

Columnar phases of three-fold molecular structures

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We study the occurrence of both positional and helical orders, for three-fold symmetric flat molecules in a columnar liquid crystal phase D_{hd} . Working in the group-theoretical Landau's framework, we identify a set of three order parameters giving rise to supercells of intercalated column with helical order and opposite helicities, as observed experimentally. The first-order nature of the transition is also discussed. The degrees of freedom introduced give rise to various other phases, including a new type, having helical order but no positional order along the columns.

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I. INTRODUCTION

In the framework of understanding the thermodynamical properties of aggregates of disk-shaped molecules, the study of phase transitions between columnar liquid crystal phases [1,2] is of fundamental interest. On the other hand, as organic materials with unusual properties such as high anisotropy in elasticity and electric conductivity [3], the columnar liquid crystals are currently seen as candidates for molecular electronic applications such as fast photoconductors, molecular wires and light emitting diodes [4]. While implications to other materials will be pointed out, the present work is justified primarily by the results for hexahexylthiotriphenylene (HHTT) liquid crystal made of molecules having a rigid core of aromatic cycles with six flexible tails of hydrocarbon chains.

By means of high resolution x-ray diffraction on both powders [5] and freely suspended strands [6,7], a number of phases have been identified for HHTT. In addition to the high temperature isotropic liquid I phase ($T > 93^\circ\text{C}$) and the low temperature monoclinic crystalline K phase ($T < 62^\circ\text{C}$), two intermediate phases have been observed. In the temperature range $T = [70, 93]^\circ\text{C}$, the D_{hd} phase is formed with a two-dimensional hexagonal ordering of disordered columns. In the temperature range, $T = [62, 70]^\circ\text{C}$, the more intricate D_{ho} (also called H) phase sets in. In what may be called the main feature of the D_{ho} phase, HHTT molecules are ordered or quasiordered along the columns, with one out of three columns displaced along the columnar axis by half the intermolecular distance, hence forming a $\sqrt{3} \times \sqrt{3} R 30^\circ$ (or honeycomb) superlattice in the hexagonal plane. This frustration-relieving intercolumn intercalation was recently studied in a phenomenological approach [8]. Starting with the symmetry group $G_0 = (R \otimes Z^2) \wedge D_{6h}$ and density $\rho_0(\mathbf{x})$ of the parent D_{hd} phase, the irreducible representation (IR) involved in the density increment $\delta\rho(\mathbf{x})$, appearing at the transition, was identified together with other related phases. Only an orientationally isotropic density increment was considered in the treatment. However, an important additional feature of the D_{ho} phase remains to be considered: helical ordering of the molecular tails sets in along each column at the phase transition. Lowering the temperature, a stiffening and extension of the six tails is ob-

served at the approach to the transition, with formation of a propeller-type conformation, in which every second tail is bended above the molecular plane with the next one bended below, resulting in a D_3 invariant structure. After consideration of various structures based on a detail mapping of the molecule's structure functions, the best-fitting model for the D_{ho} phase has a helical order present on each column. Adjacent molecules within a stack have a relative tail rotation of nearly 45° , in line with the analysis of intermolecular pairwise interactions and minimization of steric hindrance between tails for similar derivatives [16]. The vertically displaced column is found to have opposite helicity from the other two. Recent studies [9] have focused on this orientational order, assuming fixed crystalline molecular positions. Consequently, no theory has so far been proposed to account for the simultaneous occurrence of positional and orientational orders at the $D_{hd} \leftrightarrow D_{ho}$ transition in a phenomenological, symmetry-based description, as opposed to a detailed microscopic analysis. Our objective, in the present work, is to provide such a description. To account for both positional and helical orders occurring at the same temperature, a minimum of two IR's are expected to be involved at the phase transition, given the two independently measured wave vectors appearing along the broken columnar direction in the D_{ho} phase. Theories with more than one IR's have been invoked in other structural phase transitions, and are generally associated with strong coupling between the IR's [15]. In the present work, such coupling reflects the tail extension near the transition, and will be shown to play an important role as well.

The paper is organized as follows. In Sec. II, we present the model used to study the $D_{hd} \leftrightarrow D_{ho}$ transition, a model involving contributions from a total of three IR's with a free energy expansion developed to fourth order in the order parameter coefficients. In Sec. III, we obtain and describe a number of phases from the model, and point out salient symmetry features. Then in Sec. IV, we show how our model provides the lowest harmonics of an intercalated set of columns, with counter-rotating helical structures on each column, as experimentally observed in HHTT. Concluding remarks follow in Sec. V.

II. MODEL

The parent phase D_{hd} , composed of disordered columns on a triangular lattice (hence, featuring a continuous symme-

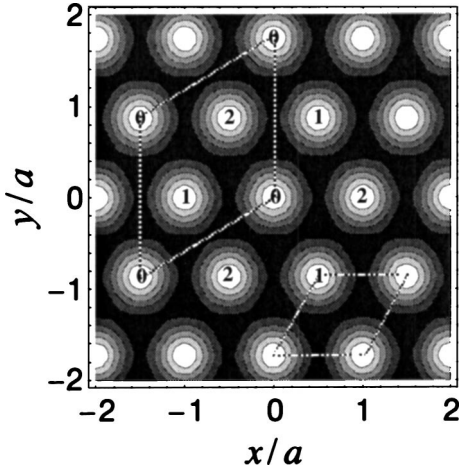


FIG. 1. Contour plot of the D_{hd} phase, after Eq. (2) (using $r_0 = 3/2$, $r_1 = 1$). Lighter regions are of higher density. Also shown are the D_{hd} and D_{ho} primitive cells and the column numbering.

try axis) has been classified as $G_0 = (R \otimes Z^2) \wedge D_{6h}$ [10]. To describe the D_{hd} phase in the plane orthogonal to columns, we pick for lattice generators

$$\begin{aligned} \mathbf{b}_1 &= a \hat{\mathbf{e}}_x, & \mathbf{b}_2 &= \frac{a}{2} \hat{\mathbf{e}}_x + \frac{\sqrt{3}}{2} a \hat{\mathbf{e}}_y, \\ \mathbf{B}_1 &= \frac{2\pi}{a} \left(\hat{\mathbf{e}}_x - \frac{1}{\sqrt{3}} \hat{\mathbf{e}}_y \right), & \mathbf{B}_2 &= \frac{4\pi}{\sqrt{3}a} \hat{\mathbf{e}}_y. \end{aligned} \quad (1)$$

