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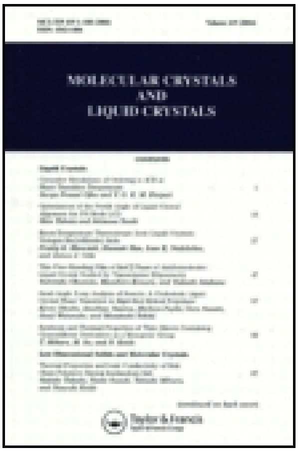

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
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A Molecular Mean Field Model for a Rectangular to Hexagonal Phase Transitionin Discotic Liquid Crystals

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A Molecular Mean Field Model for a Rectangular to Hexagonal Phase Transition in Discotic Liquid Crystals

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A mean field model for a rectangular columnar to hexagonal columnar phase transition, assuming that the molecules are biaxial in both the phases, is presented. The theory is developed for a face centered rectangular lattice taking the molecular cores to be tilted in a particular direction with respect to the column axis by the same angle at each lattice site. Phase diagrams for a homologous series for two values of biaxiality parameter are presented. With increasing temperature a phase sequence rectangular–hexagonal–nematic–isotropic is found for shorter members while for higher members of a homologous series the nematic phase is absent in the calculated phase sequence.

Keywords: discotic phase, biaxial mean field

I. INTRODUCTION

A. Classification of phases

The majority of the discotic liquid crystals so far discovered are of columnar (D) type, in which the disc like molecules are stacked one on top of the other. Various columnar mesophases are classified according to the two dimensional arrangement of the columns e.g. hexagonal (D_{hd}), rectangular (D_{rd}) etc. While the initial suffix specifies the type of lattice, the second suffix "*d*" indicates a disordered stacking in a column. The rectangular phase is further subclassified[1] according to the space group symmetry of the lattice namely $D_{rd(P2_1/a)}$, $D_{rd(P2/a)}$, $D_{rd(C2/m)}$ [Figure 1]. It is important to note that in all the rectangular varieties[1] the average molecular plane is not perpendicular to column axis. In $D_{rd(P2_1/a)}$ phase the tilted molecules forms a "herring bone" arrangement as observed in HAT series.[2,3] The $D_{rd(C2/m)}$ phase is often referred as D_t phase in many papers.[3,4,5] For the sake of brevity we shall drop the second suffix "*d*" in our subsequent discussions.

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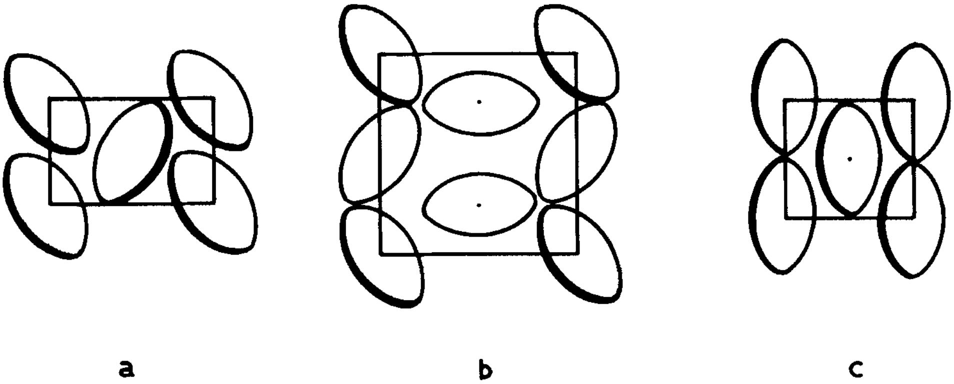

FIGURE 1 Three different types of two dimensional rectangular lattices (a) $D_{rd(\mathrm{P21/a})}$, (b) $D_{rd(\mathrm{P2/a})}$, (c) $D_{rd(\mathrm{C2/m})}$.

Very few samples actually exhibit discotic nematic (N_D) phase, which is an orientationally ordered arrangement of the discs with no long range translational order. Clearly the N_D and D_h phases are uniaxial while all the D_r phases are biaxial.

B. Experimental situation

Amongst the various discotic liquid crystals, some exhibit only a single type of mesophase but many are polymorphic in character. To give an idea, we cite a few typical examples in which biaxial columnar phases are involved.

