Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

To cite this article: Y. F. Sun & J. B. Swift (1985): Landau Theory of Transitions from the D_{rd} Phase of Columnar Liquid Crystals, Molecular Crystals and Liquid Crystals, 126:2-4, 131-141

To link to this article: http://dx.doi.org/10.1080/00268948508084785

Mol. Cryst. Liq. Cryst., 1985, Vol. 126, pp. 131–141
0026-8941/85/1264–0131/$20.00/0

Landau Theory of Transitions from the D_{rd} Phase of Columnar Liquid Crystals

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(*Received November 14, 1984*)

Possible symmetry patterns of disordered columnar phases associated with the continuous symmetry breaking of the D_{rd} (pgg) phase are given. The results may be used to predict new mesophases which are as yet undiscovered and should be of aid in identifying unconfirmed phases. The universality classes of the possible transitions are also given.

I. INTRODUCTION

Several homologous series of disc-like mesogens which form a new type of columnar-mesophase have been discovered[1-3] and experiments on polymorphism and the sequences of the possible phase transitions in the various homologous series have been reported.[2-10] Very recently, Landau theory[11] and group theoretic techniques have been used[12] to give a theoretical discussion of the disordered-hexagonal-disordered-rectangular (D_{rd}-D_{rd}) transition in HAT series (hexa-n-alconoylaxy-triphenylens) based on experimental results of the Bordeaux group[2]. This work was based on the symmetry group of the D_{hd} phase given in the classification of Kleman and Michel.[13]

In this paper we consider the possible symmetry patterns in the low temperature phase (say, D_x) following a D_{rd}-D_x transition which is continuous. There have already been some experimental reports on such kinds of transitions. For example, in addition to the D_{hd} (or D_2) and D_{rd} (or D_1) phases in HAT series there exists another phase, denoted by D_o. A direct D_{rd}-D_o transition was reported[3] with no latent heat measured through the transition. The symmetry pattern of the D_o phase remains to be determined.

Another interesting phase and transition are the D_c phase and D_B (or D_{rd}(pgg))-D_c transition in the RHO (hexa-n-octanoate of rufigallol) series.[5,9] The D_c phase was suggested[5] to be D_{rd} (pmg) (i.e. a disordered rectangular with pmg symmetry) and the D_B-D_c transition is second order[9].

Below, we will give all the possible symmetry patterns of the low temperature phases following the symmetry breaking of the D_{rd} (pgg) phase by means of Landau's theory and group theoretic techniques. In addition to predicting new mesophases which are as yet undiscovered, the results should be of aid in identifying unconfirmed phases.

To simplify our discussion, we ignore the effect of the elastic degrees of freedom in the present work, and suppose that the distortions of the two dimensional lattice sites are small. However, these latter are inevitable when the transitions are between different two dimensional crystal systems, e.g., rectangular to oblique.

In section 2, we give all the possible symmetry patterns which may be obtained through a continuous phase transition from the D_{rd} (pgg) phase. A brief discussion of the results will be given in section 3.

2. POSSIBLE SYMMETRY PATTERNS OF THE LOW TEMPERATURE PHASES

If we denote the symmetry group of the high temperature phase (D_{rd}) as G_o', then for $g \in G_o'$, g is given[12] by

$$g = (h_i \mid \vec{\sigma}_i + m\vec{a}_1 + n\vec{a}_2 + \mu\hat{a}_3)\ i = 1,2,3,4,25,26,27,28 \quad (1a)$$

$$\vec{\sigma}_i = \begin{cases} \vec{0} & \text{if } i = 1,4,25,28 \\ \vec{\sigma}_o & \text{if } i = 2,3,26,27 \end{cases} \quad (1b)$$

where $\vec{\sigma}_o = \vec{a}_1/2 + \vec{a}_2/2$, and $\vec{a}_1$, $\vec{a}_2$ are basis vectors of the two dimensional lattice of the D_{rd} phase, $\hat{a}_3$ is the unit vector along the column axes; an orthogonal coordinate frame will be adopted with x_1, x_2 and x_3 axes parallel to $\vec{a}_1$, $\vec{a}_2$, and $\hat{a}_3$ respectively (see Figure 1), and with its origin fixed on a given column axis; the meaning of the h_i are as in Ref. [6], and the operations of the h_i are defined with respect to the chosen coordinate origin and axes; m, n are integers and μ is any real number.

