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Liquid Crystals of Disc-Like Molecules [and Discussion]

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Liquid crystals of disc-like molecules

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Liquid crystals of disc-like molecules fall into two distinct structural types, the columnar and the nematic. The columnar phase in its simplest form consists of discs stacked aperiodically in columns, the different columns constituting a two-dimensional array, whereas the nematic phase is an orientationally ordered arrangement of discs without any long-range translational order. After a brief review of the structures of the various mesophases, two topics are considered in somewhat greater detail.

(i) An extension of McMillan's mean field model of smectic A to liquid crystals of disc-like molecules. The translational order is now assumed to be periodic in two dimensions. Calculations show that when the lattice is hexagonal, or departs from it only slightly, the transition from the columnar to the isotropic phase may take place either directly or via a nematic phase, depending on the model potential parameters α. Interpreting α to be a measure of the chain lengths as in McMillan's model, the theoretical phase diagram is shown to be in broad agreement with the experimental trends. As the asymmetry of the lattice is increased the theory predicts the occurrence of a smectic A phase as well. The new smectic A phase is biaxial.

(ii) A theoretical study of fluctuations in the columnar liquid crystal. It is shown that the Frank elasticity of the liquid-like columns stabilizes the two-dimensional order, a result that was in fact envisaged by Peierls and Landau in the 1930s. The mean-square fluctuation of the lattice as well as the Debye–Waller factor show a certain dependence on the linear dimensions of the sample.

Introduction

The shape of the molecule is an important criterion for determining liquid crystalline behaviour. Until quite recently, the accepted rule was that the molecule has to be elongated and rod-like for thermotropic mesomorphism to occur, but it has emerged in the last few years that *pure* compounds composed of relatively simple disc-like molecules may also form *stable* liquid crystals. The first example of this kind of mesomorphism was observed in the hexa-substituted esters of benzene. These compounds were prepared by my colleague B. K. Sadashiva at my instance, and from optical, thermodynamic and X-ray studies we concluded that they form an entirely new type of liquid crystal, quite unlike the classical nematic or smectic types that have been investigated for over 90 years. The structure that we proposed is illustrated in figure 1: the discs are stacked *aperiodically* in columns, the different columns constituting a two-dimensional array (Chandrasekhar *et al.* 1977). Thus the mesophase has translational periodicity in two dimensions but liquid-like disorder in the third. It has been variously designated as 'canonic' (from the Greek κανων = rod (Sir Charles Frank, personal communication 1978); see also Frank & Chandrasekhar (1980) and Helfrich (1980)), 'columnar' (Helfrich 1979) and 'discotic' (Billard *et al.* 1978), the last often being used to describe the molecules as well as the mesophases formed by them.

A number of other disc-like mesogens have since been found, notably by the Paris and Bordeaux groups (Dubois 1978; Billard *et al.* 1978; Destrade *et al.* 1979*a*), the canonic or columnar structure has been confirmed by the very fine X-ray work of Levelut (1979, 1980, 1982) and in particular, in the last 2 years or so, it has been established that these compounds exhibit a rich polymorphism, comparable with that observed in systems of rod-like molecules. The aim of the present paper is to review the current situation in the field. I shall first describe briefly what is known about the structures of these mesophases and then proceed to discuss some aspects of the physics of these new systems.

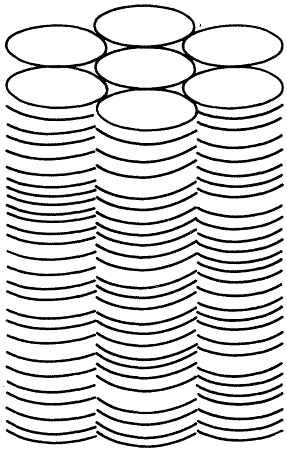

Figure 1. Schematic representation of the structure of the columnar liquid crystal.

Brief description of the liquid crystalline structures

Figure 2 presents the chemical formulae of the disc-like mesogens reported to date. The mesophases so far discovered fall into two distinct categories, the columnar and the nematic.

The basic columnar structure (hereafter designated by the symbol D) is as shown in figure 1, but a number of variants have been identified: hexagonal, rectangular, tilted, etc. (figure 3*a–f*). In all of them except one the columns are 'liquid-like', i.e. there is no long-range translational order along the axes of the columns. The one exception is the hexagonal phase of the hexa-*n*-alkoxytriphenylenes. From an X-ray study of the pentyl derivative, Levelut (1979) has inferred that there is a certain degree of regularity in the stacking of the triphenylene cores in each column, but that the chains are in a relatively disordered state and the molecular centres in neighbouring columns *uncorrelated*.