1) Hexa-n-alkanoates of Benzene (HAB).[6,7] This substance (for $n = 6,7,8$) undergoes the phase sequence $K \rightarrow D_{r(C2/m)} \rightarrow I$ with increase in temperature. The tilt angle measured by optical methods[8] is of the order of ~35°. If the molecules are regarded as thin rigid discs, all tilted by ~35° in the same direction, the lattice will be appreciably distorted from hexagonal type which is not corroborated by X-ray measurements.[7] This anomaly can be resolved if it is assumed that the benzene core (which is approximately about one third of the whole molecule) is only tilted with respect to columnar axis, but the aliphatic side chains are quite flexible and not necessarily tilted.

2) Hexa alkoxy benzoates of triphenylene (HBT).[3,4] This is one of the very few series in which the N_D phase is observed. With increasing temperature this series shows the following phase sequence:

$K \rightarrow N_D \rightarrow I$ for $n = 4$, 5 and 7

$K \rightarrow D_{r(C2/m)} \rightarrow N_D \rightarrow I$ for $n = 6$

$K \rightarrow D_{r(P2_1/a)} \rightarrow N_D \rightarrow I$ for $n = 8$ to 11.

As observed by X-ray measurements,[9] the deviation from hexagonal lattice is not so large in $D_{r(P2_1/a)}$ phase (for $n = 11$, $b/a = 1.59$ as compared to 1.73 for ideal hexagonal lattice), (b and a defined in Figure 3(a)) but quite appreciable in

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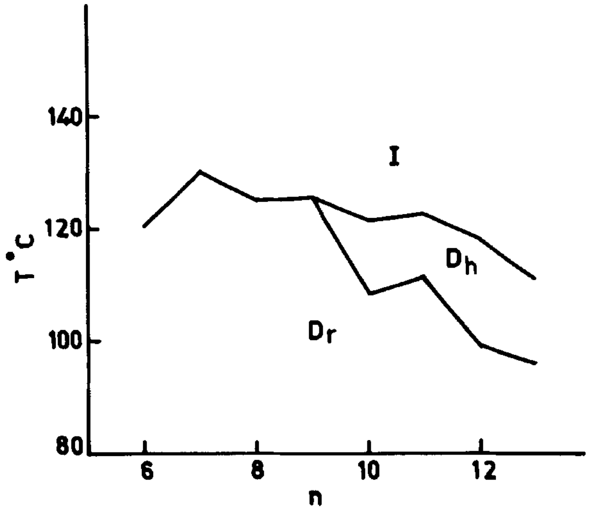

FIGURE 2 Experimental phase diagram of HAT series. Transition temperature (T) in °C is plotted against number of carbon atom (*n*) in the alkyl chain of HAT. [*I* = Isotropic, D_r = rectangular columnar, D_h = hexagonal columnar.

$D_{r(C2/m)}$ phase (for $n = 6$, $b/a = 1.081$; tilt angle ~55°). Various theoretical attempts[5,10,11] have been made to explain this homologous series behavior by extending McMillan's theory[12] of smectic ordering to a two-dimensionally periodic lattice.

3) Hexa-n-alkanoates of Triphenylene (HAT).[2,3] In this series mesomorphic polymorphism is observed among columnar discotics for long alkyl chain length as shown in the phase diagram (Figure 2). There is direct $D_{r(P2_1/a)}$–I transition for short alkyl chain lengths ($n = 6$ to 9). For long alkyl chain lengths ($n = 10$ to 13) there are $D_{r(P2_1/a)}$–D_h–I transitions also.

Here also the deviation of rectangular lattice ($b/a \simeq 1.7$) from hexagonal lattice is quite small as found by X-ray measurements,[3,13] though optical microscopy[14] reveals ~28° tilt of the optic axis with respect to columnar axis in rectangular (D_r) phase. Thus it was suggested[13] that only the central core is tilted but the flexible aliphatic side chains need not be tilted. Moreover it is found that the molecular tilt angle remains finite in the hexagonal phase (D_h) also. From these observations they[13] proposed that the D_h–D_r phase transition is characterized primarily by the onset of the intercolumn ordering of the molecular tilt angle about the columnar axis.