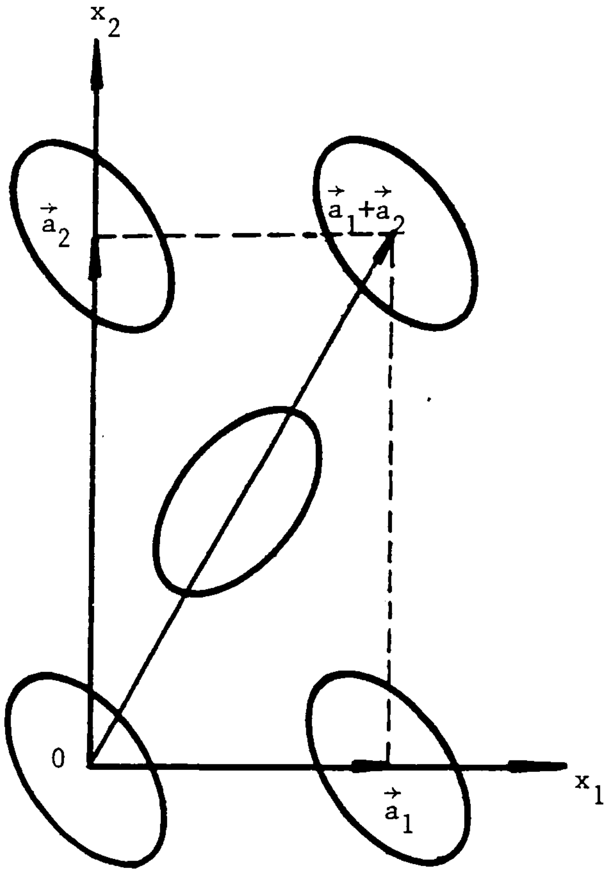

FIGURE 1 pgg pattern of the D_{rd} phase in the plane perpendicular to the column axes; x_1 and x_2 are coordinates in the plane which are along the basis vectors $\vec{a}_1$ and $\vec{a}_2$ respectively; the x_3 axis is perpendicular to the x_1-x_2 plane.

Since the translational invariant sub-group $T_3 = \{(h_1|\mu\hat{a}_3)\}$ is supposed to be preserved through the transition between two different disordered columnar phases, we can therefore use G_o rather than G_o' as the high temperature symmetry group for our purposes without loss of generality. For $g \in G_o \subset G_o'$, we have

$$g = (h_i|\vec{\sigma}_i + m\vec{a}_1 + n\vec{a}_2) \tag{2}$$

where i and $\vec{\sigma}_i$ are the same as in Eqs. (1a) and (1b). Using arguments similar to those in Ref. [12], we can further express G_o as a direct product of two invariant sub-groups G_1 and G_2, i.e., $G_o = G_1 \otimes$

G_2. For $g_1 \in G_1$, $g_2 \in G_2$, we have

$$g_1 = (h_\alpha | \vec{\sigma}_\alpha + m\vec{a}_1 + n\vec{a}_2) \quad \alpha = 1, 4, 26, 27 \tag{3a}$$

$$\vec{\sigma}_\alpha = \begin{cases} \vec{0} & \text{if } \alpha = 1, 4 \\ \vec{\sigma}_o & \text{if } \alpha = 26, 27 \end{cases} \tag{3b}$$

$$g_2 = (h_\beta \mid 0) \quad \beta = 1, 28. \tag{4}$$

G_1 is isomorphic to the two dimensional space group pgg, and G_2 is an Abelian group of order two. The irreducible representations of G_o are determined by those of G_1 and G_2, i.e.,

$$\Gamma_{\vec{k}}^{n,m}(G_o) = \Gamma_{\vec{k}}^{n}(G_1) \otimes \Gamma^m(G_2). \tag{5}$$

