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Disordered hexagonal-disordered rectangular phase transitions in HAT series

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Résumé. — La transition entre phases liquide-cristallines columnaires hexagonale/rectangulaire désordonnées (D_{hd}-D_{rd}) dans la série HAT est analysée en appliquant les techniques de la théorie des groupes. La théorie de Landau prédit que la transition doit être du deuxième ordre. L'hamiltonien de Ginzburg-Landau-Wilson correspond à une classe d'universalité ayant un paramètre d'ordre de composante $n = 3$ et une anisotropie cubique. Le comportement critique près de la transition D_{hd}-D_{rd} est étudié à partir des résultats de Aharony et d'autres auteurs sur le groupe de renormalisation et il apparaît qu'une valeur critique de n, n_c, supérieure à 3, est possible. Une transition du deuxième ordre entre la phase D_{hd} et une phase pas encore mise en évidence expérimentalement est prédite.

Abstract. — Group theoretical techniques are used to discuss the disordered hexagonal columnar-disordered rectangular columnar (D_{hd}-D_{rd}) liquid crystal phase transition in HAT series. On the basis of Landau theory the transition is predicted to be second order. The Ginzburg-Landau-Wilson Hamiltonian corresponds to a universality class with an $n = 3$ component order parameter and with cubic anisotropy. The critical behaviour near the D_{hd}-D_{rd} transition is discussed by referring to the renormalization group results of Aharony and other authors and we present evidence in favour of the critical value of n, n_c, being greater than 3. It is also predicted that a second order transition from the D_{hd} phase to an as yet experimentally undiscovered phase is possible.

1. Introduction.

Since the first discovery of a new type of mesophase in liquid-crystals composed of disc-like molecules [1], at least five homologous series of disc-like mesogens have been reported. A classification of these mesogens was suggested by Destrade *et al.* [2]. According to their notation, the mesogens are called HAB, HET, HAT, HBT and HATX, and the corresponding compounds and molecular structures are presented in figure 1 of reference [2]. A rich polymorphism has been found in these homologous series. At least five different mesophases have been discovered, referred to as D_{hd} (disordered hexagonal), D_{rd} (disordered rectangular), D_{ho} (ordered hexagonal), D_t (tilted) and N_D (nematic disc-like). The D_0 phase in HAT series has not been definitely identified yet [2, 3] and other mesophases are also possible; e.g. the D_c phase, which is suggested to have a pmg symmetry in the hexa-*n*-octanoate of rufigallol (RHO) [4], and the $D_{ob,d}$ (disordered oblique) phase in the *n*-hexalkanoyloxybenzo trisbenzofurans [5] were reported recently.

For some homologous series, e.g. HAT, HBT, and HATX (see Table IX of Ref. [2]), the polymorphism in a given series and the possible phase transitions in the same series were also investigated by several authors [2]-[5]. Usually the following sequence of phase transitions is observed as temperature is increased : HAT(C-D_0-D_{rd}-D_{hd}-I), HBT(C-D_t-D_r-N_D-I); where C represents the crystal phase, and I the isotropic phase. But for the HATX series, the order is reversed; i.e. HATX(C-N_D-D_r-D_h-I). This was reported as the first example of a reentrant nematic phase in disc-like mesogens [6]. On the other hand, few theoretical discussions have been published in this area.

Some phase transitions in a given series are second order (or nearly so) according to the experimentally measured latent-heat [2], [4]. Because the phase transitions among the different mesophases in a given series just correspond to changes of symmetries, one then can expect that in some cases (second order transitions), Landau's theory [7] may be employed to construct a suitable Ginzburg-Landau-Wilson Hamiltonian. The critical behaviour can then be analysed by means of the renormalization group theory [8]. Such a discussion may be used to : a) compare with the experimental results; b) predict the critical behaviour where there is a lack of experimental reports so far; c) predict new possible mesophases which have not been found yet.

In this paper, we will study the D_{hd}-D_{rd} phase transition in HAT series [2] as our model system. The ana-

lysis of symmetries shows that the irreducible representation of the space group of the high temperature phase, which is associated with D_{hd}-D_{rd} transition, can be identified by a wave vector star $\{ \mathbf{k}^* \} = \{ \frac{1}{2}\mathbf{b}_1, \frac{1}{2}\mathbf{b}_2, -\frac{1}{2}\mathbf{b}_1 + \frac{1}{2}\mathbf{b}_2 \}$ and an irreducible representation A_2 of the C_{2v} point group (see section 3 for notation). If the coefficient v (see Eq. (3)) is negative, the symmetry of the low temperature phase in the plane perpendicular to the column axes corresponds to the two dimensional space group p2gg which has been observed experimentally. If v is positive, the symmetry of the low temperature phase corresponds to the two dimensional space group p6; such a phase has not yet been found experimentally.