C. Earlier theoretical models

The first theoretical mean field model for the biaxial rectangular discotic phase (D_r) was proposed by S. Chandrasekhar *et al.*[5] This is essentially an extension of McMillan's model[12] of smectic ordering to a face-centered rectangular lattice composed of liquid like columns. They assumed that the molecular cores are circular discs normal to the columnar axes, but with an asymmetrical disposition of the

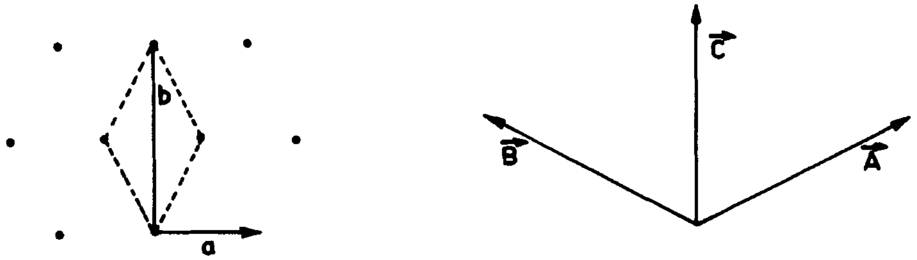

FIGURE 3 (a) Face centered rectangular (FCR) lattice of the D_r phase. The dotted region shows the unit cell. (b) Reciprocal lattice vectors of the FCR lattice.

chains. When the *b*/*a* ratio (defined in Figure 3(a)) of the face centered rectangular (F.C.R.) lattice departs slightly from $\sqrt{3}$, the calculated phase diagram is similar to the hexagonal case, i.e. the transitions from the D_r to isotropic (I) phase may take place either directly or via a N_D phase, depending on the length parameter "α". For values of (*b*/*a*) slightly higher than $\sqrt{3}$ the theory predicts a D_r–S_A (Smectic A) transition as well. In this model the D_r–D_h transitions are not however reproduced.

II. PRESENT MODEL

We have developed our model considering three important experimental observations:

1. Optical microscopy[8,14] suggests that the average molecular plane is not perpendicular to columnar axis for the D_r phase.
2. X-ray measurements[3,9,13] give relatively small deviation of rectangular lattice from hexagonal lattice.
3. Molecular tilt angle remains finite[13] even in the D_h phase.

Out of the three types of molecular arrangements mentioned earlier we have restricted ourselves, for the sake of simplicity, to $D_{r(C2/m)}$ alone. In this phase the molecular cores are tilted in a particular direction with respect to the column axis by the same angle at each lattice site. The extension of the model to explicitly take into account the herring bone arrangement ($D_{r(P2_1/a)}$) or the $D_{r(P2/a)}$ phase is quite difficult and even if it is possible it will result in a very large number of order parameters as well as free parameters.[5] The structure we have taken up has the least number of free parameter (only the tilt angle of molecular core) and that is also seen to involve a sizable amount of computation. In other words, the rectangular phase we discuss here is a $D_{r(C2/m)}$ phase which will henceforth be referred to as D_r phase.

With the above considerations we thus assume the disc-like molecule basically as a biaxial object whose central core is tilted only, but flexible aliphatic side chains are extended in a plane perpendicular to the columnar axis. The tilt angle of the central core is considered as a measure of the biaxiality and taken constant for all the members of the homologous series. Though the central core remains tilted

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even in D_h phase, the uniaxiality of the phase can be achieved if we consider that the tilted molecule is rotating about the columnar axis.

A. Pair potential

The anisotropic intermolecular potential between two biaxial objects can be expanded[15] in a complete set of functions of the Euler angles $\hat{\Omega}(\Phi,\theta,\psi)$, which specify the orientations of the molecules with respect to space-fixed co-ordinate axes and functions of intermolecular distance $\mathbf{r}_{12}$. This can be expressed[16] as

$$V_{12} = -J(\mathbf{r}_{12}) \sum_{l} a_l \sum_{m} (-1)^m Q_{lm}(\hat{\Omega}_1) \cdot Q_{l-m}(\hat{\Omega}_2) \qquad (1)$$

where $Q_{lm}(\hat{\Omega})$'s are the molecular moments with respect to space fixed co-ordinate axes and these can be expressed in terms of molecular multipolar moments (Q'_{lm}) with respect to the molecular axes.

$$Q_{lm}(\hat{\Omega}) = \sum_{m'} D^{l}_{m'm}(\hat{\Omega}) \cdot Q'_{lm} \qquad (2)$$

where, $D^{l}_{m'm}(\hat{\Omega})$ are the elements of the representation of the rotation group.[17] $J(\mathbf{r}_{12})$ is the space dependent part of the interaction potential.