The labels n and m in Eq. (5) and hereafter should not be confused with the n and m of the translations in Eq. (2), (3a), and (10). Here, the irreducible representation of G_1 is labeled by two indices $\vec{k}$ and n where $\vec{k}$ is a two dimensional wave vector limited to the first Brillouin zone and n enumerates the small representation of the group of $\vec{k}$. The irreducible representation of G_2 is labeled by m. The basis functions of $\Gamma_{\vec{k}}^{n,m}(G_o)$ are

$$\phi_{\vec{k}_i\upsilon}^{n,m} = \Psi_{\vec{k}_i\upsilon}^{n} \chi^m$$

where $\vec{k}_i \in \{\vec{k}\}$ (the star of $\vec{k}$), υ indicates the degeneracy of the nth small rep. of the group of $\vec{k}$. Also, $\Psi_{\vec{k}_i\upsilon}^{n}$ and χ^m are the bases of $\Gamma_{\vec{k}}^{n}(G_1)$ and $\Gamma^m(G_2)$ respectively. A central quantity in Landau theory is the density function which reflects the symmetry of the system. In liquid crystal systems, this should have a somewhat different meaning from that in crystal systems.[14,15] According to Landau theory, the density function $\rho(\vec{r})$ can be expanded as

$$\rho(\vec{r}) = \rho_o(\vec{r}) + \delta\rho(\vec{r}) \tag{6}$$

$$\delta\rho(\vec{r}) = \Sigma_{\vec{k}_i} \Sigma_\upsilon \eta_{\vec{k}_i\upsilon}^{n,m} \phi_{\vec{k}_i\upsilon}^{n,m}(\vec{r}) \tag{7}$$

where the $\phi_{\vec{k}_i\upsilon}^{n,m}(\vec{r})$'s are the basis functions of a given irreducible representation which is associated with the phase transition under consideration. The indices n and m are fixed in Eq. (7). Bearing this in mind, we will hereafter suppress these indices for the sake of compactness. In Eq. (6) $\rho_o(\vec{r})$ is invariant under the action of all $g \in G_o$. Near the transition point, the Landau Hamiltonian, H_L, can be expanded as a power series in $\eta_{\vec{k}_i\nu}$.[11] In the high temperature phase, the $\eta_{\vec{k}_i\nu}$'s are equal to zero; in the low temperature phase, the symmetry is determined by $\delta\rho_{eq.}(\vec{r})$ (i.e. the $\eta_{\vec{k}_i\nu}$'s take the values which minimize H_L and are not all equal to zero).

Because we are interested in the irreducible representations which correspond to second order phase transitions and to low temperature phases in which the two dimensional periodic structures are not modulated, both the Landau condition (no cubic invariant of $\eta_{\vec{k}_i\nu}$) and Lifshitz condition (no antisymmetric quadratic terms in $\eta_{\vec{k}_i\nu}$ can be formed which transform as components of a vector) should be satisfied.[11] In other words, we only discuss the so-called active irreducible representatives which are induced by a very few wave vectors located at high symmetry points in the first Brillouin zone. Two cases arise if we consider active representations.

(1) $\vec{k} = \vec{k}_o = \vec{0}$

The irreducible representations of G_1 with $\vec{k} = \vec{0}$ can be constructed from the point group $C_{2\nu}$ whose elements are $\{h_1, h_4, h_{26}, h_{27}\}$ (the isogonal point of group G_1). This induces four one dimensional irreducible representation of G_1, denoted by $n = 1$ through 4, and can be proved active. G_2 always has two one-dimensional irreducible representations. $\Gamma^1(G_2)$ and $\Gamma^2(G_2)$, i.e. $m = 1,2$, and for $g_2 = (h_{28}|0)$, we have $g_2\chi^{(1)} = \chi^{(1)}$ and $g_2\chi^{(2)} = -\chi^{(2)}$ where $\chi^{(1)}$ and $\chi^{(2)}$ are basis functions of $\Gamma^1(G_2)$ and $\Gamma^2(G_2)$ respectively. The $\Gamma^{n,m}_{\vec{k}_o}(G_o)$ are then given by all the possible combinations of $\Gamma^n_{\vec{k}_o}$ and Γ^m. So there are eight one dimensional irreducible representations of G_o which we denote as Γ_1 through Γ_8. These are shown in Table I and are all active. The associated Ginzburg-Landau-Wilson Hamiltonian is in the universality class of the three dimensional Ising model.

The possible symmetry patterns of the low temperature phases can be easily found from Table I. All the results are listed in Table II and Figures 2(a) through (e). We note that Γ_4 will give the same pattern as Γ_6, and Γ_5 will give the same pattern as Γ_3.