$\mathbf{B}_1, \mathbf{B}_2$ are the two basic vectors in the reciprocal space. To the lowest order in the modulation, one may express the density as

$$\rho_0(\mathbf{x}) = r_0 + r_1 \sum_{i=1}^3 \cos(\mathbf{B}_i \cdot \mathbf{x}), \quad (2)$$

where $\mathbf{B}_3 = -(\mathbf{B}_1 + \mathbf{B}_2)$. A contour plot of ρ_0 is shown in Fig. 1. In the Landau's framework, the modification in density taking place at the transition point is written as

$$\rho(\mathbf{x}) = \rho_0(\mathbf{x}) + \delta\rho(\mathbf{x}), \quad (3)$$

where the density increment $\delta\rho$ is expanded on a basis spanning at least one IR of G_0 . Following the symmorphic nature of G_0 , IR's are identified by a vector \mathbf{k} of high symmetry in the first Brillouin zone of the parent phase along with an IR of the corresponding little group [11]. The IR suitable for positional order, IR1, is associated with the positioning of the disk-shaped molecules [8]. It is obtained from the vector $\mathbf{k}_0 = \mathbf{A}_1 + \mathbf{C}_1$, with \mathbf{A}_1 on the edge of the Brillouin zone and $\mathbf{C}_1 = (2\pi/c_1)\hat{\mathbf{e}}_z$ along the columnar direction. Specifically, we introduce the second set of reciprocal space vectors $\mathbf{A}_1 = \frac{2}{3}\mathbf{B}_1 + \frac{1}{3}\mathbf{B}_2 + \mathbf{C}$, $\mathbf{A}_2 = (\mathbf{B}_2 - \mathbf{B}_1)/3$, and $\mathbf{A}_3 = -(\mathbf{A}_1 + \mathbf{A}_2)$, making 120° between themselves. The associated little group is C_{3v} , whose characters are provided in Table I. Picking the invariant representation A_1 , one may write a density increment as

TABLE I. Character table of C_{3v} .

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$$\delta\rho_1 = (\gamma_+ u_+ + \gamma_- u_-) + \text{c.c.}, \quad (4)$$

with basis functions $u_{\pm}(\mathbf{x}) = \sum_{i=1}^3 e^{i(\mathbf{A}_i \pm \mathbf{C}_1) \cdot \mathbf{x}}$ and complex order parameters γ_+ and γ_- . Minimization of the free energy for IR1 has been shown [8] to lead to three distinct phases, all featuring a $\sqrt{3} \times \sqrt{3} R$ 30° superlattice and breaking of the z -translation symmetry. Among them, phase 2A was identified with the intercalated columnar positioning of the molecules in the D_{ho} phase. Namely, the pattern $(0, \frac{1}{2}, \frac{1}{2})$ was found, where the relative positions of the density increment maxima are indicated in units of the period c_1 along the z axis, for columns 0, 1, and 2.

In order to treat the orientational aspects, the essential step is to invoke one or more IR's of G_0 appropriate to account for the additional symmetry breaking brought about by the counter-rotative helicoidal structure present in the D_{ho} phase [7]. Based on the three-fold symmetry of the HHTT molecules, along with the Bragg peak structure found experimentally [7], the helicoidal phase is expected to preserve $2C_3$, but break all σ_{A_i} , σ_{B_i} , σ_H , $2S_6$, i , $2S_3$, and C_2 . Here, σ_{A_i} are vertical mirrors cutting through \mathbf{A}_i , and similarly for σ_{B_i} . σ_H is the horizontal plane perpendicular to the columnar direction. Other operations follow Shoenflies's notation with the rotation axis along a column.

The natural starting point is among the IR's based on the similar wave vector $\mathbf{k}_0 = \mathbf{A}_1 + \mathbf{C}_1$ and little group C_{3v} that was used in finding IR1. So after selecting a different wave vector $\mathbf{C}_2 = (2\pi/c_2)\hat{\mathbf{e}}_z$ along the columnar direction (z axis), we form $\mathbf{k}_1 = \mathbf{A}_1 + \mathbf{C}_2$ and form IR2 based on A_1 of the little group C_{3v} . The star ensemble has four components, $\mathbf{k}_1^* = \{\pm \mathbf{A}_1 \pm \mathbf{C}_2\}$, and we use basis functions Sv_+ and Sv_- along with their complex conjugates, where

$$v_{\pm}(\mathbf{x}) = \sum_{i=1}^3 e^{i(\mathbf{A}_i \pm \mathbf{C}_2) \cdot \mathbf{x}} \quad (5)$$

and

$$S = R^{*3} - R^3, \quad R = \sum_{n=1}^3 e^{i(2\pi n/3)} \sin \mathbf{B}_n \cdot \mathbf{x}. \quad (6)$$

The function S , invariant under the small lattice translations, preserves the C_3 symmetries along the z axis and the vertical mirror σ_{A_i} , but nevertheless breaks the vertical mirrors σ_{B_i} . It will be seen, however, that the combination IR1 and IR2 are by themselves insufficient to reproduce the rotational degrees of freedom of the HHTT molecules.