In section 2 we will discuss a possible mechanism which leads to the D_{hd}-D_{rd} phase transition; in section 3 we use Landau's theory and group theoretic techniques to obtain the relevant Ginzburg-Landau-Wilson Hamiltonian and the possible symmetries of the low temperature phases; in section 4 we give the symmetry elements and pattern of the as yet undiscovered mesophase; in section 5 critical behaviour near the transition will be discussed by referring to Aharony's and others' work.

2. Mechanism of D_{hd}-D_{rd} transition in HAT series.

The molecular structure of HAT derivatives consists of a hard triphenylene core, attached to which are six *n*-alcanoyloxy chains $R(=OCOC_nH_{2n+1})$. The molecular core has a threefold axis perpendicular to the plane of the core. In the D_{hd} phase, the molecular planes are irregularly spaced with respect to each other to form disordered columns. In the plane perpendicular to the columns, they form a two-dimensional hexagonal lattice. The symmetry of the D_{hd} phase requires the column axes to be sixfold-axes (C_6). As a simple way to realize such an arrangement, one can imagine that along the column axes both the triphenylene core and the flexible chains are randomly oriented with equal probabilities in any direction in the plane perpendicular to the columns. In other words, the orientations of the molecules in the plane do not exhibit long-range correlations along the C_6 axes. Only in this sense can the molecules be considered as disc-like circles from which are constructed a D_{hd} phase at high temperature. Below and close to $T = T_c$ the molecular chains start to orient with larger probability along some easy directions than along other directions in order that the minimum free energy be reached. No matter how small such an effect is, once it appears the molecules can no longer be considered as circle-like and the symmetry is changed. In the process, the state of the system has changed continuously. This gives a possible mechanism for a phase change from D_{hd} to a lower symmetry phase by a second order phase transition. Two points need to be added.

2.1 For HAT derivatives with short chain length, the orientations of the chains are mainly dominated by triphenylene cores, so the orientational arrangement of the chains along some easy directions may be hindered by the random orientations of the cores. On the contrary, for long length chains which are more flexible than the short ones, we can suppose that the outer parts of the chains are free from the core influences so that the orientational arrangements along the easy directions can be realized. This qualitative argument may be used to explain table III of reference [2] which shows the polymorphism only appears when the chain length is greater than ten in HAT series.

2.2 We suppose that the position of the lattice sites are unchanged through the transition. The X-ray experiments measured in different homologous series do show the changes of the lattice site positions [2]; however, the measured change in HAT system is tiny. We ignore this small change in our model.

3. Analysis of symmetries.

The method we employ here is one which has been widely used to discuss structural phase transitions in crystals. We give a brief description of the theoretical framework based on references [7], and [9-12]. The application of this theory to our model system with a few special considerations will be given later on.

According to Landau's theory of second order phase transitions, different phases before and after a transition can be described by a density functional $\rho(\mathbf{r})$. The symmetry of a given system and its Hamiltonian in either phase can be characterized by the respective symmetry group; say, G_0 for the high temperature phase, and G for low temperature phase, $G \subset G_0$. Such a symmetry should be reflected by $\rho(\mathbf{r})$. In the equilibrium state $\rho(\mathbf{r})$ takes the form $\rho_{eq}(\mathbf{r})$ which minimizes the Hamiltonian, and $\rho_{eq}(\mathbf{r})$ is invariant under all of the operations in the symmetry group of the given phase. In the terminology of group theory, $\rho_{eq}(\mathbf{r})$ is the base-function of the unit representation of the symmetry group. Based on the arguments given in reference [7], for ordinary second order phase transitions (excluding multi-critical points), near the transition point, ρ can be written as

$$\rho = \rho_0 + \delta\rho \tag{1}$$

and

$$\delta\rho = \sum_{i=1}^{m} \eta_i \phi_i . \tag{2}$$

Here ρ_0 is supposed to be invariant under G_0 (i.e. ρ_0 is the base-function of the unit representation of G_0), the ϕ_i's are the base-functions of one of the *m*-dimensional irreducible representations of G_0, which is relevant to the phase transition under consideration. Obviously, in the high temperature phase $\rho_{eq} = \rho_0$; i.e., minimizing the Hamiltonian requires all η_i to be zero. In the low temperature phase the η_i's are non-zero, but they continuously approach

zero when the system is close to its transition point. The symmetry at low temperature is therefore determined by $\delta\rho_{eq}$.

Near the transition, the Hamiltonian H_L can be expanded as a power series in the η_i. Since H_L is a scalar, such an expansion should consist of various invariants; i.e.

$$H_L = \frac{1}{2} r \sum_i \eta_i^2 + \sum_\alpha C_\alpha^{(3)} f_\alpha^{(3)}(\eta_i) + \\ + \sum_\alpha C_\alpha^{(4)} f_\alpha^{(4)}(\eta_i) + \cdots \quad (3)$$

where $f_\alpha^{(3)}(\eta_i)$ and $f_\alpha^{(4)}(\eta_i)$ are the αth third order and fourth order invariants of η_i respectively, the summation index α is over all possible invariants. The coefficients r, $C_\alpha^{(3)}$, $C_\alpha^{(4)}$ are functions of temperature and other state parameters. If the phase transition is second order, there must be no $f_\alpha^{(3)}(\eta_i)$ terms (Landau condition).