(2) $\vec{k} = \vec{k}_s = 1/2\ \vec{b}_1 + 1/2\ \vec{b}_2$ where $\vec{b}_1$ and $\vec{b}_2$ are basis vectors of the reciprocal lattice

TABLE I

Irreducible representations of the symmetry group of D_{rd} phase with $\vec{k} = \hat{O}$.

	$(h_1\|0)$	$(h_2\|\vec{\sigma}_0)$	$(h_3\|\vec{\sigma}_0)$	$(h_4\|0)$	$(h_{25}\|0)$	$(h_{26}\|\vec{\sigma}_0)$	$(h_{27}\|\vec{\sigma}_0)$	$(h_{28}\|0)$
Γ_1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	-1	-1	-1	-1
Γ_3	1	1	-1	-1	1	1	-1	-1
Γ_4	1	1	-1	-1	-1	-1	1	1
Γ_5	1	-1	1	-1	1	-1	1	-1
Γ_6	1	-1	1	-1	-1	1	-1	1
Γ_7	1	-1	-1	1	1	-1	-1	1
Γ_8	1	-1	-1	1	-1	1	1	-1

TABLE II

Symmetry groups at low temperature phase obtained from the irreducible representations with $\vec{k} = \vec{0}$. The operation $(h_1|t)$, which always exists, is not listed in the table; $\vec{t} = m\vec{a}_1 + n\vec{a}_2$ with m, n being integers.

irreducible representation	symmetry operations of the low temperature phase	pattern of low temperture phase
Γ_2	$(h_2\|\vec{\sigma}_0+\vec{t}), (h_3\|\vec{\sigma}_0+\vec{t}), (h_4\|\vec{t})$	Fig. 2(a)
Γ_3	$(h_2\|\vec{\sigma}_0+\vec{t}), (h_{25}\|\vec{t}), (h_{26}\|\vec{\sigma}_0+\vec{t})$	Fig. 2(b)
Γ_6	$(h_3\|\vec{\sigma}_0+\vec{t}), (h_{26}\|\vec{\sigma}_0+\vec{t}), (h_{28}\|\vec{t})$	Fig. 2(c)
Γ_7	$(h_4\|\vec{t}), (h_{25}\|\vec{t}), (h_{28}\|\vec{t})$	Fig. 2(d)
Γ_8	$(h_4\|\vec{t}), (h_{26}\|\vec{\sigma}_0+\vec{t}), (h_{27}\|\vec{\sigma}_0+\vec{t})$	Fig. 2(e)