We then add IR3 built from yet another different wave vector $\mathbf{k}_2 = \mathbf{C}_2$, whose vanishing in-plane component has

been shown to obey Lifshitz condition in two dimensions [12]. In this case, the star space is two dimensional $\mathbf{k}_2^* = \{\pm \mathbf{C}_2\}$ and the (larger) little group C_{6v} has a total of six possible IR's. Among them, we pick the one-dimensional B_2 , whose characters are listed in Table II, forming basis functions $T e^{i\mathbf{C}_2 \cdot \mathbf{x}}$ and its complex conjugate, where $T = R^{*3} + R^3$. Putting together the three IR's, one has in total $\delta\rho = \delta\rho_1 + \delta\rho_2 + \delta\rho_3$, with expansions given by Eq. (4), along with

$$\begin{aligned} \delta\rho_2 &= S(\eta_+ v_+ + \eta_- v_-) + c.c., \\ \delta\rho_3 &= \varepsilon T e^{i\mathbf{C}_2 \cdot \mathbf{x}} + c.c. \end{aligned} \quad (7)$$

for IR2 and IR3, respectively. The complex order parameters γ_{\pm} , η_{\pm} , ε are of total dimension ten. We define their phase angles through $\gamma_{\pm} = |\gamma_{\pm}| e^{i\varphi_{\pm}}$, $\eta_{\pm} = |\eta_{\pm}| e^{i\theta_{\pm}}$, $\varepsilon = |\varepsilon| e^{i\phi}$, and also introduce mean and differential phase angles

$$\varphi_{\pm} = \varphi_m \pm \frac{1}{2} \varphi_d, \quad \theta_{\pm} = \theta_m \pm \frac{1}{2} \theta_d. \quad (8)$$

Up to fourth order, the free energy has the following order parameter expansion:

$$\begin{aligned} F_4 &= \alpha(|\gamma_+|^2 + |\gamma_-|^2) + \frac{\beta_1}{2}(|\gamma_+|^4 + |\gamma_-|^4) + \beta_2 |\gamma_+|^2 |\gamma_-|^2 \\ &+ \alpha'(|\eta_+|^2 + |\eta_-|^2) + \frac{\beta'_1}{2}(|\eta_+|^4 + |\eta_-|^4) \\ &+ \beta'_2 |\eta_+|^2 |\eta_-|^2 + \alpha'' |\varepsilon|^2 + \frac{\beta''}{2} |\varepsilon|^4 + \mu_1 (|\eta_+|^2 |\gamma_+|^2 \\ &+ |\eta_-|^2 |\gamma_-|^2) + \mu_2 (|\eta_+|^2 |\gamma_-|^2 + |\eta_-|^2 |\gamma_+|^2) \\ &+ \lambda_1 |\varepsilon|^2 (|\gamma_+|^2 + |\gamma_-|^2) + \lambda_2 |\varepsilon|^2 (|\eta_+|^2 + |\eta_-|^2) \\ &+ \lambda_3 (\eta_- \eta_+^* \varepsilon^2 + c.c.), \end{aligned} \quad (9)$$

where the individual parts of each IR has been included, along with the lowest order coupling between one another. Note that the last term is the only one involving the phase angles of the order parameters.

TABLE II. Character table for representation B_2 of point group C_{6v} .

C_{6v}	E	C_2	$2C_3$	$2C_6$	$3\sigma_v$	$3\sigma_d$
B_2	1	-1	1	-1	-1	1

III. STABLE PHASES

Depending on the signs and magnitudes of the expansion coefficients, the free energy (9) admits a number of stable phases. In this section, we study many of these phases, always demanding the presence of C_3 symmetry. We consider the results for one and two IR's, keeping the case of three IR's for the following section, where references to the experimental results for HHTT will be made explicitly. We also focus on the lowest order stable point in coefficient's space. In general, of course, higher order terms in the free energy could provide additional stable points and consequently affect the nature of the transition between different phases.

A. Single IR solutions

The stable phases with $(\eta_+ = \eta_- = \varepsilon = 0)$ involving only the degrees of freedom of IR1 have already been studied [8]. Of the three phases found, one has the columnar pattern $(0, \frac{1}{3}, \frac{2}{3})$ and two have the pattern $(0, \frac{1}{2}, \frac{1}{2})$. In the latter, phase 2A was found to display the intercalated column pattern occurring in the D_{ho} phase of HHTT. Turning to the solutions, where $\gamma_+ = \gamma_- = \varepsilon = 0$ involving only IR2, it is to be noted that the free energy for IR2 is identical to that for IR1. As such, the stable phases are identical, as far as symmetries are concerned (up to the change of $c_1 \rightarrow c_2$). However, chosen to describe helical order, our basis functions (5) for IR2 are quite different than that for IR1, and the actual density configurations look fairly different as a result. The first such phase, R2-1, has $|\eta_+| = \sqrt{-\alpha'/\beta'_1}$ and $\eta_- = 0$ (or vice versa) and a density increment $\delta\rho_2$ given by

$$\delta\rho_2 = 2|\eta_+| i S \sum_{i=1}^3 \sin(\mathbf{A}_i + \mathbf{C}_2) \cdot \mathbf{x}, \quad (10)$$

with contour plots as shown in Fig. 2, where the unmodu-

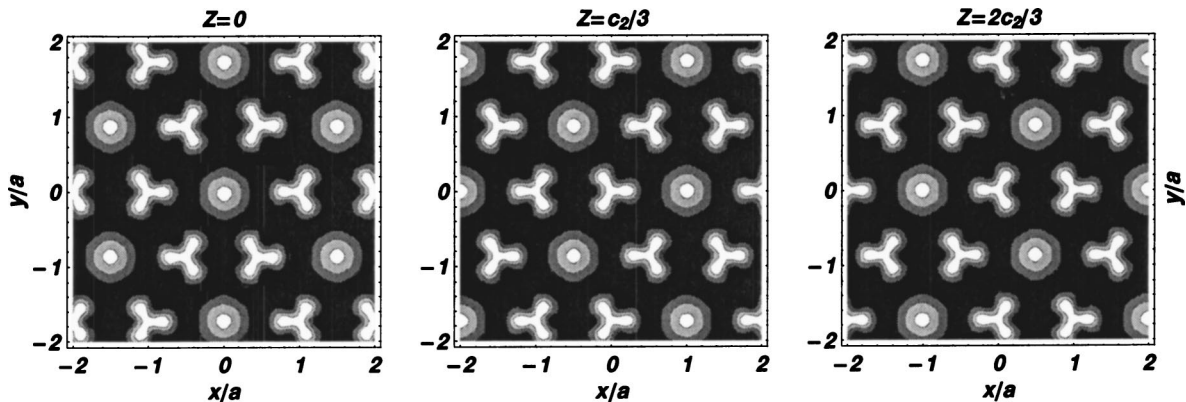


FIG. 2. Plots of phase R2-1: $\rho_0 + \delta\rho_2$, with $\delta\rho_2$ given in Eq. (10), and using $|\eta_+| = 0.06$.