The nematic (N_D) phase is an orientationally ordered arrangement of the discs with no long-range translational order (figure 4*a*). Unlike the usual nematic of rod-like molecules, the N_D phase is optically negative. A twisted nematic or cholesteric (N_D^*) phase has also been found (Destrade *et al.* 1980*b*; Malthete *et al.* 1981): compound (*c*) of figure 2 with the optically active chain R = S-(+)CH_3-CH_2-$CH(CH_3)$ $(CH_2)_3O$- exhibits such a phase, the helical configuration of which is depicted in figure 4*b*. For more detailed information on these different structures, the temperatures and entropies of transition, etc., reference may be made to recent review articles on the subject (Chandrasekhar 1982; Levelut 1982).

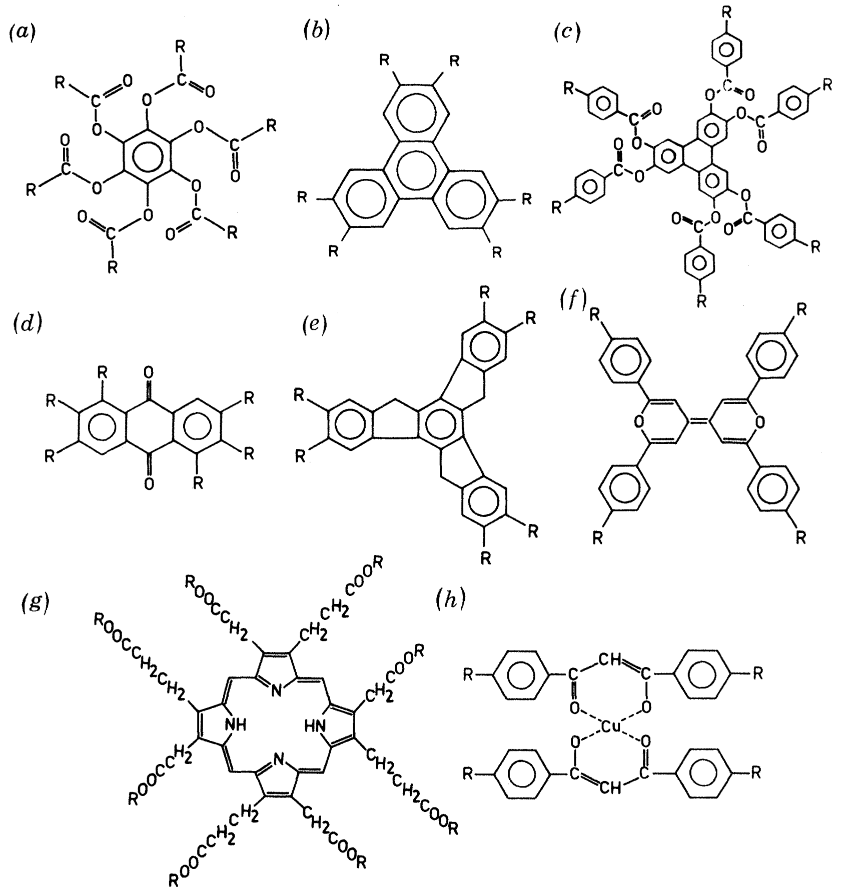

Figure 2. Disc-like mesogens: (*a*) hexa-*n*-alkanoates of benzene (Chandrasekhar *et al.* 1977, 1979); (*b*) hexa-*n*-alkanoates of triphenylene and hexa-*n*-alkoxytriphenylene (Dubois 1978; Billard *et al.* 1978; Destrade *et al.* 1979*a*, *b*); (*c*) hexa-*n*-alkyl and alkoxybenzoates of triphenylene (Tinh *et al.* 1979; Destrade *et al.* 1980*a*; Tinh *et al.* 1981); (*d*) rufigallol-hexa-*n*-octanoate (Queguiner *et al.* 1980; Billard *et al.* 1981); (*e*) hexa-*n*-alkanoates of truxene (Destrade *et al.* 1981*a*); (*f*) 2,2′,6,6′-tetra-arylbipyran-4-ylidenes (Fugnitto *et al.* 1980); (*g*) uroporphyrin I octa-*n*-dodecyl ester (Goodby *et al.* 1980); (*h*) bis(*p*-*n*-decylbenzoyl)methanato copper(II) (Girod-Godquin & Billard 1981).