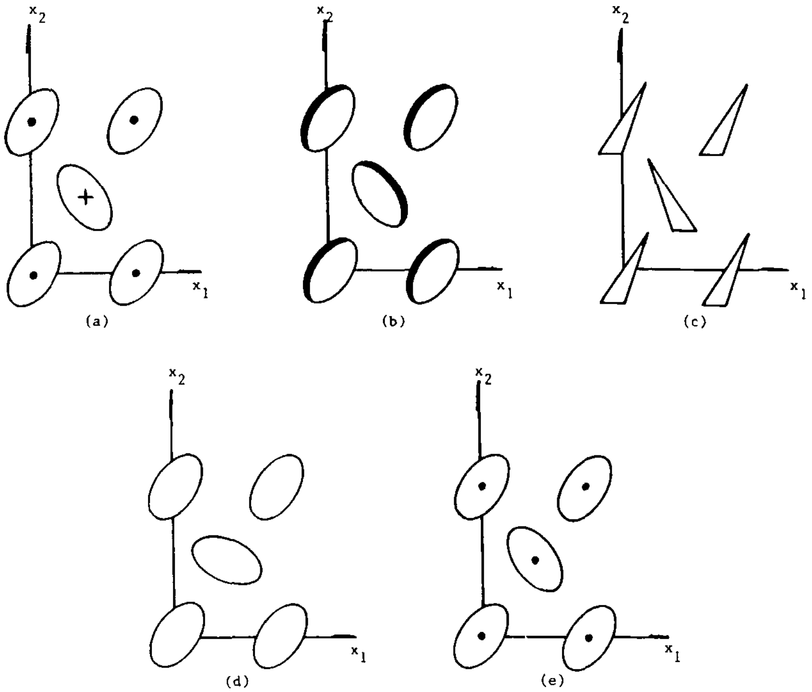

FIGURE 2 Five possible patterns of the D_x phase with the unit cell unchanged after the D_{rd}-D_x transition. The definition of the coordinate frame x_1, x_2, and the basis vectors $\vec{a}_1$ and $\vec{a}_2$ are the same as in Figure 1; the symbols + and · represent the polarization of the columns in two opposite directions along x_3 axis; the molecular planes in Figure (2b) are inclined; the triangles in Figure (2c) only mean that the two-fold rotation axes of the molecules are lost by rearrangements of the molecular chains.

The two-dimensional physical real irreducible representation of G_1 can be formed,[17] and will be denoted by $\Gamma^1_{\vec{k}_s}$ and $\Gamma^2_{\vec{k}_s}$. The representation matrix of G_1 can be easily obtained by choosing the basis functions given in Ref. [18]. Combining with Γ^1 and Γ^2 of G_2, we have four two dimensional irreducible reps. of G_o. The Landau Hamiltonian can be written as

$$H_L = \frac{1}{2}r \sum_{\upsilon=1}^{2} \eta_\upsilon^2 + u \sum_{\mu=1}^{2} \sum_{\upsilon=1}^{2} \eta_\mu^2 \eta_\upsilon^2 + v \sum_{\upsilon=1}^{2} \eta_\upsilon^4; \qquad (8)$$

here we dropped $\vec{k}_i$ because there is only one wave vector in the star. Allowing for a spatial dependence of η_υ we can read off the

Ginzburg-Landau-Wilson Hamiltonian, H, from Ref. [18] as

$$H = \frac{1}{2}\gamma\int d^3x \sum_{\upsilon=1}^{2} \eta_\upsilon^2 + \frac{1}{2}c\int d^3x \sum_{\upsilon=1}^{2}\sum_{\alpha=1}^{3} \nabla_\alpha\eta_\upsilon\nabla_\alpha\eta_\upsilon + u\int d^3x \sum_{\mu=1}^{2}\sum_{\upsilon=1}^{2} \eta_\mu^2\eta_\upsilon^2 + v\int d^3x \sum_{\upsilon=1}^{2}\eta_\upsilon^4 \tag{9}$$

where u, v, and c are constants. Eq. (9) shows that the system belongs to the universality class of the three dimensional x-y model with cubic anisotrophy.

The symmetry properties of the possible low temperature phases are now determined by $\delta\rho_{eq}$ which is obtained by minimizing H_L with respect to η_υ.

Four possible cases can be obtained according to different irreducible representations, $\Gamma_{\vec{k}}^{n,m}$ (G_o), and the symmetry operations of the low temperature phases. These are:

Case 1) $\Gamma_{\vec{k}_s}^{1,1}$

$(h_1\vert m\vec{a}_1 + n\vec{a}_2)$	$m + n$ = even
$(h_4\vert m\vec{a}_1 + n\vec{a}_2)$	$m + n$ = even
$(h_{25}\vert m\vec{a}_1 + n\vec{a}_2)$	$m + n$ = even
$(h_{28}\vert m\vec{a}_1 + n\vec{a}_2)$	$m + n$ = even

where m, n are integers. Now, we rewrite the translational operations $m\vec{a}_1 + n\vec{a}_2$ as $(m-n)\vec{a}_1 + n(\vec{a}_1 + \vec{a}_2)$, $m-n$ is even because $m + n$ is even. We further define $m-n = 2\ell$, $\vec{a}_1' = 2\vec{a}_1$ and $\vec{a}_2' = \vec{a}_1 + \vec{a}_2$, then, $m\vec{a}_1 + n\vec{a}_2 = 2\ell\vec{a}_1 + n(\vec{a}_1 + \vec{a}_2) = \ell\vec{a}_1' + n\vec{a}_2'$. The above symmetry operations are now:
$(h_1\vert\ell\vec{a}_1' + n\vec{a}_2')$, $(h_4\vert\ell\vec{a}_1' + n\vec{a}_2')$, $(h_{25}\vert\ell\vec{a}_1' + n\vec{a}_2')$, $(h_{28}\vert\ell\vec{a}_1' + n\vec{a}_2')$ with n, ℓ being arbitrary integers. $\vec{a}_1'$ and $\vec{a}_2'$ are the basis vectors of the new two dimensional lattice structure, which gives an oblique unit cell with a size twice that in the high temperature phase as shown in Figure (3a). The mechanism for realizing such a pattern is that the molecular planes below the transition temperature are rotated about an axis parallel to the columns when compared to the configuration at high temperatures. The molecules may have four different orientations labelled by A,B,C,D in Figure (3a).