For centrosymmetric molecules, terms with odd values of l will not occur in the Equation (1). So to develop a mean field model of liquid crystal composed of centrosymmetric molecules, in the lowest order approximation, we shall restrict only to $l = 2$ terms. a_2 is absorbed in $J(\mathbf{r}_{12})$.

From the molecular shape of any biaxial object, we can always choose the principal axes of molecules so that

$$Q'_{2,\pm 1} = 0$$

$$Q'_{2,0} \neq 0 \qquad \text{and real.}$$

$$Q'_{2,2} = Q'_{2,-2} \neq 0 \qquad \text{and real.}$$

This last term is zero for axially symmetric molecules. So we require only two independent parameters to describe these molecules. For convenience let us assume

$$\left.\begin{aligned} Q'_{2,0} &= Q\cos\xi \\ Q'_{2,2} &= Q'_{2,-2} = (Q/\sqrt{2})\sin\xi \end{aligned}\right\} \qquad (3)$$

where ξ is a molecular parameter representing the biaxiality of the molecule. In our model, we have phenomenologically assumed ξ as the tilt angle of the central core of the disc-like molecules with respect to the director (z-axis). This ξ is assumed to be constant for all the members of the homologous series.

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B. Mean field

The mean field for the pair potential (1) can be obtained by averaging V_{12} for all positions of the second particle. So

$$\begin{aligned} V_1 &= n\,\langle V_{12}\rangle_2 \\ &= -n \sum_m (-1)^m\, Q_{2m}(\hat{\Omega}_1) \int d\,\mathbf{r}_2\, J(\mathbf{r}_{12}) \cdot Q_{2,-m}(\hat{\Omega}_2) \cdot f(\mathbf{r}_2, \hat{\Omega}_2) \end{aligned} \tag{4}$$

where, $f(\mathbf{r}, \hat{\Omega})$ is the distribution function given by

$$f(\mathbf{r}, \hat{\Omega}) = \exp\{-V_1(\mathbf{r}, \hat{\Omega})/kT\}/Z; \tag{5}$$

Z is the partition function.

The local orientational order parameters are defined as

$$\langle Q_{2m}(\hat{\Omega})\rangle = \int d\hat{\Omega}\; Q_{2m}(\hat{\Omega})\, f(\mathbf{r}, \hat{\Omega}) \tag{6}$$

Due to the symmetry of the problem, we can suitably choose the laboratory frame of reference so that

$$\left.\begin{aligned} &\langle Q_{2,\pm 1}(\hat{\Omega})\rangle = 0 \\ &\langle Q_{2,0}(\hat{\Omega})\rangle \neq 0, \text{ real} \\ &\langle Q_{2,2}(\hat{\Omega})\rangle = \langle Q_{2,-2}(\hat{\Omega})\rangle \neq 0, \text{ real} \end{aligned}\right\} \tag{7}$$

Thus, for the expansion of $Q_{2,m}(\hat{\Omega})$'s we require only four rotation matrices $D^{(2)}_{0,0}$, $D^{(2)}_{0,2}$, $D^{(2)}_{2,0}$ and $D^{(2)}_{2,2}$. Putting the values of rotation matrices[17] in Equation (2), we get

$$\begin{aligned} Q_{2,0}(\hat{\Omega}) &= Q\left[\operatorname{Cos}\xi \cdot P_2(\operatorname{Cos}\theta) + \operatorname{Sin}\xi \cdot \frac{\sqrt{3}}{2} \cdot \operatorname{Sin}^2\theta \cdot \operatorname{Cos} 2\Phi\right] \\ &= Q \cdot F_1(\theta,\Phi) \text{ say} \end{aligned} \tag{8}$$

and

$$\begin{aligned} &Q_{2,2}(\hat{\Omega}) + Q_{2,-2}(\hat{\Omega}) \\ &= \sqrt{2}\cdot Q\left[\frac{\sqrt{3}}{2}\sin^2\theta\cdot\cos 2\psi\cdot\cos\xi + \sin\xi\{\cos 2\Phi\cdot\cos 2\psi \right. \\ &\quad \left. \times ((1+\cos^2\theta)/2) - \sin 2\Phi\cdot\sin 2\psi\cdot\cos\theta\}\right] \\ &= \sqrt{2}Q\cdot F_2(\Phi,\theta,\psi) \text{ say} \end{aligned} \tag{9}$$

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To describe the biaxial phase two orientational order parameters are sufficient and defined as

$$\eta = \langle F_1(\theta,\Phi)\rangle \tag{10}$$

and

$$\eta_b = \langle F_2(\Phi,\theta,\psi)\rangle \tag{11}$$

In uniaxial phase the last term vanishes due to symmetry.