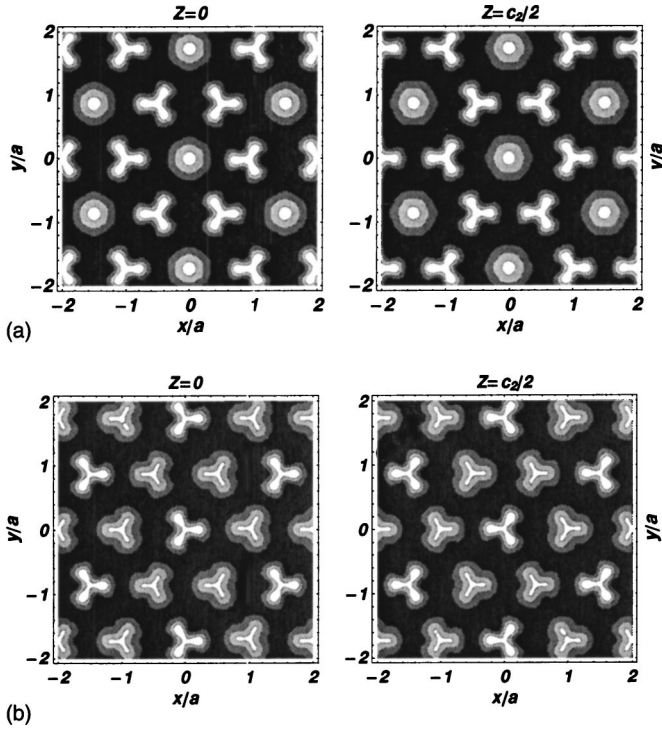


FIG. 3. Plots $\rho_0 + \delta\rho_2$, where $\delta\rho_2$ is given in Eq. (11) with $\eta = 0.03$. (a) Phase R2-2 with $\theta_m = 0$ and (b) Phase R2-3 with $\theta_m = \pi/2$.

lated column number shifts from 0, to 2, to 1, as one moves along the z axis in steps of $c_2/3$. As discussed previously, the degenerate phase $|\eta_-| = \sqrt{-\alpha'/\beta'_1}$ and $\eta_+ = 0$ are similar to the above, but are nevertheless topologically distinct [8].

A different set of solutions for IR2 has two nonvanishing and equal amplitudes $|\eta_+| = |\eta_-| \equiv \eta = \sqrt{-\alpha' / (\beta'_1 + \beta'_2)}$ giving rise to a density increment

$$\delta\rho_2 = 4\eta i S \cos \mathbf{C}_2 \cdot \mathbf{x} \sum_{i=1}^3 \sin(\mathbf{A}_i \cdot \mathbf{x} + \theta_m), \quad (11)$$

where the mean phase angle θ_m is determined by the sixth-order term $\nu_2(\eta_+^3 \eta_-^3 + \text{c.c.}) = 2\nu_2 \eta^6 \cos 6\theta_m$. The sign of ν_2 allows for two groups of degenerate configurations,

$$\theta_m = \begin{cases} 0, \pm \frac{\pi}{3}, \pm \frac{2\pi}{3}, \pi, & \text{degenerate} \\ \pm \frac{\pi}{6}, \pm \frac{\pi}{2}, \pm \frac{5\pi}{6} & \text{degenerate,} \end{cases} \quad (12)$$

where the first group is favored for $\nu_2 < 0$. All degenerate configurations in Eq. (12) are equivalent, being related through a column translation or shifted along the z axis by half a period $c_2/2$. The contour plots for both cases $\theta_m = 0$ and $\theta_m = \pi/2$ are shown in Fig. 3. It is seen that for $\theta_m = 0$ (Phase R2-2), $\delta\rho(x=y=0) = 0$. That is, column 0 remains completely disordered. For each period c_2 , columns 1 and 2 are stacks of three-fold molecules, with a 60° phase shift between adjacent molecules in a column and between columns 1 and 2 at the same vertical level. Phase R2-2 is highly

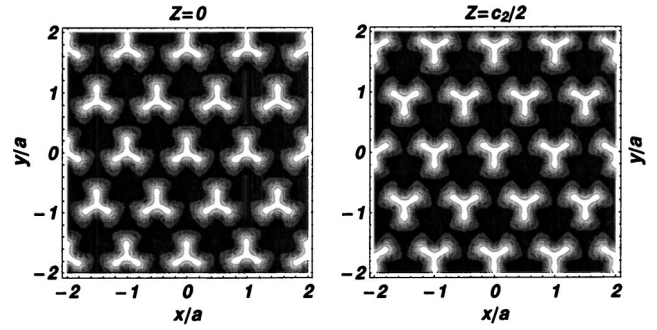


FIG. 4. Plots of phase R3: $\rho_0 + \delta\rho_3$ with $\delta\rho_3$ given in Eq. (13), where $|\varepsilon| = 0.1$.

symmetric and the entire point group D_{6h} of G_0 is preserved. Only translation symmetries are broken (i.e., continuous z translations and discrete in-plane hexagonal Bravais lattice vector translations). For $\theta_m = \pi/2$ (phase R2-3), column 0 is also changed. All three columns are modulated along the z axis and column 0 is phase shifted by 60° with respect to columns 1 and 2. Phase R2-3 has fewer symmetries left, with $C'_2(\mathbf{A}_i)$ (C_2 rotations around \mathbf{A}_i 's axis), $\sigma_{\mathbf{A}_i}$, $2S_3$, and σ_h surviving.

A solution exists, for IR3 alone with $|\varepsilon| = \sqrt{-\alpha''/\beta''}$ and

$$\delta\rho_3 = 2|\varepsilon| T \cos \mathbf{C}_2 \cdot \mathbf{x}, \quad (13)$$

where the phase angle ϕ of ε was “gauged away” by shifting the z axis. Plots of phase R3 from Eq. (13) are shown in Fig. 4, where it is seen how all the three columns in a superlattice cell have three-fold molecules at the same height. Within a given column, adjacent molecules are phase shifted by 60° . We note that by itself, phase R3 leaves both $\sigma_{\mathbf{B}_i}$ and σ_h unbroken, and it is thus unsuitable to describe helical structures. Nevertheless, these phases are allowed based on symmetry considerations for the two-dimensional hexagonal structure in the plane. To our knowledge, they have not been observed.