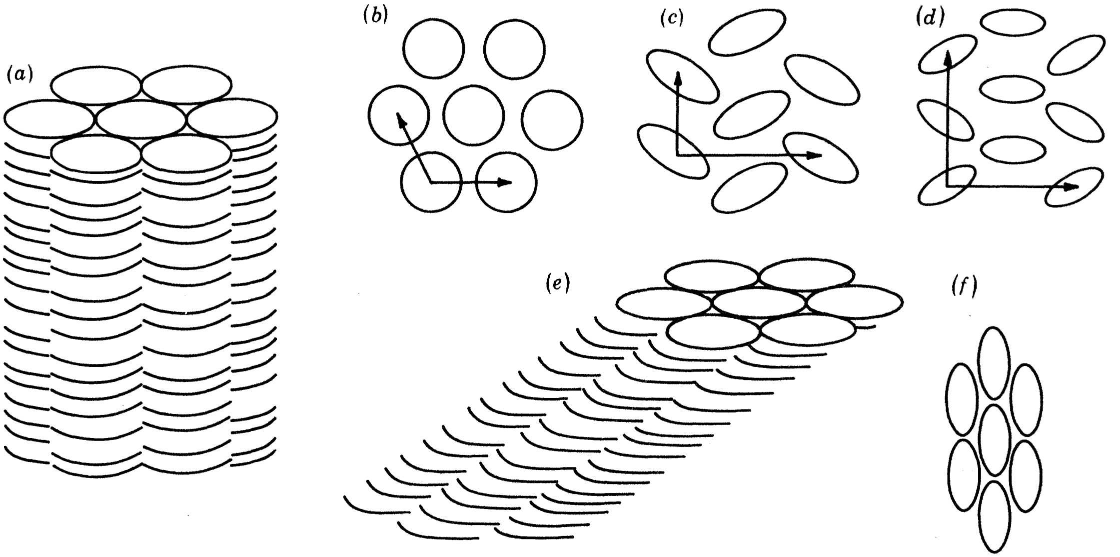

Figure 3. Columnar phases of disc-like molecules: (*a*) upright columnar structure; (*b*) its hexagonal and (*c*), (*d*) rectangular modifications; (*e*) tilted columnar structure; (*f*) its face-centred rectangular lattice.

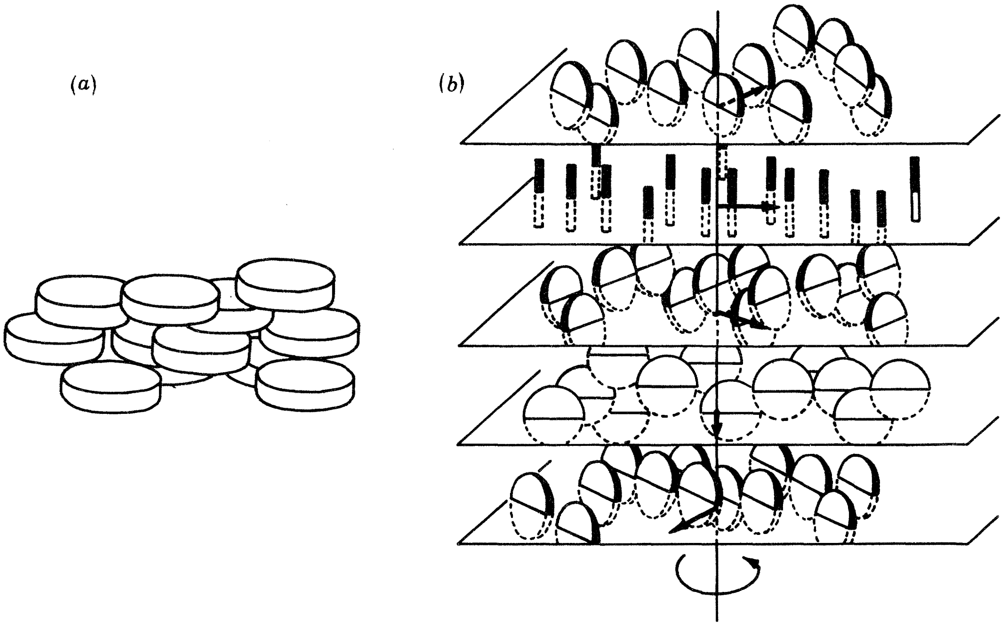

FIGURE 4. (*a*) The nematic phase N_D and (*b*) the twisted nematic or cholesteric phase N_D^* of disc-like molecules.

