol{n})]\ [\hat{\boldsymbol{p}}\cdot(\boldsymbol{k} \times \boldsymbol{l}_{\mathbf{2}})]\ [\hat{\boldsymbol{p}}\cdot(\boldsymbol{n} \times \boldsymbol{l}_{\mathbf{2}})]$. The symmetry properties of the polar columnar phases are summarized in Table 1.

Because Col$_{Pi}$ and Col$_{Pi2}$ possess a polar vector, this has interesting macroscopic electric and electromechanical properties. In the free energy they show up as

$$\begin{aligned}\Phi = \int d\tau[\epsilon_{ij}^{E} E_i E_j + P_i E_i + E_i(\zeta_i^T \delta T + \zeta_i^p \delta p + \zeta_i^c \delta c) \\ + d_{ijk} E_i \nabla_j u_k + \chi_{ijk}^{(2)} E_i E_j E_k]\end{aligned} \tag{1}$$

where the contribution $\sim \epsilon_{ij}^{E}$ is the usual dielectric term with six (4) independent coefficients for triclinic C_1 (monoclinic C_2) symmetry [16].

TABLE 1 This Table Shows the Symmetries and the Physical Properties of the Classical Columnar Phases without a Macroscopic Polarization as well as those of the Novel Phases discussed here. $\boldsymbol{k}$, $\boldsymbol{l_1}$, and $\boldsymbol{l_2}$ are the Column axis, and the Preferred Directions of the 2D Lattice, respectively. n is the Non-Polar "Disk" Axis.

Class	Symmetry	Polarization P	2D Lattice	First-rank tensor
Col$_{\boldsymbol{h}}$	D_{6h}	none	hex	none
Col$_{\boldsymbol{r}}$	D_{2h}	none	rect	none
Col$_{\boldsymbol{Ph}}$	C_{6v}	parallel to $\boldsymbol{k}$	hex	1D along $\boldsymbol{k}$
Col$_{\boldsymbol{Ph2}}$	C_{2v}	parallel to $\boldsymbol{l_1}$ or $\boldsymbol{l_2}$ ($\boldsymbol{n}$ untilted)	hex	1D along $\boldsymbol{l_1}$ or $\boldsymbol{l_2}$
Col$_{\boldsymbol{Ph1}}$	C_{1h}	in the $\boldsymbol{k}/\boldsymbol{l_1}$, $\boldsymbol{k}/\boldsymbol{l_2}$, or $\boldsymbol{l_1}/\boldsymbol{l_2}$ plane, but oblique to $\boldsymbol{k}$, $\boldsymbol{l_1}$,and $\boldsymbol{l_2}$	hex	2D in the plane
Col$_{\boldsymbol{Pr}}$	C_{2v}	parallel to $\boldsymbol{k}$	rect	1D along $\boldsymbol{k}$
Col$_{\boldsymbol{Pr2}}$	C_{2v}	parallel to $\boldsymbol{l_1}$ or $\boldsymbol{l_2}$	rect	1D along $\boldsymbol{l_1}$ or $\boldsymbol{l_2}$
Col$_{\boldsymbol{Pr1}}$	C_{1h}	as in Col$_{Ph1}$	rect	2D in the plane
Col$_{\boldsymbol{Pi2}}$	C_2	parallel to $\boldsymbol{l_1}$ or $\boldsymbol{l_2}$($\boldsymbol{n}$ tilted)	any	1D along $\boldsymbol{l_1}$ or $\boldsymbol{l_2}$
Col$_{\boldsymbol{Pi}}$	C_1	inclined to any of the planes $\boldsymbol{k}/\boldsymbol{l_1}$, $\boldsymbol{k}/\boldsymbol{l_2}$, or $\boldsymbol{l_1}/\boldsymbol{l_2}$ ($\boldsymbol{n}$ untilted) or inclined to any of the directions $\boldsymbol{k}$, $\boldsymbol{l_1}$or $\boldsymbol{l_2}$ ($\boldsymbol{n}$ tilted)	any	3D any orientation

The next term is characteristic of all ferroelectric materials. The terms $\sim\zeta_i^T$, ζ_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 second last term in Eq. (1) is related to piezoelectric effects coupling the electric field to in-plane deformations of the lattice built by the columns. This results in 9 (4) independent piezoelectric constants for C_1 (C_2) symmetry. In addition to these linear electric and electromechanical effects, the last term describes second harmonic generation, where $\chi_{ijk}^{(2)}$ contributes 10 (4) independent coefficients.

We note one important difference in this respect between smectic and columnar phases. For columnar phases, tilting the disk-shaped objects once can be sufficient to reach the lowest symmetry level, while in the smectic C_G phase, banana-shaped molecules have to be tilted twice, i.e. about two different orthogonal axes.

It should be noted however, that the homogeneous state as depicted in Figure 2 might not be the true ground state of that phase, because – due to the low C_1 symmetry – there are a host of possible first order gradient invariants in the free energy, allowing for spontaneous twist, splay and splay-bend structures [17] possibly leading to textured and frustrated structures.

