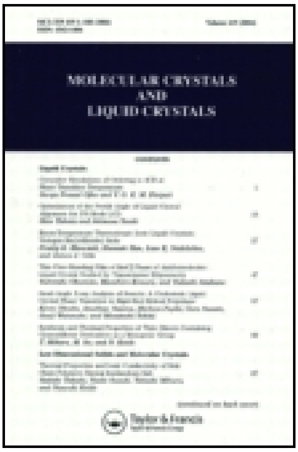

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A Molecular Meanfield Model for the Biaxial Rectangular Discotic Phase with Herring-Bone Packing of Tilted Molecules

D. Ghose [a] [b] , T. R. Bose [a] [c] , J. Saha [a] , C. D. Mukherjee [a] [d] , M. K. Roy [a] & M. Saha [a]

[a] Department of Physics, Calcutta University, 92, A. P. C. Road, Calcutta, 700 009, India

[b] R. K. Mission Vidyamandira, Belur Math, Howrah, 711202, India

[c] Scottish Church College, Calcutta, 700006, India

[d] Saha Institute of Nuclear Physics, Calcutta, 700064, India

To cite this article: D. Ghose , T. R. Bose , J. Saha , C. D. Mukherjee , M. K. Roy & M. Saha (1995): A Molecular Meanfield Model for the Biaxial Rectangular Discotic Phase with Herring-Bone Packing of Tilted Molecules, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 264:1, 165-179

To link to this article: http://dx.doi.org/10.1080/10587259508037310

Mol. Cryst. Liq. Cryst., 1995, Vol. 264, pp. 165–179
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A Molecular Meanfield Model for the Biaxial Rectangular Discotic Phase with Herring-Bone Packing of Tilted Molecules

D. GHOSE*, T. R. BOSE⁺, J. SAHA, C. D. MUKHERJEE#, M. K. ROY and M. SAHA
Department of Physics, Calcutta University, 92, A. P. C. Road, Calcutta 700 009, India

(Received January 24, 1994; in final form July 1, 1994)

A molecular meanfield model for a rectangular columnar to hexagonal columnar phase transition, as observed in case of the HAT series, is presented here assuming the molecules basically to be biaxial objects. The theory is developed for a rectangular lattice having herring-bone packing of the tilted molecules. Various types of phase diagrams for a homologous series are reproduced for different values of molecular biaxiality. Some of them are very similar to the experimentally observed cases but others, particularly involving biaxial nematic phase, are not yet observed. It is shown that a gradual lowering of biaxiality with the addition of flexible chain segments can lead to the full phase sequence observed in the HAT series.

I INTRODUCTION

Among the various discotic mesophases (i.e., the phases generated by disc-shaped molecules), the majority are of columnar type.[1,2] In columnar phases, the disk-like molecules are stacked one on top of the other to form a column and these columns are arranged in different types of two dimensional lattices. The most commonly observed hexagonal disordered (D_{hd}) and rectangular disordered (D_{rd}) phases consist of hexagonal and rectangular array of columns with liquid-like intracolumn order.[1,2] In the D_{hd} phase, disk-shaped molecules are arranged in a two-dimensionally periodic hexagonal lattice. The hexagonal phase is uniaxial in nature and many mean field theories[3–5] have been developed to explain the associated phase transitions. Crystallographic studies[2] of the biaxial D_{rd} mesophase showed it to possess a $P2_1/a$ space group symmetry with two inequivalent (but symmetry related) molecular sites '1' and '2' in a unit cell (Figure 1). In this phase, the molecules in neighbouring columns are oppositely tilted with respect to the column axis to form a herring-bone arrangement.

Chandrasekhar *et al.*[4] developed the first molecular mean field model of the rectangular discotic phase, but they did not take into consideration the herringbone packing

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[*] Permanent Address: R. K. Mission Vidyamandira, Belur Math, Howrah-711202, India.
[+] Permanent Address: Scottish Church College, Calcutta-700006, India.
[#] Permanent Address: Saha Institute of Nuclear Physics, Calcutta-700064, India.

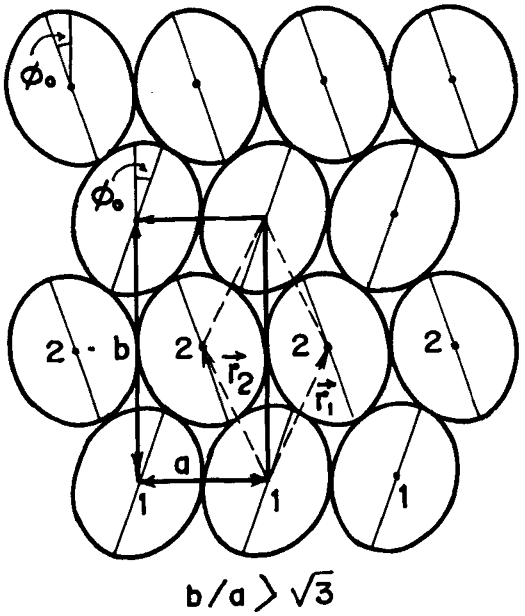

FIGURE 1 Arrangement of tilted molecules in D_{rd} phase. Conventional unit cell of the rectangular lattice (shown by bold lines of length '*a*' and '*b*') contains two molecules '1' and '2' as basis. If we assume the two lattice sites 1 and 2 as equivalent then the lattice can be considered as a FCR lattice whose unit cell is denoted by dotted lines.