B. Two IR solutions

A few solutions are possible with $\varepsilon = 0$ (involving only IR1 and IR2). One of them has $\gamma_- = \eta_- = 0$ and

$$|\gamma_+| = \sqrt{\frac{\alpha' \beta_1 - \alpha \mu_1}{\mu_1^2 - \beta_1 \beta'_1}}, \quad (14)$$

$$|\eta_+| = \sqrt{\frac{\alpha' \mu_1 - \alpha \beta'_1}{\mu_1^2 - \beta_1 \beta'_1}}.$$

The associated modulation is

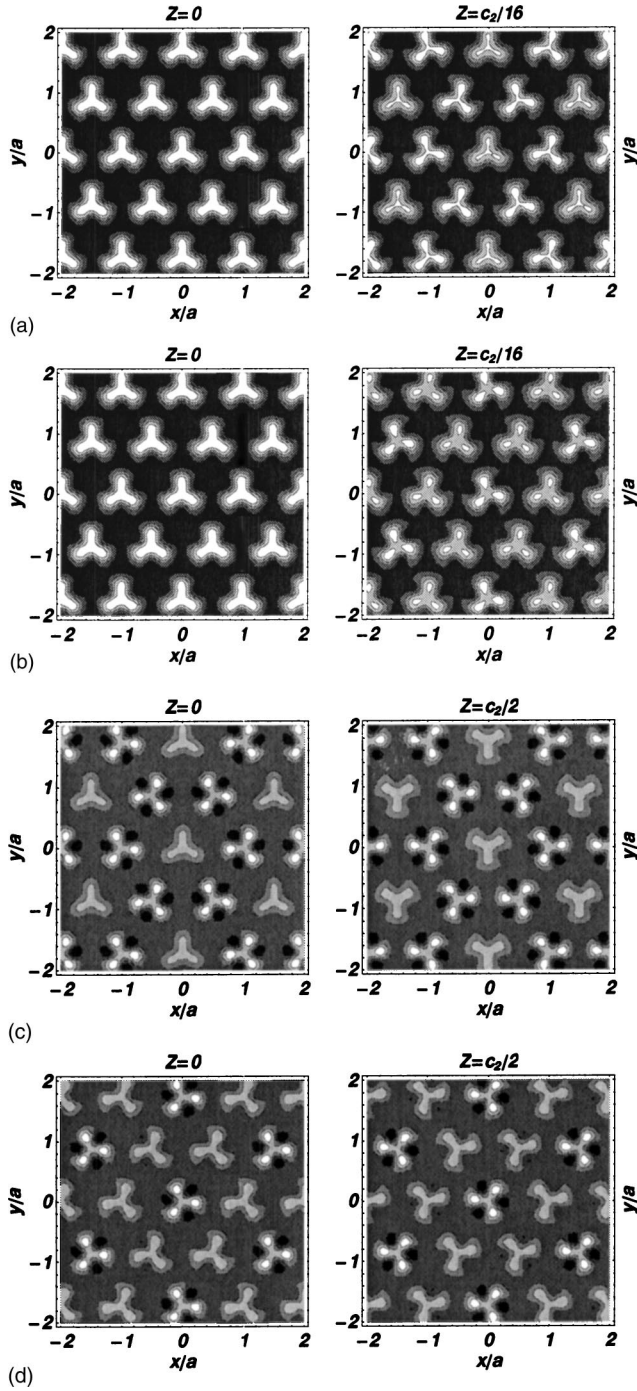


FIG. 5. Plots of $\rho_0 + \delta\rho_2 + \delta\rho_3$ in Eq. (17), with $\eta = 0.06$ and $|\varepsilon| = 0.09$. (a) Phase R23-1 with $n = -1$ and $\theta_m = 0$, (b) phase R23-2 with $n = -1$ and $\theta_m = \pi/2$, (c) phase R23-3 with $n = 0$ and $\theta_m = 0$, and (d) phase R23-4 with $n = 0$ and $\theta_m = \pi/2$.

$$\delta\rho = 2|\gamma_+| \sum_{i=1}^3 \cos[(\mathbf{A}_i + \mathbf{C}_1) \cdot \mathbf{x}] + 2|\eta_+| iS \times \sum_{i=1}^3 \sin[(\mathbf{A}_i + \mathbf{C}_2) \cdot \mathbf{x} + \theta_+ - (c_1/c_2)\varphi_+], \quad (15)$$

with a degenerate configuration having instead $\gamma_+ = \eta_+ = 0$ and $|\gamma_-|, |\eta_-|$ given by Eq. (15), with the change in sub-

scripts $+\leftrightarrow-$ and $\mathbf{C}_2 \rightarrow -\mathbf{C}_2$. In order to fix the phase angle $\theta_+ - (c_1/c_2)\varphi_+$ in Eq. (15), a term of the form $\gamma_+^n \eta_+^{*m} + \dots$ is necessary in the free energy. From the z translation invariance, the condition $n/m = c_1/c_2$ must be obeyed between integers n and m . Also, m must be even owing to the sign reversal of η_+ under the vertical mirror symmetries. Moreover, in-plane lattice translations by $n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2$ imposes the condition $n - m = 3p$, where p is an integer. Under these constraints, the possible ratios $3c_2/c_1$ are then the fractions $3(4)$, $\frac{6}{5}(7)$, $\frac{3}{4}(10)$, $\frac{12}{7}(11)$, etc., where the number in parenthesis is the (lowest) order of appearance in the expansion of the free energy. Physically realized helical order should have $3c_2 > c_1$, where the factor 3 in the period ratio originates in the three-fold helix structure [13]. The first case (with $3c_2/c_1 = 3$) indicates a rotation of 120° between adjacent molecules in a column (and hence, no rotation at all). The second possibility with $3c_2/c_1 = 6/5$ comes with an angle of $\pi/3$ between consecutive molecules representing only a molecular inversion rather than a rotation. A complementary solution to the free energy minimization is instead with $\gamma_- = \eta_+ = 0$. In that case, the phase angle $\theta_+ + (c_1/c_2)\varphi_-$ is fixed by a term in the free energy of the form $\gamma_+^n \eta_-^m + \dots$. The allowed ratios $3c_2/c_1$ are then $6(3)$, $\frac{3}{2}(6)$, $\frac{4}{7}(9)$, $\frac{12}{5}(9)$, etc. But in both cases with $3c_2/c_1 > 1$, only molecular inversion is again present. Thus, despite a large amount of symmetry breaking taking place in phases arising from IR1 and IR2, none of them is suitable for the type of helical order observed in HHTT. We also note how by construction, in all such cases, the ratio c_1/c_2 can only be a rational number, contrary to the experimental results for helical order in HHTT.