THEORY OF THE COLUMNAR–NEMATIC–ISOTROPIC TRANSITIONS

Transitions between the D and N_D phases have been observed in a few compounds (Tinh *et al.* 1981; Destrade *et al.* 1981 *a*, *b*). As an example, I present in table 1 the data for the hexa-*n*-alkoxybenzoates of triphenylene, the structure of which is shown in figure 2*c* (Tinh *et al.* 1981). Here D_t signifies tilted columns and a face-centred rectangular lattice (figure 3*e*, *f*), D_r upright columns and a rectangular arrangement as in figure 3*c*. X-ray studies have shown that in the latter structure the discs are *normal* to the columnar axes, implying thereby that there is an asymmetric disposition of the chains about the molecular cores (Levelut 1980; Destrade *et al.* 1981 *b*). In both D_t and D_r the columns themselves are liquid-like. For the $n = 11$ homologue the lattice parameters have been determined to be $a = 32.6$ Å and $b = 51.8$ Å (Tinh *et al.* 1981; Destrade *et al.* 1981 *b*), which represents only a very slight departure from true hexagonal symmetry.

TABLE 1. HEXA-*n*-ALKOXYBENZOATES OF TRIPHENYLENE: TRANSITION TEMPERATURES IN DEGREES CELSIUS

$R = C_nH_{2n+1}O$	K		D_t		D_r		N_D		I
$n = 4$	.	257	—		—		.	> 300	.
5	.	224	—		—		.	298	.
6	.	186	.	193	—		.	274	.
7	.	168	—		—		.	253	.
8	.	152	—		.	168	.	244	.
9	.	154	—		.	183	.	227	.
10	.	142	—		.	191	.	212	.
11	.	145	—		.	179	.	185	.
12	.	146	—		.	174	—		.

K, crystal; D_t, tilted columnar; D_r, rectangular columnar; N_D, nematic; I, isotropic. The phases exhibited by a compound are indicated by points in the appropriate columns.

It is seen from table 1 that the lower members of the homologous series, $n = 4$ and 5, show only the N_D phase. The next few members (with the exception of $n = 7$) show both D and N_D phases, the temperature range of the N_D phase decreasing with increasing chain length till at $n = 12$ the D phase transforms directly to the isotropic (I) phase. Broadly the trend is reminiscent of the behaviour of the smectic A–nematic–isotropic (S_A–N–I) transitions in systems of rod-like molecules. This suggests that one may be able to give a qualitative description of the D–N_D–I transitions by extending McMillan's mean field model of S_A (McMillan 1971) so that the density wave is now periodic in two dimensions (Kats 1978; Feldkamp *et al.* 1981; Chandrasekhar *et al.* 1982).

Consider a face-centred rectangular lattice composed of liquid-like columns, the molecular cores being assumed to be circular discs normal to the columnar axes. Such a lattice can be described by a superposition of three density waves with wavevectors (figure 5)

$$\boldsymbol{A} = 2\pi(\boldsymbol{i}/a+\boldsymbol{j}/b);$$

$$\boldsymbol{B} = 2\pi(-\boldsymbol{i}/a+\boldsymbol{j}/b);$$

and

$$\boldsymbol{C} = 4\pi\boldsymbol{j}/b = (\boldsymbol{A}+\boldsymbol{B}).$$

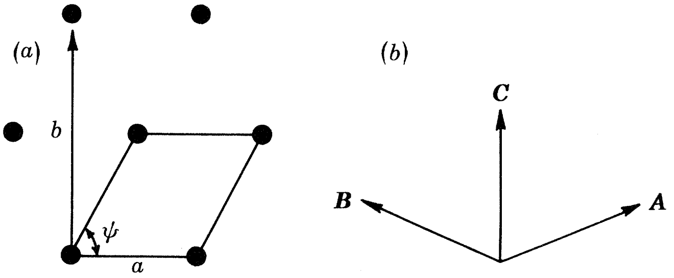

FIGURE 5. Two-dimensional face-centred rectangular lattice showing (*a*) the lattice parameters *a* and *b* and the primitive cell of the direct lattice, (*b*) the reciprocal lattice vectors ***A***, ***B*** and ***C***.

Because orientational ordering is obviously necessary for the existence of the columnar structure, we couple each density wave to the appropriate component of the orientational order parameter along ***A***, ***B*** or ***C***. Retaining only the leading terms in the Fourier expansions of the density waves, the single particle potential in the mean field approximation may be taken to be of the form (Chandrasekhar *et al.* 1982)

$$\begin{aligned} V_1(r,\theta,\phi) = {} & -V_0[-\eta_1 P_2(\sin\theta\cos\phi)-\eta_2 P_2(\sin\theta\sin\phi) \\ & -2\alpha_1\sigma_1 P_2(\sin\theta\cos\phi)\cos(\boldsymbol{C}\cdot\boldsymbol{r})-2\alpha_2\sigma_2\{P_2(\sin\theta\cos(\psi+\phi))\cos(\boldsymbol{A}\cdot\boldsymbol{r}) \\ & +P_2(\sin\theta\cos(\psi-\phi))\cos(\boldsymbol{B}\cdot\boldsymbol{r})\}], \end{aligned}$$

where V_0 determines the nematic–isotropic transition temperature T_{NI}, α_2 is an interaction strength related to the density waves along ***A*** and ***B*** and α_1 to the wave along ***C***, $\psi = \tan^{-1}(b/a)$, θ and ϕ are the polar angles, $\boldsymbol{r}$ is the position vector, and P_2 is the Legendre polynomial of order two. This form of the potential ensures that the energy of the molecule is minimum when the disc is centred in the column with its plane normal to the z axis.