of the molecules. The $D_{rd} - D_{hd}$ phase transition is not reproduced by their model. In a series of papers,[6] Y. F. Sun and J. Swift developed a Landau theory of the $D_{rd} - D_{hd}$ phase transition taking into consideration the herringbone arrangement of the tilted molecules in a rectangular lattice. However, the homologous series behaviour of the HAT series[1] is not reproduced in their theory. In an earlier attempt[7] the present authors developed a molecular meanfield model for the biaxial rectangular phase having D_t-phase-like molecular arrangement i.e., the disk normal is on the average tilted in a particular direction with respect to the column axis by the same angle at each lattice site. In this paper a meanfield model of the D_{rd} phase is presented for the first time in which the herringbone arrangement of the biaxial molecules is taken into consideration. This model reproduces the $D_{rd} - D_{hd}$ phase transition as observed in case of the HAT series.[1]

In the case of Hexa-*n*-alkanoates of Triphenylene (HAT) series, there are direct $D_{rd} - I$ (Isotropic) transitions for short alkyl chain length ($n = 6$ to 9) and $D_{rd} \rightarrow D_{hd} - I$ transitions for long alkyl chain length ($n = 10$ to 13) as shown in Figure 2. From X-ray measurements[8,9] of the D_{rd} phase, it was found that the deviation of the rectangular lattice from the ideal hexagonal lattice is quite small. Optical microscopy[10] reveals $\sim 28^\circ$ tilt of the optic axis with respect to the column axis. Thus it was suggested by C. R. Safinya *et al.*[9] that only the central core of the disk-like molecule is tilted but the flexible aliphatic side chains need not be tilted. Various measurements[11-13] on different columnar mesophases suggest that the tails are disordered, producing a nearly

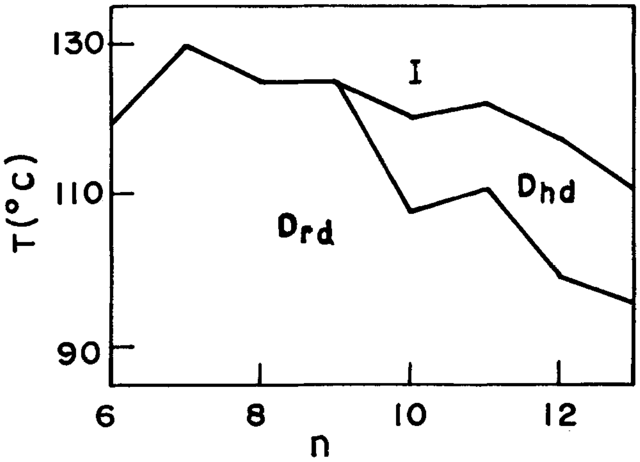

FIGURE 2 Experimental phase diagram of the HAT series. Transition temperature 'T' in °C is plotted against number of carbon atom 'n' in the alkyl chain of HAT.

isotropic fluid. So it is not a realistic model for this type of phases to have the whole molecular disk tilted with respect to the column axis. It was also found, that the molecular tilt angle remains finite in the hexagonal phase. From their observations, Safinya *et al.* proposed that the $D_{rd} - D_{hd}$ phase transition is characterised primarily by the onset of the intercolumn ordering of the molecular tilt angle about the column axis. In the D_{rd} phase, the columns of tilted molecules are close packed with herringbone order. In the D_{hd} phase, random fluctuations[9] between the two inequivalent lattice sites '1' and '2' (Figure 1) destroys the herringbone structure and brings in a uniaxial hexagonal structure with an optic axis along the column axis.

II OUR MODEL

Considering all of these experimental observations we have developed a mean field model of the biaxial D_{rd} phase on the following assumptions:

(i) The central cores of the disk-shaped molecules are tilted and the flexible aliphatic side chains are extended in a plane perpendicular to the column axis just for space filling purposes (Figure 3(a)). We think that the steric effect, apart from the dispersive forces, plays important role in this kind of molecular configuration. We treat these molecules as biaxial objects having the symmetry of a rectangular parallelopiped and the corresponding principal axis system, say, is labelled as (x', y', z'). To simulate the combined effect of the induced polarisation and the steric hindrance (to generate the tilted configuration of the molecules in D_{rd} phase) we assume that the maximum diagonal component of the molecular quadrupole moment is along the z'-axis (of the principal axis system) of the molecule and the core normal $\hat{n}$ makes an angle ξ with this axis. In laboratory frame the z'-axis of the molecules will tend to align along some direction which in case of the D_{rd} phase is the column axis (Lab z-axis).