To determine the form of H_L, and the symmetry of G, we need the representation theory of groups. The symmetry group of D_{hd} has been classified as $H = R \times Z^2 \wedge D_{6h}$ [13], i.e., a semi-direct product of a translational sub-group $T_H = R \times Z^2$ and a point group D_{6h}, and will be taken as the symmetry group G_0 of the high temperature phase. By using the Sietz notation [10], for $g \in G_0$, we have $g = (h_i \mid \mathbf{t}_H)$. The h_i ($i = 1$ through 24) on the left-hand side in the parenthesis represents a symmetric operation of D_{6h}, which has the same meaning as in Kovalev's book [14]. The $\mathbf{t}_H$ on the right-hand side represents a simultaneous translational operation applied after the h_i on the left side, and $\mathbf{t}_H = m\mathbf{a}_1 + n\mathbf{a}_3 + \mu\hat{\mathbf{a}}_3 \in T_H$, where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the basis vectors of the two dimensional lattice in the plane perpendicular to the C_6 axis, $\hat{\mathbf{a}}_3$ is a unit vector along the C_6 axis, m, n are integers and μ is an arbitrary real number. The multiplication rules are

$$gg' = (h_i \mid \mathbf{t}_H)(h_j \mid \mathbf{t}'_H) = (h_i h_j \mid \mathbf{t}_H + h_i \mathbf{t}'_H). \quad (4)$$

Now, we consider two subgroups of $G_0 (\equiv H)$, G_1 and G_2. For $g_1 \in G_1$ and $g_2 \in G_2$, we have

$$g_1 (h_\alpha \mid m\mathbf{a}_1 + n\mathbf{a}_2)\ \alpha = \begin{matrix} 1, 2, 3, 4, 5, 6, \\ 19, 20, 21, 22, 23, 24 \end{matrix} \quad (5)$$

$$g_2 = (h_\beta \mid \mu\hat{\mathbf{a}}_3) \qquad \beta = 1, 16 \quad (6)$$

Obviously

$$G_1 \cap G_2 = (h_1 \mid 0). \quad (7)$$

According to the multiplication table of D_{6h} [14] it is clear that $h_\alpha h_\beta = h_\beta h_\alpha$ for the given values of α and β as in equations (5) and (6). Also, $h_\alpha(\mu\hat{\mathbf{a}}_3) = \mu\hat{\mathbf{a}}_3$, $h_\beta(m\mathbf{a}_1 + n\mathbf{a}_2) = m\mathbf{a}_1 + n\mathbf{a}_2$, it is easy to prove that $g_1 g_2 = g_2 g_1$. All the symmetric operations $g \in G_0$ can be expressed as $g = g_1 g_2 \in G_0$. So, G_0 is a direct product of G_1 and G_2,

$$G_0 = G_1 \otimes G_2 . \quad (8)$$

The irreducible representations of $G_0(\Gamma(G_0))$ are totally determined by that of $G_1(\Gamma(G_1))$ and $G_2(\Gamma(G_2))$ [10], and

$$\Gamma(G_0) = \Gamma(G_1) \otimes \Gamma(G_2) .$$

In this paper, our interests will focus on the irreducible representation of G_0 which is relevant to the D_{hd}-D_{rd} transition. Through the transition all the symmetric operations in G_2 should be preserved in the low temperature phase. This requires that $\Gamma(G_2) \equiv 1$ (the unit representation of G_2). The required irreducible representation of G_0 which describes the phase transition will then be determined by that of G_1. From the definition of equation (5), one can identify that G_1 is isomorphic to the two dimensional symmorphic space group P6mm. The suitable irreducible representations of such a space group can be found in reference [11]. A difference from the real two dimensional systems discussed in reference [11] is that the Landau condition of the second order transition should still be satisfied. This is because our model system has three spatial dimensions and only in the sense of symmetry changes through the D_{hd}-D_{rd} transition can we consider the system to be two dimensional.

The irreducible representations of a space group are classified by two indices, $\mathbf{k}$ and τ, and are denoted by $\Gamma^\tau_{\mathbf{k}}$. Here $\mathbf{k}$ is a wave vector in the first Brillouin zone in reciprocal space. For a chosen $\mathbf{k}$, a proper symmetry group of $\mathbf{k}$, $G_{\mathbf{k}}$, can be defined. For a symmorphic space group, $G_{\mathbf{k}}$ is a point group and is composed of all those rotational operations under which $\mathbf{k}$ is unchanged or changed into an equivalent wave vector $\mathbf{k}' = \mathbf{k} + \mathbf{K}_n$ ($\mathbf{K}_n$ is a reciprocal lattice vector). We will not discuss the irreducible representations of a non-symmorphic space group here. Also, τ is an irreducible representation of $G_{\mathbf{k}}$. Further, we can define a set of non-equivalent wave vectors $\{\mathbf{k}^*\}$, called the star of $\mathbf{k}$, which are produced by the action of all of the rotational operations of the space group on $\mathbf{k}$. So long as $\mathbf{k}$ and τ are determined, the irreducible representation of the symmorphic space group $\Gamma^\tau_{\mathbf{k}}$ can be loaded by choosing a set of base-functions ϕ_i^α given by