Because the molecular core is assumed to be circularly symmetric, we get

$$\alpha_1 = 2\exp\{-(2\pi r_0/b)^2\},$$

$$\alpha_2 = 2\exp[-\{\pi r_0(a^2+b^2)^{\frac{1}{2}}/ab\}^2],$$

where r_0 is the range of the intermolecular attractive potential.

In general there are four order parameters, η_2 and η_1, the orientational order parameters measured along the x and y axes, and σ_2 and σ_1, the order parameters coupling the orientational and the translational ordering along the $\boldsymbol{A}$ (or $\boldsymbol{B}$) and $\boldsymbol{C}$ directions respectively. We have chosen to define the order parameters in such a way that they vary from 0 in the disordered system to $+1$ in the perfectly ordered system. We then have

$$\eta_1 = \langle -2P_2(\sin\theta\cos\phi)\rangle,$$

$$\eta_2 = \langle -2P_2(\sin\theta\sin\phi)\rangle,$$

$$\sigma_1 = \langle -2P_2(\sin\theta\cos\phi)\cos(\boldsymbol{C}\cdot\boldsymbol{r})\rangle,$$

$$\sigma_2 = \langle -[P_2\{\sin\theta\cos(\psi+\phi)\}\cos(\boldsymbol{A}\cdot\boldsymbol{r}) + P_2\{\sin\theta\cos(\psi-\phi)\}\cos(\boldsymbol{B}\cdot\boldsymbol{r})]\rangle,$$

where the angular brackets represent a statistical average, and the normalized single partition distribution function

$$f_1(\boldsymbol{r},\theta,\phi) = \frac{\exp\{-V_1(\boldsymbol{r},\theta,\phi)/k_\mathrm{B}T\}}{\int \mathrm{d}\boldsymbol{r}\int_0^1 \mathrm{d}(\cos\theta)\int_0^{2\pi}\mathrm{d}\phi\exp\{-V_1(r,\theta,\phi)/k_\mathrm{B}T\}},$$

where $\int \mathrm{d}\boldsymbol{r}$ is over the primitive cell, and k_B is the Boltzmann constant. The molar internal energy of the oriented system can now be written as

$$\frac{\Delta U}{Nk_\mathrm{B}T} = -\frac{V_0}{2k_\mathrm{B}T}(\tfrac{1}{2}\eta_1^2 + \tfrac{1}{2}\eta_2^2 + \alpha_1\sigma_1^2 + 2\alpha_2\sigma_2^2),$$

where N is the Avogadro number, the entropy as

$$\frac{\Delta S}{Nk_\mathrm{B}} = -\int_0^1\int_0^{2\pi}\int f(\boldsymbol{r},\theta,\phi)\ln f(\boldsymbol{r},\theta,\phi)\,\mathrm{d}(\cos\theta)\,\mathrm{d}\phi\,\mathrm{d}\boldsymbol{r}$$

$$= -\frac{V_0}{k_\mathrm{B}T}(\tfrac{1}{2}\eta_1^2 + \tfrac{1}{2}\eta_2^2 + \alpha_1\sigma_1^2 + 2\alpha_2\sigma_2^2) + \ln\frac{1}{\pi ab}\int_0^1\int_0^{2\pi}\int \exp\{-V_1(\boldsymbol{r},\theta,\phi)/k_\mathrm{B}T\}\mathrm{d}(\cos\theta)\,\mathrm{d}\phi\,\mathrm{d}\boldsymbol{r},$$

and hence the molar free energy as

$$\frac{\Delta F}{Nk_\mathrm{B}T} = \frac{\Delta U - T\Delta S}{Nk_\mathrm{B}T} = \frac{V_0}{2k_\mathrm{B}T}(\tfrac{1}{2}\eta_1^2 + \tfrac{1}{2}\eta_2^2 + \alpha_1\sigma_1^2 + 2\alpha_2\sigma_2^2)$$
$$-\ln\frac{1}{\pi ab}\int_0^1\int_0^{2\pi}\int \exp\{-V_1(\boldsymbol{r},\theta,\phi)/k_\mathrm{B}T\}\,\mathrm{d}(\cos\theta)\,\mathrm{d}\phi\,\mathrm{d}\boldsymbol{r}.$$