3. THE TETRAHEDRATIC PHASE

In the tetrahedratic phase one has – in addition to the usual fields describing isotropic fluids – a third rank tensor T_{ijk} characterizing the tetrahedratic order. T_{ijk} is symmetric in all indices and traceless $T_{iik}=0$, i.e. it does not contain any vectorial quantity. Since it transforms under an $l=3$ representation of spherical harmonics, it is odd under parity and thus allows coupling terms not possible in ordinary simple liquids. It can be written as [7] $T_{ijk}=\sum_{\alpha=1}^{4} n_i^\alpha n_j^\alpha n_k^\alpha$ in terms of the 4 vectors n_i^α that form a tetrahedron. A tetrahedron has neither a mirror plane nor inversion symmetry and so does the tetrahedratic phase. Note that we deal only with the so-called nonchiral tetrahedratic phase, T_d, made by achiral molecules. The lack of inversion symmetry of a tetrahedron requires a tensor of odd rank as order parameter. Since the phase is not polar, which would contradict isotropy, a third rank tensor is the simplest possibility to describe tetrahedratic order. This third rank tensor cannot influence the form of second rank material tensors, like the dielectric tensor, and the tetrahedratic phase appears to be isotropic optically. However, there are other material properties described by higher-ranked tensors, like viscosity, where the non-isotropic nature of this phase becomes manifest.

In addition, the existence of T_{ijk} allows couplings described by third rank material tensors not possible in ordinary isotropic phases. When comparing the tetrahedratic phase to an ordinary isotropic phase in the dynamic regime, we have reversible couplings of velocity gradients $\sim T_{ijk}\nabla_j v_k$ [6] to the electric, entropy (energy), and concentration current and, vice versa, contributions to the stress tensor from electric fields $\sim T_{ijk}E_k$, temperature and concentration gradients $\sim T_{ijk}\nabla_k T$ and $\sim T_{ijk}\nabla_k c$.

This leads to simple experimentally testable predictions to enable a distinction between the novel tetrahedratic phase and the usual isotropic liquid. Applying, for example, a simple shear flow with the shear rate S to a tetrahedratic phase, this results in a reversible heat current as well as an electric current perpendicular to the shear plane $\sim S$. Reciprocally, one can apply an electric field in (z-direction), E_z (or a temperature, or a concentration gradient) to a sample in the tetrahedratic phase. The flow behavior is then affected by non-vanishing components of the stress tensor $\sigma_{yx}^R=\sigma_{xy}^R \sim E_z$. This result shows that an applied electric field gives rise to a shear stress in the plane perpendicular to the field. And this shear stress can in turn lead for spatially varying situations – via the dynamic equation for the linear momentum density or the velocity field – to a flow in the plane perpendicular to the direction of the applied field. The same applies to external gradients of temperature and concentration.

If the tetrahedratic phase is not built by rigid objects, but rather made of soft aggregates, as may expected for banana molecules, there is the possibility that the tetrahedratic structure is deformed by external forces [8]. Applying an external electric field, not only is the tetrahedratic structure oriented, but it is also deformed into a pyramidic structure of C_{3V} symmetry, which actually lowers the free energy of the system. The phase has then (induced) pyroelectricity and an (induced) macroscopic polarization. The effects of shear flow are even more drastic. Upon the tumbling of the structure, which is optically not detectable, there is time dependent periodic structural oscillation into a C_1-symmetric deformed structure. This can be detected as an oscillating birefringence, whose frequency is twice the shear rate [8]. Extensional flow, on the other hand, leads to a static deformation of the tetrahedral structure into a C_1-symmetric one.

4. THE B7 PHASE AND ITS ISOTROPIC NEIGHBOR

In the last section we discussed how the new terms in the tetrahedratic phase coupling flow to an external electric field as well as to temperature gradients could be experimentally detected. Here we suggest that a good candidate for the tetrahedratic phase may be the isotropic liquid state above the B7 phase for the following reasons.

Allowing for deformations of the tetrahedratic entities under external fields one can show [8] that T_d-symmetric structure may actually be transformed to a C_{3V}-symmetric one under a static electric field or to a locally C_1-symmetric (time-dependent) one under shear flow. Then, as temperature is lowered above an isotropic – B7 phase transition, one generates flow if an electric field or temperature variations are applied, provided the optically isotropic phase observed is tetrahedratic. For a deformable tetrahedratic phase the symmetry is then reduced drastically to C_1 in the presence of flow. Given the fact that the heat of transition observed for this phase transition is rather large [2,3,5] and comparable in magnitude to that observed for isotropic – pyramidic transitions [11], this leads us to suggest that the B7 phase could be a columnar phase with a macroscopic polarization [18]. This suggestion is further supported by the observation that B7 forms strands rather than freely suspended films [3,19] indicating at least locally a columnar structure. We also note that the same local C_1 symmetry (or rather the absence of any symmetry) will facilitate locally the transition from a deformed tetrahedratic structure to a columnar structure with an 'oblique' polarization.

To experimentally test the scenario outlined above a few crucial experiments are important. First, the question whether the B7 phase has a macroscopic polarization must be addressed. At this time there is no clearcut experimental result in the literature concerning this point. Second, it would be important to study in detail the physical properties of the optically isotropic phase above the B7 phase. Key question: is its symmetry reduced drastically when external forces are applied? Third, we predict in this scenario a phase transition from a classical isotropic fluid to a tetrahedratic phase.

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