In D_r phase, the liquid like columns form a face centered rectangular lattice (FCR) as shown in Figure 3(a). Corresponding reciprocal lattice vectors (Figure 3(b)) are given by

$$\begin{aligned} \mathbf{A} &= 2\pi\left(\frac{\hat{\imath}}{a} + \frac{\hat{\jmath}}{b}\right) \\ \mathbf{B} &= 2\pi\left(-\frac{\hat{\imath}}{a} + \frac{\hat{\jmath}}{b}\right) \\ \mathbf{C} &= \mathbf{A} + \mathbf{B} = \frac{4\pi\hat{\jmath}}{b} \end{aligned} \tag{12}$$

Since the distribution function is also periodic having the periodicity of the lattice, it can be expanded in a Fourier series. In lowest order Fourier expansion it can be expressed as

$$f(\mathbf{r}) = f_0 + 2\,[f_1\{\mathrm{Cos}(\mathbf{A}\cdot\mathbf{r}) + \mathrm{Cos}(\mathbf{B}\cdot\mathbf{r})\} + f_2\,\mathrm{Cos}(\mathbf{C}\cdot\mathbf{r})] \tag{13}$$

where f_0, f_1 and f_2 are Fourier coefficients.

In our model, we have assumed the space dependent part of the interaction potential as

$$J(r_{12}) = -v_0\cdot\exp\left[-(r_{12}/r_0)^2\right] \tag{14}$$

where v_0 is a constant, r_0 is the range of interaction and assumed to be of the order of core size.

Following standard procedure, we can arrive at the mean field

$$\begin{aligned} V_1(\mathbf{r},\hat{\Omega}) = -\frac{v}{R_L^2}[\{\eta + \alpha_1\sigma_1(\mathrm{Cos}(\mathbf{A}\cdot\mathbf{r}) + \mathrm{Cos}(\mathbf{B}\cdot\mathbf{r})) \\ + \alpha_2\sigma_2\mathrm{Cos}(\mathbf{C}\cdot\mathbf{r})\}F_1(\theta,\Phi) + \{\eta_b + \alpha_1\sigma_1^b(\mathrm{Cos}(\mathbf{A}\cdot\mathbf{r}) + \mathrm{Cos}(\mathbf{B}\cdot\mathbf{r})) \\ + \alpha_2\sigma_2^b\mathrm{Cos}(\mathbf{C}\cdot\mathbf{r})\}F_2(\Phi,\theta,\psi)] \end{aligned} \tag{15}$$

where v is the modified strength of interaction involving v_0 and few other constants like Q^2, r_0, π etc. R_L is the reduced diameter of the molecule and given by $R_L = d/r_0$, where d is the molecular diameter. The $1/R_L^2$ term[11] in Equation (15) comes from the presence of n in the mean field (Equation (4)). $n = n_x \cdot n_y \cdot n_z$, where n_x, n_y, n_z are linear densities of molecules in x, y and z direction respectively. n_z remains more or less constant for all members of a homologous series, but

$$n_x \cdot n_y \propto \frac{1}{d^2} \propto \frac{1}{R_L^2}.$$

α_1 is the length parameter associated with density waves along **A** and **B**, α_2 is the length parameter along **C**. Utilizing Equation (14), we have

$$\left.\begin{aligned} \alpha_1 &= 2 \cdot \exp\left[-\pi^2 r_0^2 \left(\frac{1}{a^2} + \frac{1}{b^2}\right)\right] \\ \alpha_2 &= 2 \cdot \exp\left[-\pi^2 r_0^2 \frac{4}{b^2}\right] \end{aligned}\right\} \tag{16}$$