$$\phi_i^\alpha = e^{i\mathbf{k}_i \cdot \mathbf{r}} \psi^\tau_{\mathbf{k}_i \alpha} , \quad (9)$$

where $\mathbf{k}_i \in \{\mathbf{k}^*\}$, $i = 1, 2, \ldots s$. (According to Ref. [7], instead of $e^{i\mathbf{k}_i \cdot \mathbf{r}}$ the linear combinations of the expressions $e^{i\mathbf{k}_i \cdot \mathbf{r}}$ (with equivalent $\mathbf{k}_i$) which are invariant with respect to the transformations in the group of $\mathbf{k}_i$ are used. So, in equations (4), (11) and (18), $e^{i\mathbf{k}_i \cdot \mathbf{r}}$ and $e^{i(\mathbf{k}_i + \mathbf{K}_n) \cdot \mathbf{r}}$ should be considered to be the same; in

other words, the $\mathbf{k}_i$'s are defined up to $\mathbf{K}_n$ [14].) The $\psi^{\tau}_{\mathbf{k}_1,\alpha}$'s are the base-functions of the irreducible representation τ of $G_{\mathbf{k}}$, $\alpha = 1, 2, \ldots m$, m is the dimension of τ and the prefactor of i in the argument of the exponential is the square root of minus one. So, the dimension of $\Gamma^{\tau}_{\mathbf{k}}$ is *sm*. Here, $\mathbf{k}_i$, $\mathbf{r}$ and $\mathbf{k}_n$ are all two dimensional vectors.

An oblique coordinate system in the plane perpendicular to C_6 axis will be used [14]. The basis-vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, the basis vectors of the reciprocal lattice $\mathbf{b}_1$ and $\mathbf{b}_2$, and the first Brillouin zone in the plane are chosen as in figure 1. We take our wave vector star $\{\mathbf{k}^*\}$ to be

$$\mathbf{k}_1 = \frac{\mathbf{b}_1}{2}, \quad \mathbf{k}_2 = \frac{\mathbf{b}_2}{2}, \quad \mathbf{k}_3 = -\frac{\mathbf{b}_1}{2} + \frac{\mathbf{b}_2}{2}. \tag{10}$$

The proper symmetry group of $\mathbf{k}_1$ includes four rotational operations h_1, h_4, h_{19}, h_{22}, and can be identified as the C_{2v} point group. This group can only have four one-dimensional irreducible representations (see Table I). We pick A_2 in table I to be our τ. Having the wave vector star $\{\mathbf{k}\}$, and the irreducible representation τ of $G_{\mathbf{k}_1}$, we use equation (10) and obtain the base-functions of $\Gamma^{\tau}_{\mathbf{k}_1}$:

$$\begin{aligned} \phi_1 &= \exp(i\mathbf{k}_1.\mathbf{r})\,\psi^{\tau}_{\mathbf{k}_1}, \\ \phi_2 &= \exp(i\mathbf{k}_2.\mathbf{r})\,\psi^{\tau}_{\mathbf{k}_2}, \\ \phi_3 &= \exp(i\mathbf{k}_3.\mathbf{r})\,\psi^{\tau}_{\mathbf{k}_3} \end{aligned} \tag{11}$$

where $\psi^{\tau}_{\mathbf{k}_1}$ is the base-function of τ.

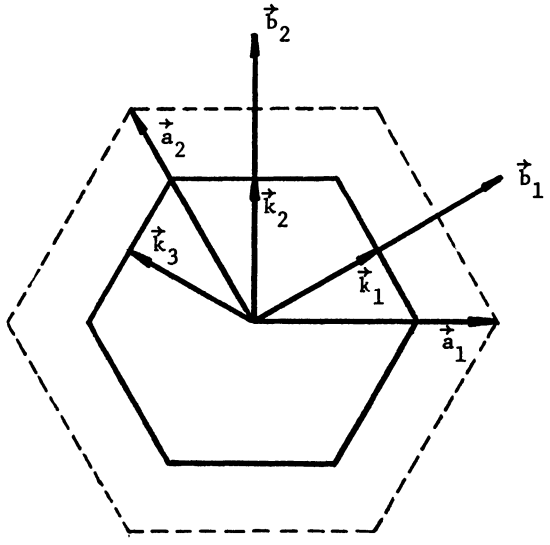


Fig. 1. — The dotted hexagon represents the Bravais cell of the two-dimensional hexagonal structure with the basis-vectors, $\mathbf{a}_1$ and $\mathbf{a}_2$, in the plane perpendicular to the C_6 axis; the bold hexagon represents the first Brillouin zone in the reciprocal space with the basis-vectors, $\mathbf{b}_1$ and $\mathbf{b}_2$; $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ are the wave vectors from which the star of $\mathbf{k}_1$ is constructed.