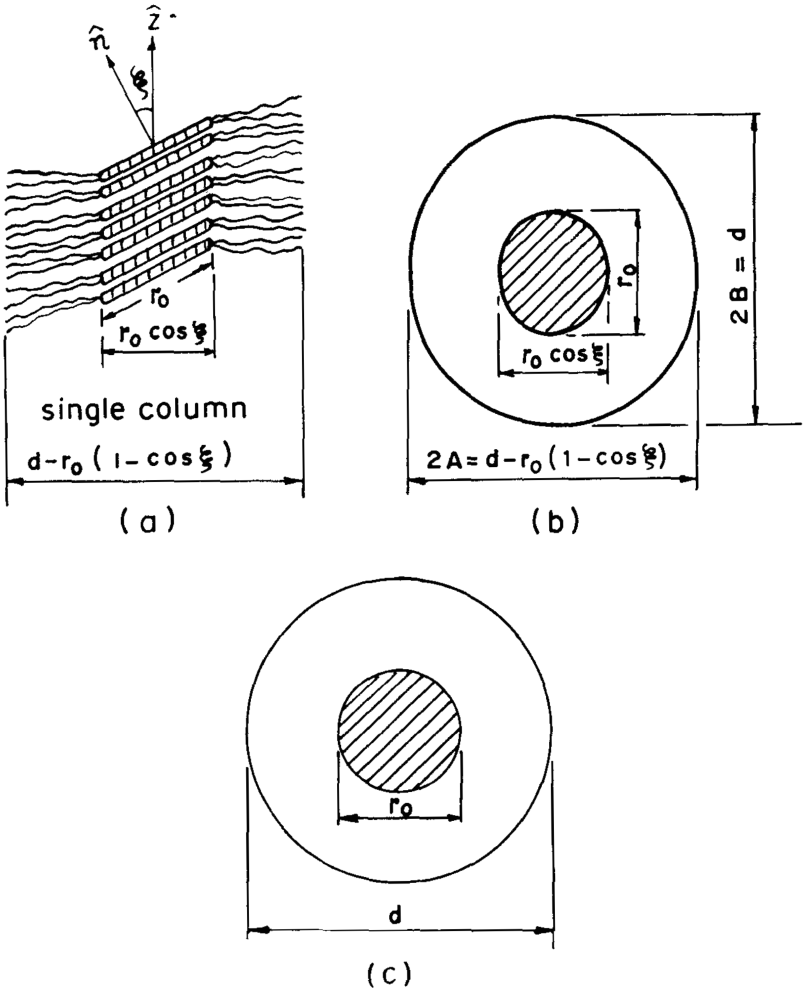

FIGURE 3 (a) Tilted core of the molecule within a column. (b) Projection of the column on X-Y plane in case of D_{rd} ph. (c) Projection of the column on X-Y plane in case of D_{hd} ph.

(ii) The tilt angle 'ξ' of the central core, i.e., the angle between the core normal $\hat{n}$ and the principal axis z', is considered as a measure of the biaxiality of the molecule. (It is to be noted that 'ξ' is also the average angle made by core normal $\hat{n}$ with column axis in the Lab-frame). This assumption is incorporated in our model by taking, on a completely ad hoc basis, the non-vanishing components of the quadrupole moment along the molecular principal axis system (x', y', z') in spherical representation as

$$\left.\begin{aligned} Q'_{2,0} &= Q(3\cos^2\xi - 1) \\ Q'_{2,2} &= Q'_{2,-2} = Q\sin^2\xi/2\sqrt{6} \end{aligned}\right\} \qquad (1)$$

It is clear from above that we have treated the tilt angle 'ξ' as a molecular parameter and it gives a measure of biaxiality of the molecule. For $\xi = 0, Q'_{2,2} = Q'_{2,-2} = 0$. In that case the only non-vanishing q.p. moment is $Q'_{2,0} = Q$, i.e., the molecule is then uniaxial in nature.

It is to be clearly stated that the form chosen in Equation (1) is totally arbitrary and its resemblance to the case of a tilted rod is a matter of choice. Any other form[7] like $Q'_{2,0} = Q\cos\xi$ and $Q'_{2,2} = Q'_{2,-2} = Q\sin\xi$ would have been good enough. Only requirement we need to have is a higher biaxiality for a higher ξ.

In D_{rd} phase, the projected dimension of the column on a x-y plane (i.e., perpendicular to the column axis) is somewhat elliptic in nature (Figure 3(b)).

(iii) The tilt angle remains constant even in the D_{hd} phase; the phase can become uniaxial by either rotation or oscillation of the tilted molecule about the column axis. In that case the average cross-section of the column will be circular (Figure 3(c)).

(iv) The rectangular unit cell (denoted by bold lines of length 'a' and 'b' in Figure 1) of the D_{rd} phase contains two inequivalent lattice sites '1' and '2'. The principal axes of the average quadrupole tensors in the laboratory frame correspond to those of the rectangular frame, and the principal values are obtained by proper averaging over the two lattice sites.[14]

Any mean field calculation is concerned only with the long range order of the system considered. So to bring the herringbone structure into the realm of meanfield, each lattice site is thought to be occupied by a molecule having the average orientational ordering appropriate for that site. Thus for the purpose of the mean field calculation, the lattice will be treated like a face centered rectangular (FCR) lattice whose unit cell is denoted by the dotted line in Figure 1; while for the calculation of the unit cell dimension in terms of molecular parameters, the actual herringbone packing of the tilted molecules will be taken into consideration.

Pair Potential

To develop the mean field theory of the D_{rd} phase according to our model, we require suitable interaction potential between two biaxial molecules. Among the various earlier works[15-18] done to consider this problem, we found two important approaches which are helpful to us. Freiser[15] expanded the orientational interaction between two biaxial molecules in a complete set of function of the Euler angles $\hat{\Omega}(\phi, \theta, \psi)$ which specify the orientations of the molecules with respect to Lab-frame. In Straley's work,[17] the angular dependence was written in terms of dot products of principal axis vectors for the molecules. We found the earlier work[15] more convenient to handle because it involves only two orientational order parameters in lowest order of approximation (in contrast to four in the work of Straley[17]). In our theory, apart from orientational order parameters, we have to introduce a few translational order parameters to represent the two-dimensionally periodic D_{rd} phase. To restrict the total number of order parameters to a minimum, we have utilised the pair potential as developed by Freiser[15] and assumed its form in the lowest order of approximation (for centro-symmetric biaxial molecules) as

$$V_{12} = -J(r_{12})\sum(-1)^m Q_{2,m}(\Omega_1)Q_{2,-m}(\Omega_2) \tag{2}$$

The space dependent part $J(r_{12})$ is expressed by a McMillan type[19] gaussian as

$$J(r_{12}) = -v_0 \exp[-(r_{12}/r_0)^2] \tag{3}$$

This constant v_0 is related to the polarisability of the central core and r_0 is the range of interaction and is assumed to be of the core size.