In hexagonal phase for compact packing of circular discs (Figure 4(a)) $a = d$, $b = \sqrt{3}\, d$. So

$$\alpha = \alpha_1 = \alpha_2 = 2 \cdot \exp\left[-\frac{4\pi^2}{3} \cdot \frac{r_0^2}{d^2}\right]$$

or,

$$\alpha = 2 \cdot \exp\left[-13.16/R_L^2\right] \tag{17}$$

In rectatngular phase, we have assumed that core of each molecule is tilted about the "b" axis by the same angle ξ. Therefore, the projection of molecule in x–y plane is somewhat elliptic in nature (Figure 4(b)), whose long and short axes are d and $(d - r_0(1 - \cos\xi))$ respectively. For compact arrangements of tilted molecules in F.C.R. lattice (Figure 4(c)),

$$a = d - r_0(1 - \cos\xi), \quad b = \sqrt{3}\, d.$$

Thus

$$\left.\begin{aligned} \alpha_1 &= 2 \cdot \exp\left[-\pi^2 \left(\frac{1}{3R_L^2} + \frac{1}{(R_L - (1 - \cos\xi))^2}\right)\right] \\ \alpha_2 &= \alpha = 2 \cdot \exp(-13.16/R_L^2) \end{aligned}\right\} \tag{18}$$

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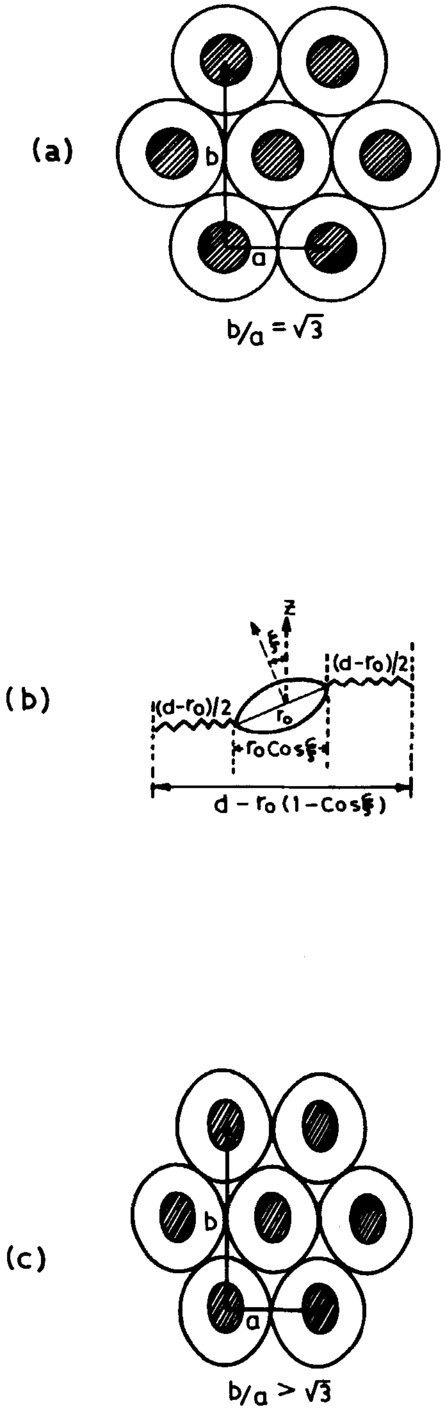

FIGURE 4 (a) Packing of molecules in D_h phase. (b) Tilted core of the molecule. (c) Packing of molecules in D_r phase.

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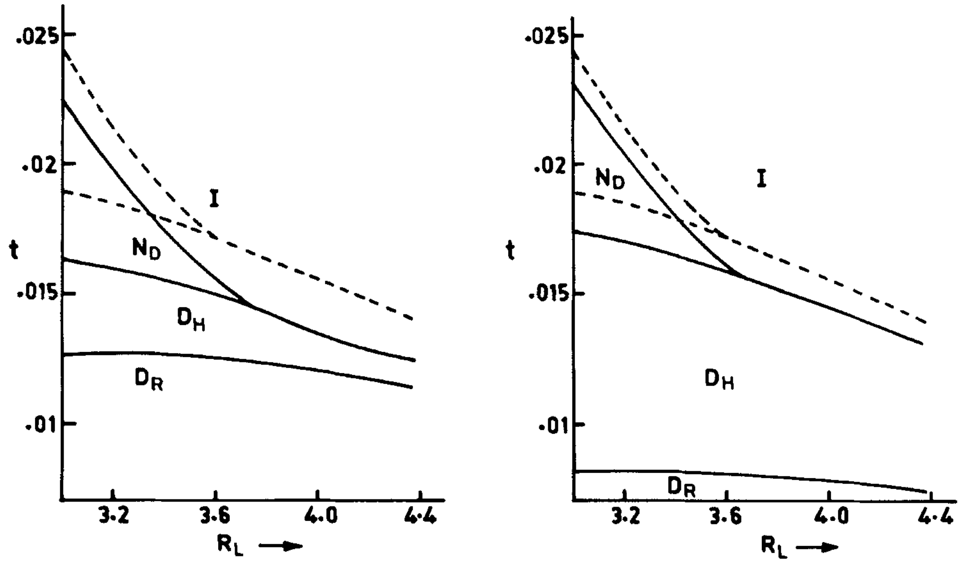
The various order parameters are defined as