Considering other solutions to the free energy minimization, none exist where only γ_+ , γ_- , and η_+ are vanishing. This is somewhat expected, since it would represent a mixture of two types of columnar modulations $[(0, \frac{1}{3}, \frac{2}{3})$ and $(0, \frac{1}{2}, \frac{1}{2})$ vertical displacements]. However, minimization of Eq. (9) admits solutions with $|\eta_+| = |\eta_-| \equiv \eta$ and $\varepsilon \neq 0$ (IR2 + IR3) as long as the relation

$$\theta_d - 2\phi = n\pi \quad (16)$$

is fulfilled between the order parameter phase angles in Eq. (8). The integer n is fixed by the sign of λ_3 in Eq. (9). For $\lambda_3 > 0$, n is odd and even for the opposite case $\lambda_3 < 0$. The increments are

$$\delta\rho_2 = 4\eta iS \cos\left(\mathbf{C}_2 \cdot \mathbf{x} + \frac{n\pi}{2}\right) \sum_{i=1}^3 \sin(\mathbf{A}_i \cdot \mathbf{x} + \theta_m), \quad (17)$$

$$\delta\rho_3 = 2|\varepsilon|T \cos \mathbf{C}_2 \cdot \mathbf{x},$$

where θ_m is fixed by Eq. (12). Consider the case where $n = -1$ and $\theta_m = 0$, which gives rise to phase R23-1 as shown in Fig. 5. It is seen that in this case, columns 1 and 2 have opposite helicities. Column 0 is not rotating but instead represents a stack of two molecules per period, equidistant and in antiphase. Of the symmetries of G_0 , only $C_2'(\mathbf{B}_i)$ (C_2

rotations around \mathbf{B}_i 's axis) is preserved but the screw symmetry, nevertheless, exists as obtained by shifting the z axis by an amount $c_2/2$ and (C_6 or C_2).

A physically more interesting case is for $n = -1$ and $\theta_m = \pi/2$, which gives rise to phase R23-2. In phase R23-2, column 0 rotates in the opposite direction with respect to columns 1 and 2. This is in line with the rotational pattern observed experimentally for HHTT. Obviously, no mirror symmetry exists in that phase. In fact, both the modulation $\delta\rho$ and its gradient $\nabla\delta\rho$ are vanishing at the column centers (i.e., $\mathbf{x} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2$), despite the orientational order. The density (17) thus models a new type of liquid crystal, which can be thought as a one-dimensional analog of the nematic order. Indeed, the columns are disordered with respect to positions, yet are ordered with respect to their azimuthal angles. It is interesting to note that while IR2 or IR3 alone is insufficient to yield molecular rotations, the sum of the two does provide the observed helical structure along the columnar axis.

Of course, this is only true because we have picked $n = -1$ in the above.

A different result is obtained when $n = 0$ and $\theta_m = 0$, which gives rise to phase R23-3. In this case, on each column, two molecules are equidistant, and stacked in antiphase. However, the molecular alignment does not coincide with the lattice geometry, breaking many more symmetries. Fourthly, in the situation where $n = 0$ and $\theta_m = \pi/2$, phase R23-4 is obtained, where once again, each column has two three-fold molecules per period.

IV. INTERCALATED HELICOIDAL ORDER

A case of special interest in the present work is the one involving all three IR's introduced in Secs. II and III. Within this set, we specialize to the case of equal amplitudes within each IR: $|\eta_+| = |\eta_-| \equiv \eta$ and $|\gamma_+| = |\gamma_-| \equiv \gamma$. To the lowest order, minimization of the free energy (9) provides values for the amplitudes η , γ , and $|\varepsilon|$ with

$$\begin{aligned}\gamma &= \sqrt{\frac{\alpha(2\lambda^2 - \beta''\beta') + \alpha'(\beta''\mu - 2\lambda\lambda_1) - \alpha''(\lambda\mu - \lambda_1\beta')}{\beta''(\beta\beta' - \mu^2) + 2\lambda_1(\lambda\mu - \lambda_1\beta') + 2\lambda(\lambda_1\mu - \lambda\beta)}}, \\ \eta &= \sqrt{\frac{\alpha(\beta''\mu - 2\lambda\lambda_1) + \alpha'(2\lambda_1^2 - \beta''\beta) - \alpha''(\lambda_1\mu - \lambda\beta)}{\beta''(\beta\beta' - \mu^2) + 2\lambda_1(\lambda\mu - \lambda_1\beta') + 2\lambda(\lambda_1\mu - \lambda\beta)}}, \\ |\varepsilon| &= \sqrt{\frac{-2\alpha(\lambda\mu - \lambda_1\beta') - 2\alpha'(\lambda_1\mu - \lambda\beta) - \alpha''(\beta\beta' - \mu^2)}{\beta''(\beta\beta' - \mu^2) + 2\lambda_1(\lambda\mu - \lambda_1\beta') + 2\lambda(\lambda_1\mu - \lambda\beta)}},\end{aligned}\quad (18)$$