There are four possible solutions to the equations:

(1) $\eta_1 \neq \eta_2 \neq 0$, $\sigma_1 \neq \sigma_2 \neq 0$ (biaxial rectangular columnar phase);
(2) $\eta_1 \neq \eta_2 \neq 0$, $\sigma_1 \neq 0$, $\sigma_2 = 0$ (biaxial smectic phase);
(3) $\eta_1 = \eta_2 \neq 0$, $\sigma_1 = \sigma_2 = 0$ (uniaxial nematic phase);
(4) $\eta_1 = \eta_2 = \sigma_1 = \sigma_2 = 0$ (isotropic phase).

When $b/a = \sqrt{3}$, $\psi = 60°$, and we have a hexagonal lattice. It then follows that $\alpha_1 = \alpha_2$ and the solutions take the simpler form

(1) $\eta_1 = \eta_2 \neq 0$, $\sigma_1 = \sigma_2 \neq 0$ (uniaxial hexagonal columnar phase);
(2) $\eta_1 = \eta_2 \neq 0$, $\sigma_1 = \sigma_2 = 0$ (uniaxial nematic phase);
(3) $\eta_1 = \eta_2 = \sigma_1 = \sigma_2 = 0$ (isotropic phase).

The free energy corresponding to the different solutions can be evaluated to determine the phase diagram as a function of the α coefficients for a given value of the axial ratio b/a.

The phase diagram for the hexagonal structure is shown in figure 6. The hexagonal–nematic transition is always first-order, as is to be expected. It is seen that the temperature range of the nematic phase decreases with increasing α, and for $\alpha > 0.64$ the columnar phase transforms directly to the isotropic phase. If, as in McMillan's theory, α is interpreted to be a measure of the chain length these results are in qualitative accord with the observed trends (table 1).

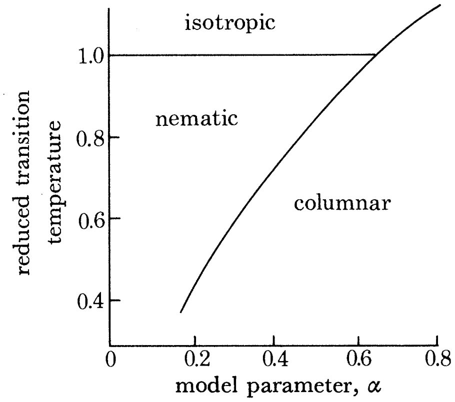

Figure 6. Theoretical plot of the reduced transition temperatures against the model parameter α showing the hexagonal, nematic and isotropic phase boundaries. All the transitions are of first order.

For the biaxial rectangular structure, the nature of the phase diagram depends on b/a. I shall confine my remarks to $b/a > \sqrt{3}$. If b/a is only slightly greater than $\sqrt{3}$, the phase diagram is similar to that for the hexagonal structure. As the asymmetry of the lattice is increased, one gets solutions corresponding to a smectic phase: the rectangular columnar phase transforms to a biaxial smectic A phase (with the layer normal along C) and this in turn undergoes a transition to a uniaxial N_D phase at a higher temperature (Chandrasekhar *et al.* 1982). Rectangular phases have been observed with molecules having essentially circular cores, but in none of them does b/a depart very much from $\sqrt{3}$. It remains to be seen whether rectangular lattices of sufficiently high anisotropy, high enough to give rise to a smectic phase, will be found. Nevertheless, our simple model serves to illustrate the fact that the origin of the two-dimensional translational order in the columnar phase is similar to that of the one-dimensional order in the smectic A phase of rod-like molecules in so far as the attraction between the aromatic cores and the role of the end chains are concerned.

Fluctuations in the columnar liquid crystal

I shall next consider the fundamental question of fluctuations in the columnar phase. This and the related problem of stability were discussed in general terms by Peierls and Landau (see Landau & Lifshitz 1970), and have recently been investigated by Ranganath & Chandrasekhar (1982) and independently and rather more thoroughly by Kammensky & Kats (1982).