Table I. — *The irreducible representation* τ *of* $G_{\mathbf{k}_1}$.

τ	h_1	h_4	h_{19}	h_{22}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

We have dropped the index α, because our τ is one-dimensional. Thus we have given a three-dimensional irreducible representation of $\Gamma^{\tau}_{\mathbf{k}_1}$ of G_1. The Landau Hamiltonian, H_L, can then be found from table II of reference [11].

$$H_L = \frac{1}{2} r\eta^2 + u\eta^4 + v(\eta_1^4 + \eta_2^4 + \eta_3^4). \tag{12}$$

If we allow for a spatial dependence of η_i, the Ginzburg-Landau-Wilson Hamiltonian, H, can be written down immediately as

$$H = \frac{1}{2} r \int \mathrm{d}^d x \sum_{i=1}^{3} \eta_i^2 + \frac{c}{2} \int \mathrm{d}^d x \sum_{i=1}^{3} \sum_{\alpha=1}^{d} \nabla_\alpha \eta_i \nabla_\alpha \eta_i + u \int \mathrm{d}^d x \sum_{i=1}^{3} \sum_{j=1}^{3} \eta_i^2 \eta_j^2 + v \int \mathrm{d}^d x \sum_{i=1}^{3} \eta_i^4 \tag{13}$$

where d is the spatial dimension ($d = 3$) and u, v, and c are constants.

Finally, we determine the possible low temperature phases. Rewriting equation (12) by changing variables [7], we have

$$H_L = \frac{1}{2} r\eta^2 + u\eta^4 + v\eta^4(\gamma_1^4 + \gamma_2^4 + \gamma_3^4) \tag{14}$$

where

$$\eta_1 = \eta\gamma_1, \quad \eta_2 = \eta\gamma_2, \quad \eta_3 = \eta\gamma_3 \tag{15a}$$

with

$$\gamma_1^2 + \gamma_2^2 + \gamma_3^2 = 1. \tag{15b}$$

The minimum value of H_L can be obtained from $\frac{\partial H_L}{\partial \gamma_2} = 0$, $\frac{\partial H_L}{\partial \gamma_3} = 0$ and $\frac{\partial H_L}{\partial \eta} = 0$ (γ_1 in H_L should be substituted from Eq. (15b)) with the conditions

$$\begin{vmatrix} \frac{\partial^2 H_L}{\partial \gamma_2^2} & \frac{\partial^2 H_L}{\partial \gamma_2 \partial \gamma_3} \\ \frac{\partial^2 H_L}{\partial \gamma_3 \partial \gamma_2} & \frac{\partial^2 H_L}{\partial \gamma_3^2} \end{vmatrix} = \text{positive definite},$$

and

$$\frac{\partial^2 H}{\partial \eta^2} > 0.$$

We obtain two possible solutions :

$$\gamma_1 = 1, \quad \gamma_2 = 0, \quad \gamma_3 = 0 \quad \text{if} \quad v < 0, \quad u + v > 0 \tag{16}$$

and

$$\gamma_1 = \frac{1}{\sqrt{3}}, \quad \gamma_2 = \frac{1}{\sqrt{3}}, \quad \gamma_3 = \frac{1}{\sqrt{3}}$$

$$\text{if} \qquad v > 0, \quad u + \frac{1}{3} v > 0 \tag{17}$$

So, if $v < 0$, we substitute equation (16) into equation (2) and have

$$\delta\rho_{eq} = \eta_{eq}\, \phi_1 = \eta_{eq} \exp(i\mathbf{k}_1 . \mathbf{r})\, \psi^{\tau}_{\mathbf{k}_1} \tag{18}$$

where η_{eq} is a constant under symmetric transformations and is obtained from $\dfrac{\partial H_L}{\partial \eta} = 0$. One can easily check that

$$\tilde{g}_1\, \delta\rho_{eq} = \delta\rho_{eq}, \quad \text{if} \quad \tilde{g}_1 \in \tilde{G}_1 \subset G_1 \tag{19}$$

and

$$\tilde{g}_1 = \begin{cases} (h_i \mid 2\, m\mathbf{a}_1 + n\mathbf{a}_2) & \text{if} \quad i = 1, 4 \\ (h_i \mid (2\, m + 1)\, \mathbf{a}_1 + n\mathbf{a}_2) & \text{if} \quad i = 19, 22 \end{cases} \tag{20}$$

where m and n are integers. We can further define

$$\mathbf{a}_0 = 2\, \mathbf{a}_1 . \tag{21}$$

Then

$$(h_i \mid 2\, m\mathbf{a}_1 + n\mathbf{a}_2) = (h_i \mid m\mathbf{a}_0 + n\mathbf{a}_2) \tag{22}$$