The $Q_{2,m}(\hat{\Omega})$'s are the molecular quadrupole (q.p) moments in the spherical representation with respect to the Lab-frame; these can be expressed in terms of the molecular quadrupole moments $Q'_{2,m}$ (defined in Equation (1)) in the molecular frame by means of the following transformation rule

$$Q_{2,m}(\hat{\Omega}) = \sum_{m'} D^2_{m'm}(\hat{\Omega})Q'_{2,m'} \tag{4}$$

where the $D^2_{m'm}(\hat{\Omega})$ are the elements of the representation of the rotation group.[20]

Orientational Order Parameter

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

$$\left.\begin{aligned} &\langle Q_{2,\pm 1}(\hat{\Omega})\rangle = 0 \\ &\langle Q_{2,0}(\hat{\Omega})\rangle \neq 0 \quad \text{and real} \\ &\langle Q_{2,2}(\hat{\Omega})\rangle = \langle Q_{2,-2}(\hat{\Omega})\rangle \neq 0 \quad \text{and real} \end{aligned}\right\} \tag{5}$$

The sign $\langle\,\rangle$ denotes the statistical average over the whole system. Putting the values of rotation matrices[20] in Equation (4) we get

$$\begin{aligned} Q_{2,0}(\hat{\Omega}) = Q[&(3\cos^2\xi - 1)P_2(\cos\theta) \\ &+ (\sin^2\xi/\sqrt{6})\cdot(\sqrt{3/2})\sin^2\theta\cdot\cos 2\phi] = QF_1(\theta,\phi) \quad \text{say} \end{aligned} \tag{6}$$

and

$$\begin{aligned} Q_{2,2}(\hat{\Omega}) + Q_{2,-2}(\hat{\Omega}) &= \sqrt{2}\cdot Q[(\sqrt{3/2})\cdot\sin^2\theta\cdot\cos 2\psi\cdot(3\cos^2\xi - 1) \\ &\quad + (\sin^2\xi/\sqrt{6})\{\cos 2\phi\cdot\cos 2\psi((1+\cos^2\theta)/2) - \sin 2\phi\cdot\sin 2\psi\cdot\cos\theta\}] \\ &= \sqrt{2}\cdot Q\cdot F_2(\phi,\theta,\psi) \quad \text{say} \end{aligned} \tag{7}$$

For a biaxial phase having an ideal FCR lattice, $\langle F_1(\theta,\phi)\rangle$ and $\langle F_2(\phi,\theta,\psi)\rangle$ serve as the two orientational order parameters of the system.[7] But here due to the herringbone ordering of the tilted molecules, the orientational order parameters of the D_{rd} phase will be obtained by averaging the quantities $F_1(\theta,\phi)$ and $F_2(\phi,\theta,\psi)$ over the lattice sites '1' and '2' (Figure 1). They are

$$\begin{aligned}\eta &= (1/2)\langle F_1(\theta,\phi+\phi_0)+F_1(\theta,\phi-\phi_0)\rangle\\ &= \langle(3\cos^2\xi-1)P_2(\cos\theta)+\cos 2\phi_0(\sin^2\xi/\sqrt{6})(\sqrt{3/2})\sin^2\theta\cdot\cos 2\phi\rangle\\ &= \langle F_u(\theta,\phi)\rangle \quad \text{say} \qquad (8)\end{aligned}$$

and

$$\begin{aligned}\eta_b &= (1/2)\langle F_2(\phi+\phi_0,\theta,\psi)+F_2(\phi-\phi_0,\theta,\psi)\rangle\\ &= \langle(\sqrt{3/2})\sin^2\theta\cos 2\psi(3\cos^2\xi-1)+\cos 2\phi_0(\sin^2\xi/\sqrt{6})\\ &\quad \{\cos 2\phi\cdot\cos 2\psi(1+\cos^2\theta)/2-\sin 2\phi\cdot\sin 2\psi\cdot\cos\theta\}\rangle\\ &= \langle F_b(\phi,\theta,\psi)\rangle \quad \text{say} \qquad (9)\end{aligned}$$

where ϕ_0 is the herringbone angle (Figure 1). The η_b vanishes in the uniaxial phase and therefore gives a measure of the biaxiality in the orientational distribution.

Translational Distribution Function

According to our model of the D_{rd} phase [assumption no. (iv)] the liquid like columns form a FCR lattice (Figure 1) whose unit cell parameters are given by

$$\vec{r}_1=(\hat{i}a+\hat{j}b)/2 \quad \text{and} \quad \vec{r}_2=(-\hat{i}a+\hat{j}b)/2 \qquad (10)$$

The normalised translational distribution function $f(\vec{r})$, which describes the tendency of the centres of mass of the molecules to lie at the lattice sites, should also have the periodicity of the FCR lattice and can be expanded in a two dimensional Fourier series. Due to the inversion symmetry of the lattice, $f(\vec{r})=f(-\vec{r})$ and so the Fourier expansion will contain only cosine terms. Following standard procedure, in lowest order of approximation, the translational distribution function $f(\vec{r})$ for the D_{rd} phase can be expressed as

$$f(\vec{r})=f_0+2f_1\{\cos(\vec{R}_1\cdot\vec{r})+\cos(\vec{R}_2\cdot\vec{r})\}+2f_2\cdot\cos(\vec{R}_3.\vec{r}) \qquad (11)$$

where f_0, f_1 and f_2 are Fourier co-efficients. The reciprocal lattice vectors of the FCR lattice are given by

$$\left.\begin{aligned}\vec{R}_1&=2\pi[(\hat{i}/a)+(\hat{j}/b)]\\ \vec{R}_2&=2\pi[-(\hat{i}/a)+(\hat{j}/b)]\\ \vec{R}_3&=\vec{R}_1+\vec{R}_2=4\pi\hat{j}/b\end{aligned}\right\} \qquad (12)$$

The coefficients f_1 and f_2 are the translational order parameters of the D_{rd} phase. In the D_{hd} phase i.e., for uniaxial system, $f_1=f_2$, so only one translational order parameter is needed to describe the phase.