Let us suppose that the liquid-like columns are along the z axis and that the two-dimensional (2D) lattice (assumed to be hexagonal) is parallel to the xy plane. We shall consider only the vibrations of the lattice in the xy plane. The free energy density may be expressed as

$$F = \tfrac{1}{2}B\left(\frac{\partial u_x}{\partial x}+\frac{\partial u_y}{\partial y}\right)^2 + \tfrac{1}{2}D\left\{\left(\frac{\partial u_x}{\partial x}-\frac{\partial u_y}{\partial y}\right)^2 + \left(\frac{\partial u_x}{\partial y}+\frac{\partial u_y}{\partial x}\right)^2\right\} + \tfrac{1}{2}k_{33}\left\{\left(\frac{\partial^2 u_x}{\partial z^2}\right)^2 + \left(\frac{\partial^2 u_y}{\partial z^2}\right)^2\right\}, \quad (1)$$

where B and D are the elastic constants for the deformation of the 2D lattice in its own plane, u_x and u_y are the displacements along x and y at any lattice point, and k_{33} is the Frank constant for the curvature deformation (bending) of the columns. (In the notation of the standard crystal elasticity theory, $B = \frac{1}{2}(c_{11}+c_{12})$ and $D = \frac{1}{2}(c_{11}-c_{12})$). We neglect here the splay and twist deformations because they give rise to a distortion of the lattice (Prost & Clark 1980). We also neglect any contributions from the surface of the sample. Writing the displacement u in terms of its Fourier components,

$$u(\boldsymbol{r}) = \sum_{\boldsymbol{q}} u(\boldsymbol{q}) \exp[\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}]; \tag{2}$$

substituting in (1) we get in the harmonic approximation

$$F = \tfrac{1}{2}\sum_{q} (B_0 q_\perp^2 + k_0 q_z^4)\langle u_q^2\rangle,$$

and from the equipartition theorem

$$\langle u_q^2\rangle = k_\mathrm{B}T/(B_0 q_\perp^2 + k_0 q_z^4),$$

where $B_0 = B + 2D$, $k_0 = 2k_{33}$ and $q_\perp = (q_x^2+q_y^2)^{\frac{1}{2}}$.

The mean square displacement at any lattice point is given by

$$\begin{aligned}\langle u^2\rangle = \sum_q \langle u_q^2\rangle &= \frac{1}{(2\pi)^3}\int \langle u_q^2\rangle \,\mathrm{d}q\\ &= \frac{k_\mathrm{B}T}{(2\pi)^3}\int_{2\pi/L}^{2\pi/d}\int_{2\pi/L'}^{\infty}\frac{2\pi q_\perp \,\mathrm{d}q_\perp \,\mathrm{d}q_z}{B_0 q_\perp^2 + k_0 q_z^4},\end{aligned}$$

where L' is the length of the columns, L the linear dimension of the lattice in the xy plane and d its periodicity. Assuming that $L' \gg L$

$$\langle u^2\rangle = \{k_\mathrm{B}T/4B_0(\lambda d)^{\frac{1}{2}}\}\{1-(d/L)^{\frac{1}{2}}\}, \tag{3}$$

where $\lambda = (k_0/B_0)^{\frac{1}{2}}$ is a characteristic length (Ranganath & Chandrasekhar 1982; Kammensky & Kats 1982). The structure is therefore stable as $L \to \infty$ (see Landau & Lifshitz 1970). As is well known (Peierls 1934; Landau 1967) the 2D lattice itself is an unstable system with $\langle u^2\rangle$ diverging as $\ln L$ (Jancovici 1967; Gunther *et al.* 1980). Thus the curvature elasticity of the liquid-like columns stabilizes the 2D order in the columnar liquid crystal.

The 'structure factor' for the intensity of X-ray scattering may be written as

$$S(\boldsymbol{K}) = \int \mathrm{d}z \sum_m \sum_n \exp[\mathrm{i}\{\boldsymbol{K}\cdot(\boldsymbol{R}_m - \boldsymbol{R}_n)\}]\exp[-\tfrac{1}{2}K_\perp\langle|u_n-u_m|^2\rangle].$$

The second exponential term on the right hand side is the familiar Debye–Waller factor $\exp(-W)$. Now

$$\begin{aligned}\langle(u_n-u_m)^2\rangle &= \langle|u(r)-u(0)|^2\rangle\\ &= \frac{2}{2\pi^3}\int\langle u_q^2\rangle\,|1-\cos(\boldsymbol{q}\cdot\boldsymbol{r})|\,\mathrm{d}\boldsymbol{q} \quad \text{(from (2))}\\ &= \frac{k_\mathrm{B}T}{2B_0(\lambda d)^{\frac{1}{2}}}\left\{1-\left(\frac{d}{L}\right)^{\frac{1}{2}}\right\} - \frac{k_\mathrm{B}T}{16\sqrt{2\pi}B_0(\lambda\rho)^{\frac{1}{2}}}\exp\left(-\frac{z^2}{4\lambda\rho}\right)\left\{U\left(\frac{1}{4},\frac{1}{2},\frac{z^2}{4\lambda\rho}\right)\right\}^2,\end{aligned} \tag{4}$$

where $\rho = (x^2+y^2)^{\frac{1}{2}}$ and U is the confluent hypergeometric Kummer function (see Abramovitz & Stegun 1965). For $z \gg (\lambda\rho)^{\frac{1}{2}}$, the second term of (4) reduces to

$$\frac{\sqrt{2}\,k_\mathrm{B}T}{16\pi B_0 z}\exp\left(-\frac{z^2}{4\lambda\rho}\right).$$