Following a similar discussion, we can obtain the other three cases. The results are

Case 2) $\Gamma_{\vec{k}_s}^{2,1}$

By choosing a translated coordinate system, and defining all the rotational operations with respect to the new frame system, we find the symmetry operations are exactly the same as in case 1. This pattern is shown in Figure (b). The triangles only mean that the two fold rotation axes of the molecules are lost by rearranging molecular chains.

Case 3) $\Gamma_{\vec{k}_s}^{1,2}$

The preserved symmetry operations are $(h_1|\ell\vec{a}_1' + n\vec{a}_2')$, $(h_4|\ell\vec{a}_1' + n\vec{a}_2')$, $(h_{25}|\frac{\vec{a}_1'}{2} + \ell\vec{a}_1' + n\vec{a}_2)$, $(h_{28}|\frac{\vec{a}_1'}{2} + \ell\vec{a}_1' + n\vec{a}_2)$. A possible mechanism for obtaining this symmetry is that the molecules are polarized in two opposite directions along the columns, as shown in Figure (3c).

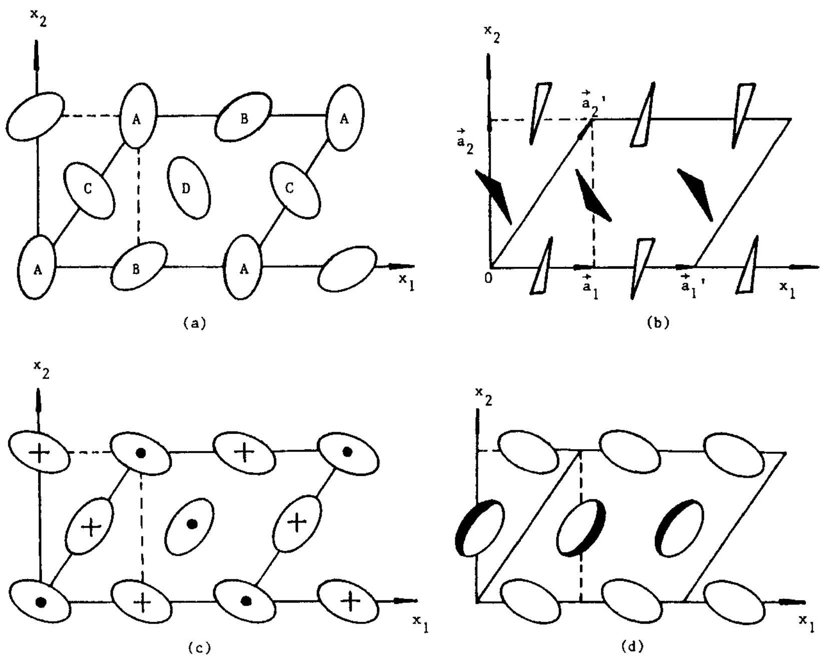

FIGURE 3 Four possible patterns of the D_x phase after the D_{rd}-D_x transition corresponding to the irreducible representations with $\vec{k} = \vec{b}_1/2 + \vec{b}_2/2$; the basis vectors $\vec{a}_1$ and $\vec{a}_2$ for the high temperature phase and $\vec{a}_1'$ and $\vec{a}_2'$ for the low temperature phases are indicated in Figure (3b); the unfilled and filled triangles in Figure (3b) indicate two different kinds of molecular configurations; the meanings of the other symbols are as in Figure 2.

Case 4) $\Gamma^{2,2}_{\vec{k}_s}$

In the translated reference frame, the symmetry operations will be the same as in case (c). This pattern may be brought about by inclinations of the molecular planes as in Figure (3d).