where use was made of the effective expansion coefficients $\mu \equiv \mu_1 + \mu_2$, $\beta \equiv \beta_1 + \beta_2$, $\beta' \equiv \beta'_1 + \beta'_2$, and $\lambda \equiv \lambda_2 + (-)^n\lambda_3$. In such phases, the total density increment takes the form,

$$\begin{aligned}\delta\rho_1 &= 4\gamma \cos \mathbf{C}_1 \cdot \mathbf{x} \sum_{i=1}^3 \cos(\mathbf{A}_i \cdot \mathbf{x} + \varphi_m), \\ \delta\rho_2 &= 4\eta i S \cos\left(\mathbf{C}_2 \cdot \mathbf{x} + \Delta + \frac{n\pi}{2}\right) \sum_{i=1}^3 \sin(\mathbf{A}_i \cdot \mathbf{x} + \theta_m), \\ \delta\rho_3 &= 2|\varepsilon| T \cos(\mathbf{C}_2 \cdot \mathbf{x} + \Delta),\end{aligned}\quad (19)$$

where $\Delta = \phi - (c_1/c_2)(\varphi_d/2)$. In obtaining Eq. (19), the condition (16) was imposed, and the z axis was shifted moving the phase angle φ_d into $\delta\rho_2$ and $\delta\rho_3$. The mean phase angles φ_m and θ_m in Eq. (19) are determined by way of the following set of sixth-order terms

$$\begin{aligned}\nu_1(\gamma_+^3\gamma_-^3 + \text{c.c.}) &= 2\nu_1\gamma^6 \cos 6\varphi_m, \\ \nu_2(\eta_+^3\eta_-^3 + \text{c.c.}) &= 2\nu_2\eta^6 \cos 6\theta_m,\end{aligned}\quad (20)$$

$$\nu_3(\gamma_+\gamma_-\eta_+^2\eta_-^2 + \text{c.c.}) = 2\nu_3\gamma^2\eta^4 \cos(4\theta_m + 2\varphi_m),$$

$$\nu_4(\gamma_+^2\gamma_-^2\eta_+\eta_- + \text{c.c.}) = 2\nu_4\gamma^4\eta^2 \cos(2\theta_m + 4\varphi_m).$$

For some subset in the range of the coefficients ν_1, ν_2, ν_3 , and ν_4 , no competition exists among the terms in Eq. (20). In Table III, the values of φ_m, θ_m are given in such cases up to equivalent configurations related by the choice of column (0, 1, or 2) and the choice of rotational direction. When the signs of the ν_1, ν_2, ν_3 , and ν_4 are not one of the combinations listed in Table III, φ_m and θ_m continue to be multiples of $\pi/6$, at the cost, however, of frustrating minimization of

TABLE III. Cases of no competition in the minimization of the sixth-order terms in the free energy.

Phase	ν_1	ν_2	ν_3	ν_4	φ_m	θ_m
R123-1	<0	<0	<0	<0	0	0
R123-2	>0	>0	>0	>0	$\pi/2$	$\pi/2$
R123-3	>0	<0	>0	<0	$\pi/2$	0
R123-4	<0	>0	<0	>0	0	$\pi/2$

least one of the terms in Eq. (20). Of course, in that case, the existence of a nonvanishing γ and η may not be energetically sustainable anymore as determined at fourth order.

Consider the case of phase *R123-4* with $\varphi_m=0$ and $\theta_m=\pi/2$. Suppose further that $\Delta=0$. The increment (19) is then further simplified into

$$\begin{aligned}\delta\rho_1 &= 4\gamma \cos \mathbf{C}_1 \cdot \mathbf{x} \sum_{i=1}^3 \cos \mathbf{A}_i \cdot \mathbf{x}, \\ \delta\rho_2 &= 4\eta i S \sin \mathbf{C}_2 \cdot \mathbf{x} \sum_{i=1}^3 \cos \mathbf{A}_i \cdot \mathbf{x}, \\ \delta\rho_3 &= 2|\varepsilon| T \cos \mathbf{C}_2 \cdot \mathbf{x},\end{aligned}\quad (21)$$

where $n=-1$ was chosen for producing the helical structure. Contour plots of $\delta\rho_1 + \delta\rho_2 + \delta\rho_3$ in Eq. (21) are presented in Fig. 6 for the case where $c_2/c_1=8/3$. The counter-rotating structure found experimentally, model III in Ref. [7], is seen to correspond to this phase *R123-4*. Namely, the helicity of columns 1 and 2 are the same and opposite to that of column 0. A helical phase shift of 60° was noted in the analysis of Ref. [7] between columns 1 and 2 on one hand and column 0 on the other. However, in view of the noncommensurate nature of the ratio c_2/c_1 , we consider the value of 60° to be rather arbitrary as all phase shift values are essentially covered as one moves along the z axis for an incommensurate situation. In the present analysis, an incommensurate value of c_2/c_1 indeed does not allow a term in the free energy to fix the value of Δ , leaving it arbitrary. The contour of Fig. 6 also differs from the one in Ref. [7] by the density obtained between molecules, for example, on column 0 at $z=c_1/2$. In the present case, working on the lowest harmonics of the modulations and focusing on the symmetries, fine features such as the molecular tails sticking out of the molecular plane are not reproduced.

Experimentally, the $D_{hd} \leftrightarrow D_{ho}$ phase transition was reported to be of weak first order [7]. To study the nature of the transition, we complement our model of F_4 in Eq. (9) with the following set of sixth-order terms, introduced to ensure stability of the phases, in each of the order parameters:

$$\begin{aligned}F' &= \chi_1(|\gamma_+|^6 + |\gamma_-|^6) + \chi_2|\gamma_+|^2|\gamma_-|^2(|\gamma_+|^2 + |\gamma_-|^2) \\ &+ \nu_1(\gamma_+^3\gamma_-^3 + \text{c.c.}) + \chi_3(|\eta_+|^6 + |\eta_-|^6) + \chi_4|\eta_+|^2 \\ &\times |\eta_-|^2(|\eta_+|^2 + |\eta_-|^2) + \nu_2(\eta_+^3\eta_-^3 + \text{c.c.}) + \chi_5|\varepsilon|^6.\end{aligned}\quad (22)$$