$$(h_j \mid (2\, m + 1)\, \mathbf{a}_1 + n\mathbf{a}_2) = \left(h_j \,\middle|\, \frac{\mathbf{a}_0}{2} + m\mathbf{a}_0 + n\mathbf{a}_2\right) \tag{23}$$

or

$$\tilde{G}_1 = \{ (h_\alpha \mid \sigma_\alpha + m\mathbf{a}_0 + n\mathbf{a}_2) \} \tag{24}$$

where $\alpha = 1, 4, 19, 22$ and

$$\sigma_\alpha = \begin{cases} \dfrac{\mathbf{a}_0}{2} & \text{if} \quad \alpha = 19, 22 \\ 0 & \text{if} \quad \alpha = 1, 4 . \end{cases} \tag{25}$$

Equation (24) means that in the low temperature phase a new Bravais lattice appears, in which the lattice constant in the $\mathbf{a}_1$ direction is doubled and that in the $\mathbf{a}_2$ direction remains the same. The meanings of the four rotational operations in $\tilde{G}_1$ are [14]

$(h_1 \mid 0)$ unit operation

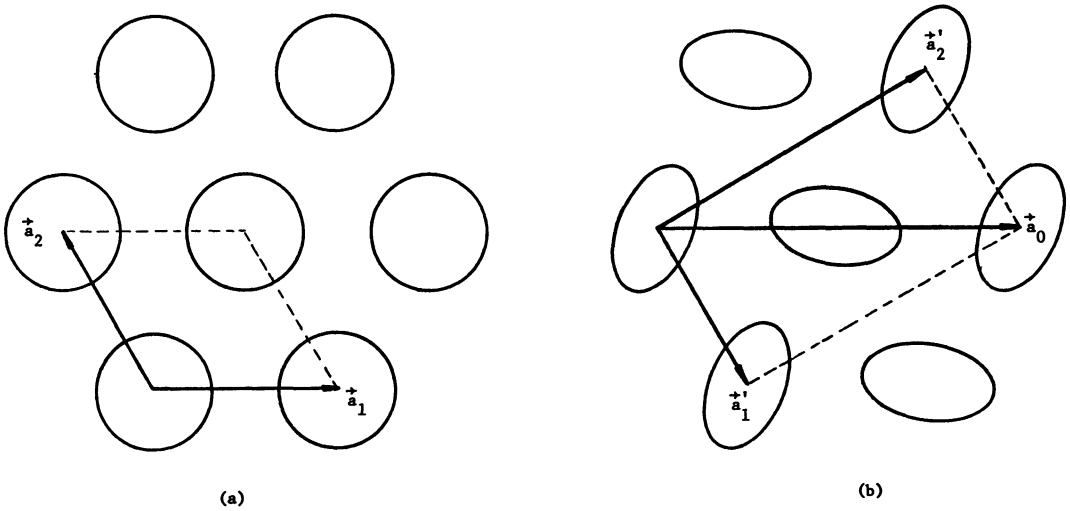
$(h_4 \mid 0)$ 180° rotation about (0, 0, 1) axis

$\left(h_{19} \,\middle|\, \dfrac{\mathbf{a}_0}{2}\right)$ reflection in (0, 1, 0) plane followed by a translation $\dfrac{\mathbf{a}_0}{2}$

$\left(h_{22} \,\middle|\, \dfrac{\mathbf{a}_0}{2}\right)$ reflection in (2, 1, 0) plane followed by a translation $\dfrac{\mathbf{a}_0}{2}$.

The pattern of the molecular arrangement in the plane perpendicular to C_6 axis at low temperature phase is shown in figure 2, which has exactly the same pattern as p2gg observed experimentally. The full symmetry of the low temperature phase then corresponds to $G = \tilde{G}_1 \otimes G_2$, or for $g \in G$, we have

$$g = (h_i \mid \sigma_i + m\mathbf{a}_0 + n\mathbf{a}_2 + \mu\hat{\mathbf{a}}_3) \tag{26}$$



(a) (b)

Fig. 2. — a) The D_{hd} phase. $\mathbf{a}_1$ and $\mathbf{a}_2$ are the basis-vectors of the two-dimensional hexagonal lattice.
b) The D_{rd} phase. $\mathbf{a}'_1$ and $\mathbf{a}'_2$ are the basis-vectors of the two-dimensional rectangular lattice. $\mathbf{a}'_1 = -\mathbf{a}_2$, $\mathbf{a}'_2 = 2\,\mathbf{a}_1 + \mathbf{a}_2$, and $\mathbf{a}_1 = \dfrac{\mathbf{a}_0}{2} = \dfrac{1}{2}(\mathbf{a}'_1 + \mathbf{a}'_2)$.

where

$$\sigma_i = \begin{cases} \frac{\mathbf{a}_0}{2} & \text{if } i = 7, 10, 19, 22 \\ 0 & \text{if } i = 1, 4, 13, 16 . \end{cases} \quad (27)$$

G is the symmetry group of the D_{rd} phase.