Mean Field

In the molecular field approximation, each molecule is assumed to experience the same average field generated via its interaction with all the other molecules. The mean field experienced by a molecule for the pair potential (Equation 2), can be obtained by averaging V_{12} for all positions and orientations of the second molecule.

Utilising the Fourier expansion (Equation 11) of the distribution function and following the standard procedure we arrive at the mean field

$$\begin{aligned} V(\vec{r},\hat{\Omega}) = & -(v/R_L^2)[\{\eta + \alpha_1\sigma_1(\cos(\vec{R}_1\cdot\vec{r}) + \cos(\vec{R}_2\cdot\vec{r})) \\ & + \alpha_2\sigma_2\cos(\vec{R}_3\cdot\vec{r})\}F_u(\theta,\phi) + \{\eta_b + \alpha_1\sigma_{1b}(\cos(\vec{R}_1\cdot\vec{r}) \\ & + \cos(\vec{R}_2\cdot\vec{r})) + \alpha_2\sigma_{2b}\cos(\vec{R}_3\cdot\vec{r})\}F_b(\phi,\theta,\psi)] \end{aligned} \tag{13}$$

Here, v is the effective strength of interaction involving v_0, Q^2, r_0.
$R_L = d/r_0 =$ the reduced diameter of the molecule, where d is the actual diameter of the molecule.
η, η_b, σ_1, σ_2, σ_{1b} and σ_{2b} are various order parameters of the D_{rd} phase and defined later on Equation 21.

$$\alpha_1 = 2\cdot\exp[-\pi^2 r_0^2\{(1/a^2) + (1/b)^2\}] \tag{14}$$

$$\alpha_2 = 2\cdot\exp[-\pi^2 r_0^2\cdot 4/b^2] \tag{15}$$

α_1 is the McMillan's length parameter associated with the density waves along $\vec{R}_1$ and $\vec{R}_2$, α_2 is the same parameter along $\vec{R}_3$. For the computation of 'a' and 'b' we assume that the area of the unit cell in D_{rd} phase is same as for D_t phase i.e. for aligned ellipses ($\phi_0 = 0$). It gives

$$ab = 4\sqrt{3}\,AB \tag{16}$$

where A and B are the lengths of the semi-minor and semi-major axes of the average cross section of the column (Figure 3b) and given by

$$2B = d \quad \text{and} \quad 2A = d - r_0(1 - \cos\xi) \tag{17}$$

Now it is straightforward to arrive at the following expression of 'a' and 'b' from simple geometrical consideration

$$\left.\begin{aligned} a &= 2AB/(B^2\cos^2\phi_0 + A^2\sin^2\phi_0)^{1/2} \\ b &= \sqrt{3}\cdot 2(B^2\cos^2\phi_0 + A^2\sin^2\phi_0)^{1/2} \end{aligned}\right\} \tag{18}$$

Thus the phase biaxiality is expressed as

$$b/a = \sqrt{3}(B/A\cos^2\phi_0 + A/B\sin^2\phi_0) \tag{19}$$

which interpolates in a sensible way between the two limits $\phi_0 = 0°$ and $\phi_0 = 90°$. In the uniaxial hexagonal phase, for compact packing of circular columns of diameter d, $a = d$ and $b = \sqrt{3}d$. So

$$\alpha = \alpha_1 = \alpha_2 = 2\cdot\exp(-4\pi^2/3R_L^2) \tag{20}$$

Self-Consistent Equations

Now, we are in a position to evaluate the various order parameters relevant to the D_{rd} phase. They are

$$\left.\begin{aligned}
\eta &= \langle F_u(\theta,\phi)\rangle \\
\eta_b &= \langle F_b(\phi,\theta,\psi)\rangle \\
\sigma_1 &= (1/2)\langle\{\cos(\vec{R}_1\cdot\vec{r})+\cos(\vec{R}_2\cdot\vec{r})\}F_u(\theta,\phi)\rangle \\
\sigma_{1b} &= (1/2)\langle\{\cos(\vec{R}_1\cdot\vec{r})+\cos(\vec{R}_2\cdot\vec{r})\}F_b(\phi,\theta,\psi)\rangle \\
\sigma_2 &= \langle\cos(\vec{R}_3\cdot\vec{r})\cdot F_u(\theta,\phi)\rangle \\
\sigma_{2b} &= \langle\cos(\vec{R}_3\cdot\vec{r})F_b(\phi,\theta,\psi)\rangle
\end{aligned}\right\} \tag{21}$$

The angular bracket symbol $\langle\,\rangle$ of the statistical average is defined as

$$\langle G(\vec{r},\hat{\Omega})\rangle = \int_{\diamond} d\vec{r}\int d\hat{\Omega}\cdot G(\vec{r},\hat{\Omega})\cdot f(\vec{r},\hat{\Omega}) \tag{22}$$

The $\vec{r}$ integration runs over a primitive cell of the FCR lattice and the $\hat{\Omega}$ integration runs over all possible values of (ϕ,θ,ψ). The normalised single particle distribution function is defined by

$$f(\vec{r},\hat{\Omega}) = \exp[-V_1(\vec{r},\hat{\Omega})/kT]/Z, \tag{23}$$

where Z is the partition function.