$$\left.\begin{aligned}
\eta &= \langle F_1(\theta,\Phi)\rangle \\
\eta_b &= \langle F_2(\Phi,\theta,\psi)\rangle \\
\sigma_1 &= \frac{1}{2}\langle\{\cos(\mathbf{A}\cdot\mathbf{r}) + \cos(\mathbf{B}\cdot\mathbf{r})\}\quad F_1(\theta,\Phi)\rangle \\
\sigma_1^b &= \frac{1}{2}\langle\{\cos(\mathbf{A}\cdot\mathbf{r}) + \cos(\mathbf{B}\cdot\mathbf{r})\}\quad F_2(\Phi,\theta,\psi)\rangle \\
\sigma_2 &= \langle\cos(\mathbf{C}\cdot\mathbf{r})\quad F_1(\theta,\Phi)\rangle \\
\sigma_2^b &= \langle\cos(\mathbf{C}\cdot\mathbf{r})\quad F_2(\Phi,\theta,\psi)\rangle
\end{aligned}\right\} \tag{19}$$

where the angular brackets ⟨ ⟩ represent a statistical average defined as

$$\langle F(\mathbf{r},\hat{\Omega})\rangle = \int_{\square} d\mathbf{r} \int d\hat{\Omega}\cdot F(\mathbf{r},\hat{\Omega})\cdot f(\mathbf{r},\hat{\Omega}) \tag{20}$$

The **r** integration runs over primitive cell of the two dimensional F.C.R. lattice. $f(\mathbf{r},\hat{\Omega})$ is the normalized distribution function defined in Equation (5). Correspond-



(a) for sinξ = 0.4; (b) for sinξ = 0.3.

FIGURE 5 Phase diagrams reproduced by the present theory. Reduced transition temperature (t = kT/v) is plotted against reduced diameter R_L. D_h–N_D and D_h–I transition temperatures for uniaxial molecule are shown by dashed line.

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ing free energy F is given by

$$\frac{F}{N\mathrm{kT}} = \frac{V}{2\mathrm{kT}}\left(\eta_1^2 + \eta_b^2 + 2\alpha_1\sigma_1^2 + \alpha_2\sigma_2^2 + 2\alpha_1\sigma_1^{b^2} + \alpha_2\sigma_2^{b^2}\right) - \ln Z \qquad (21)$$

The self-consistency Equations (19) are solved by an iterative method. There are four possible solutions to the equations:

1) $\eta \neq 0, \eta_b \neq 0, \sigma_1 \neq \sigma_2 \neq 0, \sigma_1^b \neq \sigma_2^b \neq 0$ D_r phase.
2) $\eta \neq 0, \sigma_1 = \sigma_2 \neq 0; \eta_b = \sigma_1^b = \sigma_2^b = 0$ D_h phase.
3) $\eta \neq 0, \eta_b \neq 0, \sigma_1 = \sigma_2 = \sigma_1^b = \sigma_2^b = 0$ Biaxial nematic phase.
4) $\eta \neq 0, \eta_b = 0, \sigma_1 = \sigma_2 = \sigma_1^b = \sigma_2^b = 0$ N_D phase.

The stability of a particular phase is ascertained by the minima of free energy of that particular phase.