So far, we have worked with an oblique coordinate system. Now, we choose a Bravais lattice with $\mathbf{a}'_1$ and $\mathbf{a}'_2$ as its basis-vectors (Fig. 2). Then the rotational operations should be renamed in the rectangular coordinate system [14]. The relations are as the following :

$$h_1 \to h_1 , \quad h_4 \to h_4 , \quad h_{13} \to h_{25} , \quad h_{16} \to h_{28}$$
$$h_7 \to h_3 , \quad h_{10} \to h_2 , \quad h_{19} \to h_{27} , \quad h_{22} \to h_{26} .$$

The half-integer translations after h_2, h_3, h_{26}, h_{27} will be $\frac{\mathbf{a}'_1}{2} + \frac{\mathbf{a}'_2}{2} \equiv \mathbf{a}_0/2$. If $v > 0$, we use the solutions of equation (17) instead of equation (16) and follow the similar discussions after equation (17). We obtain a new phase in which $\tilde{G}_1$ is classified by the p6 space group, with doubled lattice spacing in both $\mathbf{a}_1$ and $\mathbf{a}_2$ directions. Such a phase has not yet been observed experimentally. In section 4 we will discuss the pattern of such a phase.

4. Pattern of phase with p6 symmetry in the plane perpendicular to C_6 axis.

In this section, we give the pattern of the as yet unobserved low temperature mesophase with p6 symmetry and doubled spacing in both the $\mathbf{a}_1$ and $\mathbf{a}_2$ directions. The p6 symmetry requires the column axes to be a C_6 axis. Its symmetric elements within a Bravais cell in the plane perpendicular to the C_6 axes are shown as figure 3. (Note : inversion, reflection in the plane perpendicular to the C_6 axis, and mirror rotations about C_6 axis are not included.) It belongs to the p6 pattern [15]. Two possible orientational arrangements of the molecular plane along particular easy directions are shown in figures 4a) and b). Such arrangements

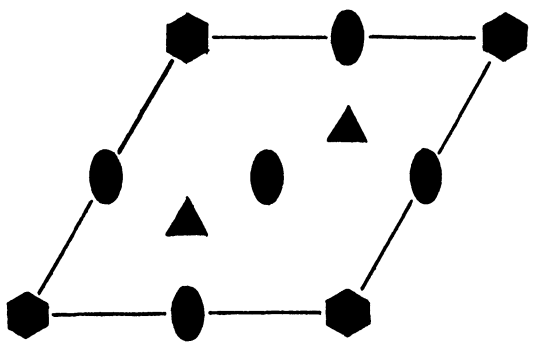


Fig. 3. — The symmetric elements of the p6 pattern. The hexagons, the triangles and the ellipses represent six, three, and twofold axes respectively.

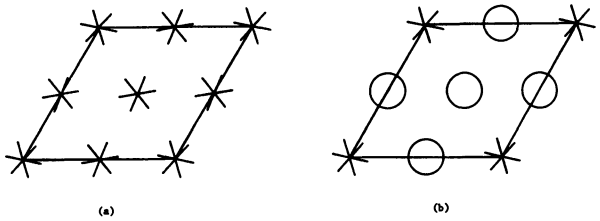


Fig. 4. — Two possible orientational arrangements which give a p6 pattern. The star-like symbols indicate the easy-directions in the sites; the circles represent random orientational arrangements.

may be formed by the molecular core or by flexible chains depending on the properties of the mesogens. On the basis of group theory arguments we can give the patterns; of course these arguments can not predict for which mesogens and temperatures, etc., this phase can be found.

5. Critical behaviour.

The Ginzburg-Landau-Wilson Hamiltonian (13) has a typical hypercubic symmetric form in order parameter space (i.e. in spin-space for magnetic systems) and has been discussed by several authors [16]-[21]. The recursion relations for u and v (Eqs. (5) and (6) of Ref. [16]), as determined by the ε expansion method of renormalization group theory [8], give four fixed points : Gaussian, Ising, Heisenberg (or isotropic), and cubic [16]. For $\varepsilon = 1$ ($d = 3$), the Gaussian and Ising fixed points are unstable, but the stability of the Heisenberg and cubic fixed points depend on n, the number of components of the order parameter. There exists a critical value n_c such that for $n < n_c$, the Heisenberg fixed point is stable, but the cubic fixed point is unstable. The exponents ν^H and η^H can then be determined by equations (7) and (13) of Ref. [16]. For $n > n_c$, the stable fixed point will be the cubic one, and the Heisenberg point becomes unstable, so the exponents cross over to ν^c and η^c (see Eqs. (14) and (15) of Ref. [16]). Of course, whether the stable fixed point in either case can be approached or not depends on the initial values of u and v (the physical values near the transition temperature). All these conclusions can be clearly seen from the schematic flow diagram of figure 3 of reference [17]. Now, the key problem is to determine n_c.