The free energy F of the system is given by

$$F/NkT = (v/2kT)\{\eta^2+\eta_b^2+2\alpha_1(\sigma_1^2+\sigma_{1b}^2)+\alpha_2(\sigma_2^2+\sigma_{2b}^2)\} - \mathrm{In}Z) \tag{24}$$

The self-consistency Equations (21) are solved by an iterative method with the help of Equation (13). There are four possible solutions:

1) $\eta\neq 0, \eta_b\neq 0, \sigma_1\neq\sigma_2\neq 0, \sigma_{1b}\neq\sigma_{2b}\neq 0 \Rightarrow$ Biaxial D_{rd} phase
2) $\eta\neq 0, \sigma_1=\sigma_2\neq 0, \eta_b=\sigma_{1b}=\sigma_{2b}=0 \Rightarrow$ Uniaxial D_{hd} phase
3) $\eta\neq 0, \eta_b\neq 0, \sigma_1=\sigma_2=\sigma_{1b}=\sigma_{2b}=0 \Rightarrow$ Biaxial Nematic (N_B) phase
4) $\eta\neq 0, \eta_b=0, \sigma_1=\sigma_2=\sigma_{1b}=\sigma_{2b}=0 \Rightarrow$ Uniaxial Nematic (N_D) phase

The stable phase is the one that gives the minimum free energy.

III RESULTS

The phase diagrams reproduced from the above meanfield (Equation 13) for three values of $\xi=40°$, $42°$ and $45°$, and for the herringbone (H. B) angle $\phi_0=10°$, are shown in Figures 4, 5 and 6 respectively. There the reduced transition temperature ($t=kT/v$) is plotted against the reduced diameter R_L. Results obtained for the H. B angle $\phi_0=0°$ are shown by the dotted line in the Figures 4 and 6 to facilitate the understanding of the change occuring in the phase diagrams by incorporating the herringbone structure of the D_{rd} phase in our previous work.

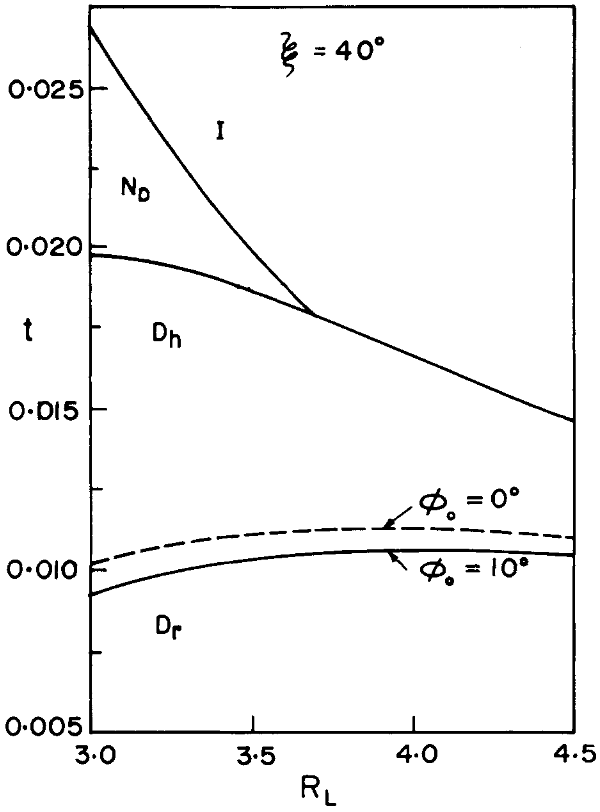

FIGURE 4 Phase diagrams reproduced by our mean field theory of D_{rd} phase in case of $\phi_0 = 10°$ and for $\xi = 40°$.

In obtaining the phase diagram, we have assumed ξ and ϕ_0 to be constant for all the members of a homologous series. Due to the above simplifying assumptions, the phase biaxiality gradually decreases with increasing R_L for a given ξ and ϕ_0 as evident from Equation (19). It is also evident from the Equation (19) that the phase biaxiality gradually increases with increasing molecular biaxiality (i.e., tilt angle 'ξ').

In the case of $\xi = 40°$ and $\phi_0 = 10°$ (Figure 4), for $R_L < 3.7$, the transition sequence (with increasing temperature) is $D_{rd} \rightarrow D_{hd} \rightarrow N_D \rightarrow I$. On the other hand, for $R_L > 3.7$, the transition sequence is $D_{rd} \rightarrow D_{hd} \rightarrow I$. The latter result matches with the experimentally observed phase sequence in HAT series[1] for long alkyl chain length ($n = 10$ to 13). In the case of $\xi = 45°$ and $\phi_0 = 10°$ (Figure 6), for $R_L < 3.95$ there is $D_{rd} \rightarrow N_b \rightarrow I$ transition with increase in temperature while for $R_L > 3.95$, there is direct $D_{rd} \rightarrow I$ transition. The high R_L result curiously simulates the experimentally observed phase sequence for the shorter members ($n = 6$ to 9) of the HAT series. The $\xi = 40°$ and $\xi = 45°$ results (Figure 4 & 6) taken together lead us to the fact that a low molecular biaxiality is needed to reproduce a $D_{rd} - D_{hd} - I$ transition while a direct $D_{rd} - I$ transition is reproduced by a high molecular biaxiality. In order to reproduce the phase