In phases *R123*'s introduced above, where no competition is present between phase angle fixing terms, the terms with coefficients ν_3 and ν_4 in Eq. (20) do not play an essential role. Along with other possible sixth-order coupling terms, they are not retained in Eq. (22) for simplicity. Specializing to the case of equal amplitudes for IR1 and IR2 (i.e., $|\eta_+|=|\eta_-|\equiv\eta$ and $|\gamma_+|=|\gamma_-|\equiv\gamma$), and also using Eq. (16), an effective free energy is obtained from $F_4 + F'$ for the order parameter's amplitudes:

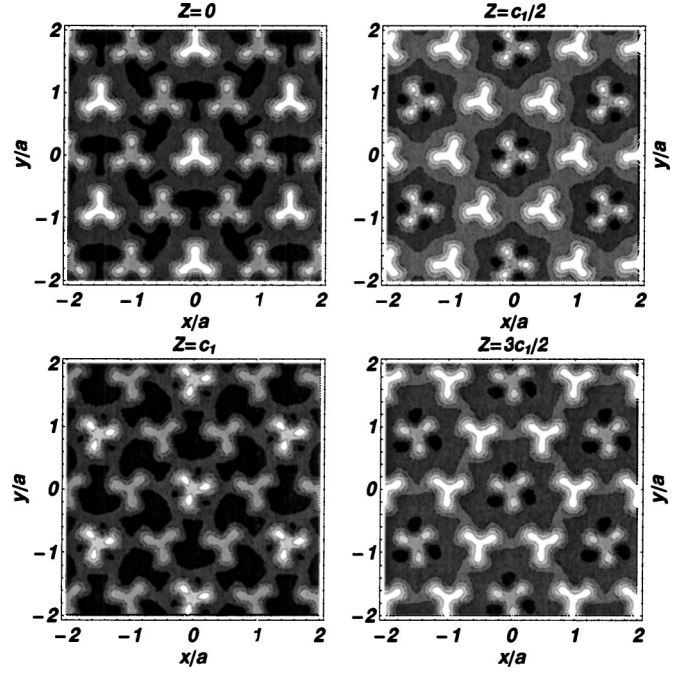


FIG. 6. Counter-rotating helical phase *R123-4* $\rho_0 + \delta\rho_1 + \delta\rho_2 + \delta\rho_3$ as specified in Eq. (21), using $\gamma=0.12, \eta=0.04, \varepsilon=0.12$.

$$\begin{aligned}F_{eff} &= 2\alpha\gamma^2 + \beta\gamma^4 + \sigma_1\gamma^6 + 2\alpha'\eta^2 + \beta'\eta^4 + \sigma_2\eta^6 \\ &+ 2\alpha''|\varepsilon|^2 + \frac{1}{2}\beta''|\varepsilon|^4 + \sigma_3|\varepsilon|^6 + 2\mu\eta^2\gamma^2 \\ &+ 2\lambda_1|\varepsilon|^2\gamma^2 + 2\lambda|\varepsilon|^2\eta^2.\end{aligned}\quad (23)$$

The potential described by Eq. (23) generalizes to three dimensions, the symmetric model studied in Ref. [15], involving the interaction of two order parameters with biquadratic coupling. The sixth-order coefficients σ_i 's are assumed to be all positive. In order to obtain a first-order transition between the parent phase with $\eta=\gamma=|\varepsilon|=0$, directly to a phase of the type *R123*, with all nonvanishing amplitudes, the fourth order coefficients β, β', β'' should be positive. However, the couplings μ, λ, λ_1 ought to be negative so as to favor simultaneous occurrence of more than one order parameter. As the temperature is modified, a trajectory is defined in the three-dimensional space of quadratic couplings $\alpha, \alpha', \alpha''$. Upon approaching the origin from the positive quadrant $\alpha, \alpha', \alpha'' > 0$ (bringing down the temperature), a first-order transition will take place provided that the following set of conditions are verified:

$$\begin{aligned}\beta\beta' - \mu^2 &> 0, \\ \beta\beta'' - 2\lambda_1^2 &> 0, \\ \beta'\beta'' - 2\lambda^2 &> 0,\end{aligned}\quad (24)$$

along with the global condition

$$\beta\beta'\beta'' - 2\beta\lambda^2 - 2\beta'\lambda_1^2 - \beta''\mu^2 + 4\mu\lambda\lambda_1 < 0. \quad (25)$$

Note how conditions (24) impose limits to the amplitude of any individual coupling between the order parameters, and serve to rule out transitions to phases with only two nonzero order parameters. The condition (25) ensures that the combination of couplings are sufficiently strong to trigger the transition.

V. CONCLUSION

We have presented a model involving a total of three irreducible representations with explicit base functions representing three-fold molecules. Fixing of angle phases and thermodynamic stability required an expansion of the Landau coefficients up to the sixth order. We have discussed a number of, hitherto unobserved phases related to the hexagonal array of liquid columns by a group-subgroup relation. For example, we have shown the possibility of a one-dimensional positional liquid having a helical order for the molecular edges. Consistent with x-ray diffraction results for the D_{ho} phase, we have shown explicitly the emergence of a stable phase with intercalated columns and counter-rotating helical structures on each columns, with arbitrary commensurability. It was seen that although a minimum of two IR's were in principle required to account for such phase, in prac-

tice, the total goes up to 3. For the density increments built on IR2 and IR3 and responsible for the helical order, each of them act as a stationary wave with a progressive wave possible only when the two are combined. We have explicitly shown the conditions, under which the phase D_{ho} may be obtained as a first-order transition from the phase D_{hd} , in agreement with experimental results. Using those conditions, the phase transition surface in the quadratic coefficient space $\alpha, \alpha', \alpha''$ may be computed numerically, once the various higher order expansion coefficients are specified.

We have also discussed how, for columnar arrangements with displacements in modulation $(0, \frac{1}{3}, \frac{2}{3})$, involving only two IR's, commensurability of the two wave numbers along the z axis was necessary, in order to produce the angle-fixing term in the free energy. Many more phases, based on neighboring IR's, were not studied in detail. But calling on molecular engineering, further study is required to determine what phase has desirable elastic, optical, and electrical properties.

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