III. RESULTS

The phase diagrams for two values of biaxial parameter sinξ = 0.4 and 0.3 are shown in Figure 5(a) and (b), where reduced transition temperature (t = kT/ν) is

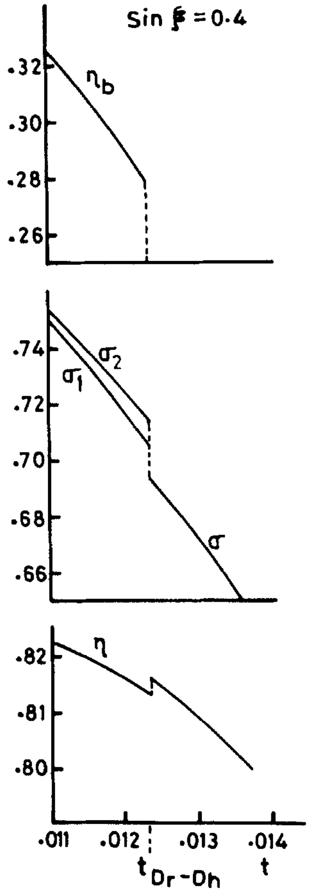

FIGURE 6 Variation of order parameters near D_r–D_h transition (for sinξ = 0.4, R_L = 3.54).

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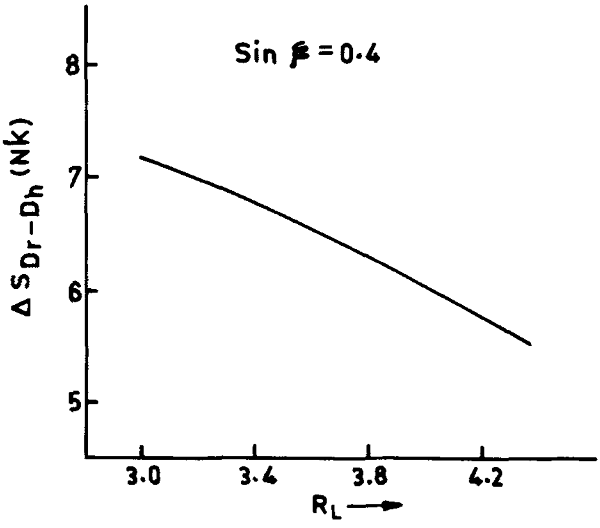

FIGURE 7 Molar transition entropy ΔS at D_r–D_h transition is plotted against R_L (for sinξ = 0.4).

plotted against the reduced diameter R_L. For low R_L ($R_L < 3.72$) in the sinξ = 0.4 case, there is I–N_D–D_h–D_r transition with decrease in temperature, but above $R_L > 3.72$, there is I–D_h–D_r transition. The latter phase sequence resembles the results experimentally obtained for HAT series (Figure 2), if one ignores the difference between D_r (C2/m) and D_r ($P2_1/a$). For sinξ = 0.3, the phase diagram is qualitatively similar but the range of D_h increases considerably. This depression of D_r–D_h transition temperature is quite understandable as the difference between D_r and D_h phases narrows down with a lowering of biaxiality parameter. So far as we know this is the first time that I–D_h–D_r phase transition for disc-like liquid crystal are reproduced within the framework of molecular meanfield model. The variation of various order parameters with temperature are shown in Figure 6. The molar transition entropy at D_r–D_h transition is found to decrease with increase in R_L as shown in Figure 7.

It should be pointed out that the existence of the D_r phase and D_r–D_h phase transition can only be reproduced if a finite tilt angle is assumed for both the D_r and D_h phases as observed by Safinya *et al.*[13] We have obtained the phase diagram assuming the tilt angle to be the same in D_r, D_h and N_D phases. However, the tilt angle is likely to decrease with increase in temperature. If we assume that the tilt angle tends to zero near about D_h–N_D or D_h–I transition the calculated D_h–N_D or D_h–I transition temperatures are shifted upwards (as shown by dashed line in Figure 5(a) and (b)). We have further assumed, for the sake of simplicity, same tilt angle for all the members of a homologous series. It is quite likely that this tilt angle will change from member to member. The effect of a change in tilt angle can be inferred from the phase diagrams for two values of biaxiality parameter (which is directly related to the tilt angle in our model). It is evident from these diagrams (Figure 5(a) and Figure 5(b)) that if the biaxiality parameter, i.e., the tilt angle is reduced, the D_h region broadens.

Finally, we wish to emphasize again that this model in its present form cannot take into consideration the herringbone arrangement of molecules as observed in HAT series (the reason for which has been briefly discussed in the text). However there exist models[18] based on Landau theory, developed by Y. F. Sun and J. Swift, in which the herringbone arrangement of tilted molecules are taken into account.

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