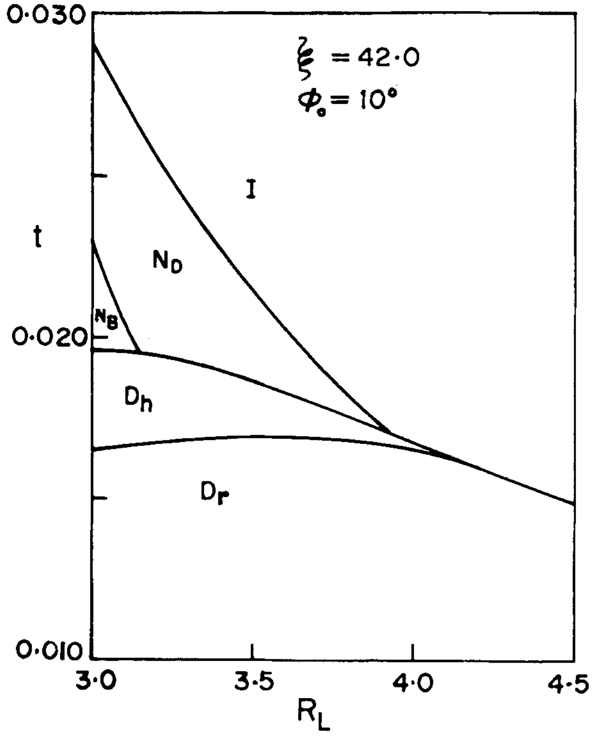

FIGURE 5 Phase diagram reproduced by our theory of D_{rd} phase for $\phi_0 = 10°$ and $\xi = 42°$.

sequence of the HAT series in full[1] (i.e., $D_{rd} - I$ for lower members and $D_{rd} - D_{hd} - I$ for higher members), an appropriate variation of molecular biaxiality has been fruitfully utilised in the following section.

Another important aspect of the phase diagram is the absence of uniaxial phases for $\xi = 45°$ (Figure 6). This disappearance of the uniaxial phases is not really unexpected. As the molecular biaxiality (ξ) increases the biaxial phases tend to dominate and gradually displace the uniaxial phases as evident from the Figures 4, 5 and 6.

The variation of the various order parameters with temperature near the $D_{rd} - D_{hd}$ and $D_{hd} - I$ transitions are shown in Figure 7 (for $R_L = 4.0$, $\xi = 40°$ and $\phi_0 = 10°$).

IV A SIMPLE MODEL OF THE HOMOLOGOUS SERIES WITH THE BIAXIALITY PARAMETER VARYING FROM MEMBER TO MEMBER

As stated earlier, for the sake of simplicity, we have assumed the same tilt angle i.e., the same molecular biaxiality for all the members of a homologous series. But it is quite likely that due to the increasing effect of the flexible aliphatic side chains in higher members of a homologous series, the biaxiality of the molecule will decrease gradually. As a simple model we are assuming that the biaxiality of the whole molecule is

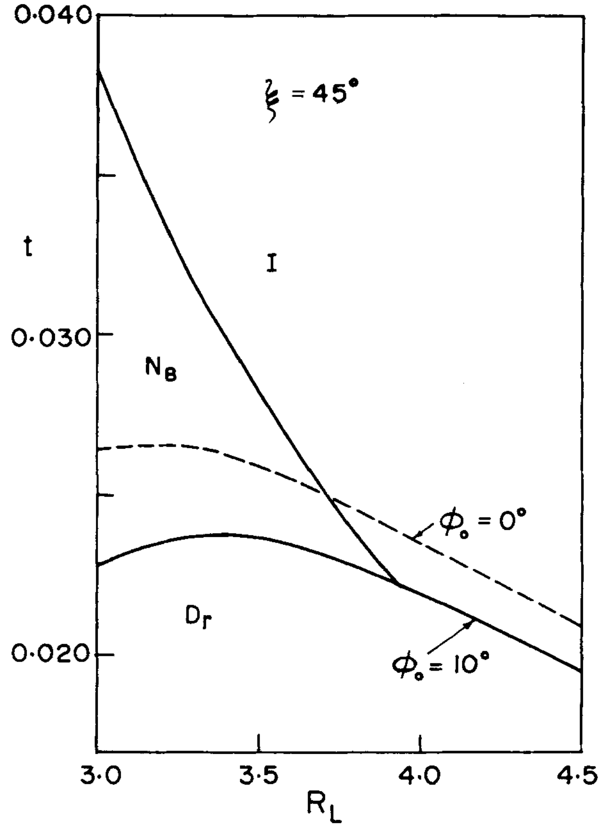

FIGURE 6 Phase diagram reproduced by our theory of D_{rd} phase for $\phi_0 = 10°$ and for $\xi = 45°$.

essentially due to the core only and therefore $\sin^2 \xi$ (which is a measure of the molecular biaxiality) is proportional to the volume fraction of the core. Since the thickness of the disc along the column axis remains more or less constant for different members of the homologous series (as evident from X-ray data),[1] $\sin^2 \xi$ will be proportional to area fraction of the core only. So

$$\sin^2 \xi \propto (r_0^2/d^2) \propto 1/R_L^2$$

Giving this input to our earlier meanfield (Equation 13) we obtained the phase diagram (Figure 8(a)) in the case of a variable biaxial parameter. We have restricted to those values of R_L for which direct $D_{rd} \rightarrow I$ or $D_{hd} \rightarrow I$ transitions are obtained in our earlier phase diagrams (Figures 4, 5 & 6). We have tentatively took $\sin^2 \xi = 8/R_L^2$ in our calculations (this will give $\sin^2 \xi = 0.5$ for $R_L = 4.0$). The phase diagram predict direct $D_{rd} \rightarrow I$ phase transition for short chain length and $D_{rd} \rightarrow D_{hd} \rightarrow I$ transition for long alkyl chain length as observed in case of HAT series (Figure 2). The H.B angle ϕ_0 was assumed to be constant for all values of R_L simply because we could not develop any realistic model by which ϕ_0 can be associated to either R_L or $\sin \xi$. The associated