In his review [17], Aharony states that, although it is probable that $n_c \gtrsim 3$, it is important to study both the Heisenbeg and cubic fixed points and let other techniques determine which one wins at $n = 3$.

In fact, if we note that the initial value of v is negative for the D_{hd}-D_{rd} transition in HAT series as we discussed in section 3, and that the phase transition is experimentally [2] found to be second order, our work, together with the report from Ref. [2b], can be considered as evidence in support of n_c being greater than 3. The arguments are as following.

First, examine the schematic flow diagram in figure 3 of reference [17] (p. 397). Cases a) and b) in the picture give two different situations for $n < n_c$ and $n > n_c$ respectively. According to equation (16) of section 3, for the D_{hd}-D_{rd} transition, v is negative and u is positive; this corresponds to the lower-right quadrant in case a) or case b). One can then clearly see that, starting from the initial value $v < 0$ and $u > 0$, the only choice which leads to a second order phase transition is case a), i.e., $n < n_c$ with $|v| < \left|\frac{v^c}{u^c}\right| u$ (if $|v| > \left|\frac{v^c}{u^c}\right| u$ the phase transition will be first order) where u^c and v^c are cubic fixed point values in the u-v plane [17]. The stable fixed point is then the Heisenberg fixed point. Since for the D_{hd}-D_{rd} transition n is equal to 3, we have $n_c > 3$. Therefore, at order ε^2, we expect the critical exponents ν and η to be [16], [22]

$$\nu = \nu^H \simeq 0.678$$

$$\eta = \eta^H \simeq 0.021 .$$

For the phase transition from D_{hd} to another possible low temperature phase with p6 symmetry discussed in sections 3 and 4, v is greater than zero. If we assume $u > 0$, the stable fixed point will again be the Heisenberg fixed point. Therefore, for this phase transition we again predict the critical exponents to be those corresponding to the Heisenberg fixed point, i.e., ν^H and η^H. If $0 > u > -\frac{1}{3} v$, although the positivity conditions (see Eq. (17)) are satisfied, no stable fixed points can be approached, and the phase transition will be first order.

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References

[1] CHANDRASEKHAR, S., SADASHIVA, B. K. and SURESH, K. A., *Pramana* **9** (1977) 471.

[2] a) DESTRADE, C., NGUYEN HUU TINH, GASPAROUX, H., MALTHETE, J. and LEVELUT, A. M., *Mol. Cryst. Liq. Cryst.* **71** (1981) 111.

b) DESTRADE, C., MONDON, M. C. and MALTHETE, J., *J. Physique Colloq.* **40** (1979) C3-17.

[3] MINORU TAKABATAKE and SHIGEO IWAYANAGI, *Japanese J. Appl. Phys.* **21** (1982) L685.

[4] BILLARD, J., DUBOIS, J. C., VAUCHER, C. and LEVELUT, A. M., *Mol. Cryst. Liq. Cryst.* **66** (1981) 115.

[5] MAMLOK, L., MALTHETE, J., NGUYEN HUU TINH and C. DESTRADE, *J. Physique Lett.* **43** (1982) 641.

[6] DESTRADE, C., MALTHETE, J., NGUYEN HUU TINH and GASPAROUX, H., *Phys. Lett.* **78A** (1980) 82.

[7] LANDAU, L. D. and LIFSHITZ, E. M., *Statistical Physics*, 3rd edition (Pergamon Press, Oxford) 1980.

[8] WILSON, K. and KOGUT, J., *Phys. Rep.* **12C** (1974) 75.

[9] TAO, R. B., « Symmetry theories in the second order phase transitions » preprint.

[10] BRADLEY, C. J. and CRACKNELL, A. P., *The Mathematical Theory of Symmetry in Solids* (Clarendon Press, Oxford) 1972.

[11] ROTTMAN, C., *Phys. Rev. B* **24** (1981) 1482.

[12] LYUBARSKII, G. Ya., *The Application of Group Theory in Physics* (Pergamon, New York) 1960.

[13] KLEMAN, M. and MICHEL, L., *Phys. Rev. Lett.* **40** (1978) 1387.

[14] KOVALEV, O. V., *Irreducible Representations of the Space Group* (Gordon and Breach, New York) 1965.

[15] KITTELL, C., *Introduction to Solid State Physics* (John Wiley and Sons, New York) 1963.

[16] AHARONY, A., *Phys. Rev. B* **8** (1973) 4720.

[17] AHARONY, A., *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London) 1976, vol. VI.

[18] KETLEY, I. J. and WALLACE, D. J., *J. Phys. A* **6** (1973) 1667.

[19] GROVER, M. K., KADANOFF, L. P. and WEGNER, F. J., *Phys. Rev. B* **6** (1972) 311.

[20] DOMANY, E. and RIEDEL, E. K., *J. Appl. Phys.* **50** (3) (1979) 1804.

[21] YALABIK, M. C. and HOUGHTON, A., *Phys. Lett.* **61A** (1977) 1.

[22] WALLACE, D. J., *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London) 1976, vol. VI.