3. DISCUSSION

(1) The existence of a mesophase with the symmetry pattern in Figure (2b) has been reported in BHA (benzene-hexa-n-alkanoate) series.[4a,4b] (see Figure 7 of Ref. [4a]). Our discussion predicts that such a phase may be obtained from D_{rd}(pgg) phase through a continuous phase transition. We notice that, if the column axes are tilted from x_3 axis along the x_2-x_3 plane with the molecular configurations unchanged so that the directions of the two dimensional descrete translations are not perpendicular to that of the continuous translations, all the preserved symmetry operations are exactly the same as in the untilted system. As pointed out by Landau and Lifshitz,[11] an arbitrary small disturbance will change the lattice system with higher symmetry to one with lower symmetry. So, distortions can be expected.

(2) For the same reasons, the phase as shown in Figure (2d) will be distorted to be oblique ($\vec{a}_1$ and $\vec{a}_2$ are not perpendicular). This phase can be employed to qualitatively explain the existence of the D_{rd}-$D_{ob.d}$ phase transition in n-hexa alkalnoyloxy-benzo series.[6]

(3) Figures (3a) through (3d) are also obtained through a transition between different two dimensional lattice systems (rectangular to oblique) and distortions are also inevitable. So those patterns are only approximately valid if the distortions are small. Taking the distortions into account, one needs to include the elastic energy and the coupling between the elastic degrees of freedom and the order parameters in the Hamiltonian. If the coupling is strong, in some cases, the elastic effects will drive the phase transition to be the first order.[19]

Acknowledgment

This research was supported in part by the Robert A. Welch Foundation under Grant No. F-767.

References

1. S. Chandrasekhar, B. K. Sadashiva, and K. A. Suresh, *Pramana*, **9**, 471 (1977).
2. C. Destrade, Nguyen Huu Tinh, H. Gasparoux, J. Malthete, and A. M. Levelut, *Mol. Cryst. Liq. Cryst.*, **71**, 111 (1981).

3. (a) C. Destrade, M. C. Mondon, and J. Malthete, *J. Physique*, **40**, C3-17 (1979). (b) C. Destrade, M. C. Mondon-Bernard and Nguyen Huu Tinh, *Mol. Cryst. Liq.-Cryst.*, **99**, L169 (1979).
4. (a) A. M. Levelut, J. Chimie *Physique*, **80**, n°1 150 (1983). (b) S. Chandrasekhan, *Mol. Cryst. Liq. Cryst.*, **63**, 171 (1981).
5. J. Billard, J. C. Dubois, C. Vaucher and A. M. Levelut, *Mol. Cryst. Liq. Cryst.*, **66**, 115 (1981).
6. L. Mamlok, J. Malthete, Nguyen Huu Tinh and C. Destrade, *J. Physique Lett.*, **43**, 641 (1982).
7. C. Destrade, J. Malthete, Nguyen Huu Tinh and H. Gasparous, *Phys. Lett.*, **78A**, 82 (1980).
8. F. C. Frank and S. Chandrasekhar, *J. Physique*, **41**, 1285 (1980).
9. C. Destrade, H. Gasparoux, P. Foucher, Nguyen Huu Tinh, J. Malthete and J. Jacques, *J. Chimie Physique*, 80 **n°1**, 137 (1983).
10. A. M. Levelut et al. *J. Phys.* **45**, 745 (1984).
11. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd Edition (Pergamon Press, Oxford (1980)).
12. Y.-f. Sun and J. Swift, *Disordered Hexagonal-Disordered Rectangular Phase—Transitions in HAT Series* to be published in J. Physique, Nov. 1984.
13. M. Kleman and L. Michel, *Phys. Rev. Lett.*, **40**, 1387 (1978).
14. S. Goshen, D. Mukamel and S. Shtrikman, *Mol. Cryst. Liq. Cryst.*, **31**, 175 (1975).
15. S. A. Pikin and V. L. Indenbom, *Soviet Phys. USP.*, **21**, 487 (1978). (Gordon and Breach, New York (1965)).
16. O. V. Kovalev, *Irreducible Representation of the space groups*. Gordon and Breach, New York (1965).
17. C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Clarendon Press, Oxford) 1972.
18. C. Rothman, *Phys. Rev.*, **B24**, 1482 (1981).
19. Y.-f. Sun and J. Swift, *J. Physique*, **45**, 1039 (1984).