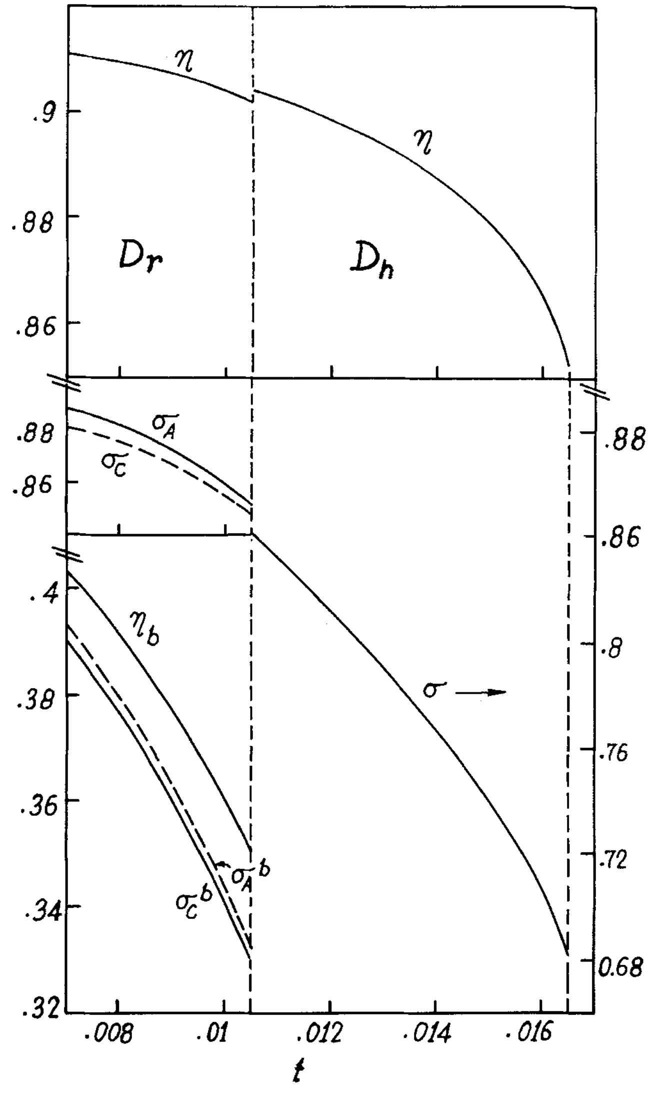

FIGURE 7 Variation of order parameters with temperature near $D_{rd} - D_{hd}$ transition and $D_{hd} - I$ transition for $R_L = 4.0$, $\xi = 40°$ and $\phi_0 = 10°$).

transition entropy for the $D_{rd} - I$, $D_{rd} - D_{hd}$ and $D_{hd} - I$ transitions are plotted as a function of R_L in Figure 8(b).

Even if this model appears very simplified, still it shows that with decreasing biaxiality with increasing chain length of the disc-shaped molecule (whatever may be the rate of decrease) it is possible to have direct $D_{rd} - I$ transition for short chain length and $D_{rd} \rightarrow D_{hd} \rightarrow I$ transition for long chain length. So far as we know this is the first time that the general nature of the phase diagram of the HAT series are reproduced within

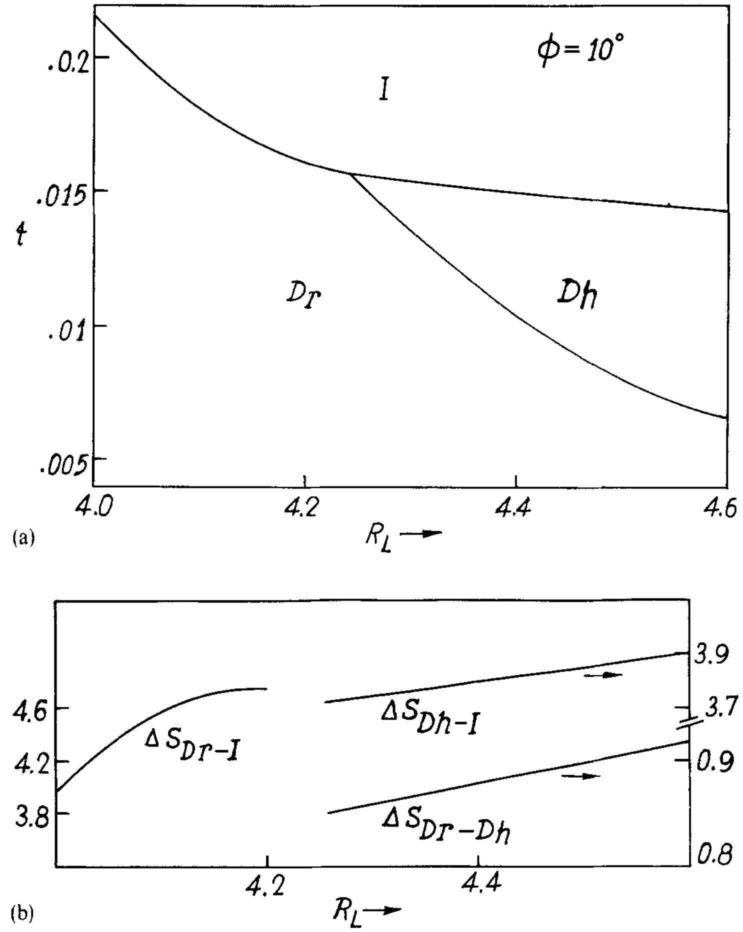

FIGURE 8 (a) Phase diagrams reproduced by our theory for variable biaxial parameter $\xi = 8.0/R_L^2$ and $\phi_0 = 10°$. (b) Associated transition entropies are plotted as a function of R_L.

the framework of molecular meanfield model. At present we are developing a model to extend the above theory to reproduce the even-odd fluctuations of the transition temperatures as observed in case of the HAT series.

Acknowledgement

One of us (J. Saha) wishes to thank the Council of Scientific and Industrial Research, India for the Senior Research fellowship offered to him.

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