In smectic A and the 2D lattice, the displacement–displacement correlation is of logarithmic form; the Bragg peaks (δ–function singularities) are therefore washed out for the infinite sample and there appears instead a strong thermal diffuse scattering with weaker singularities (Caillé 1972; Gunther *et al.* 1980; Litster 1980; Als-Nielsen 1981). On the other hand, the columnar liquid crystal does give the usual Bragg reflexions. Preliminary calculations show that the Debye–Waller factor is determined mainly by the first term of (4). Now, the lattice spacing d in any of the known columnar phases does not exceed about 5 nm, so that the size effect in (3) and (4) is quite weak in practical situations. With larger disc-like mesogens, the effect may well be observable.

I have so far considered the case of long columns ($L' \gg L$). If the columns are short ($L' \ll L$) and the sample is bounded (normal to the columnar axis on both sides), $\langle u^2 \rangle$ is independent of L' for very small L', and varies as $|\text{const.} - (\ln L'/L')|$ for larger L'. If the surfaces are free $\langle u^2 \rangle$ will have additional terms, which may be analogous to those for a 2D lattice. In any case, as far as X-ray scattering is concerned, such a thin free film may be expected to behave differently from a sample in the form of a narrow cylinder consisting of long columns.

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Discussion

Sir Charles Frank, F.R.S. (*The University, Bristol*). Professor Chandrasekhar said that with an infinite smectic sample the Bragg reflexions would disappear. Now, I grant that any such negative statement can be made about an experiment with an infinite sample, since such an experiment cannot be performed, but I presume the intended statement is about the limiting behaviour approached as the specimen is made larger and larger; and says that that reflexion does not progressively sharpen as it would with a true crystal, rather than that it disappears.

J. D. Litster. The reflexion will not disappear; it will still be rather strong. However, the line shape will be a power-law singularity instead of the delta function Bragg peak one normally observes from a system with long-range order.

Sir Charles Frank. I think that makes it a matter of semantics: wouldn't the experimentalist still say he had a Bragg reflexion?

J. D. Litster. Unless the resolution function of his spectrometer was sufficiently good to distinguish the two, he would. However, the difference is important; it is whether one has long-range order or not.

W. H. de Jeu (*Solid State Physics Laboratory, Groningen, The Netherlands*). Recently I learned that the hexa-substituted benzenes, the first compounds to show discotic mesophases, were synthesized some 50 years ago at the University of Groningen (H. J. Backer & S. van der Baan, *Rec. Trav. Chim. Pays-Bas* **56**, 1161–1174 (1937)). More interestingly they appeared to be still in stock in the Department of Organic Chemistry. We studied the compound with $O{-}CO{-}C_6H_{13}$ as substituent and observed indeed the expected columnar mesophase between 80 and 86 °C. Powder X-ray photographs (Guinier-Simon camera with $CoK\alpha_1$ radiation) showed the reflexions listed in table D1.

The first two reflexions are strong, the others rather weak. Indexing is possible on the basis of a 2D orthorhombic lattice of the columns with $\boldsymbol{a} = 28.5$ Å and $\boldsymbol{b} = 17.7$ Å. The lattice is thus not hexagonal (in which case $a/b = \sqrt{3}$), although the deviations from hexagonal are not large ($a/b = 1.61$).

TABLE D 1

hkl	$d_{\text{obs}}/\text{Å}$†	$d_{\text{calc}}/\text{Å}$†
110	15.0	15.04
200	14.3	14.27
210	11.1	11.11
020	8.86	8.85
120	8.45	8.45

† 1 Å = 10^{-10} m = 10^{-1} nm.

S. CHANDRASEKHAR. In our very first report on these compounds (Chandrasekhar *et al.* 1977) we had noted that some X-ray photographs contained a few weak diffraction spots not quite conforming to true hexagonal symmetry, but the quality of the X-ray patterns did not warrant a more refined analysis. Subsequently, from optical observations of the extinction brushes in relatively large domains in which the columnar axes are curved in circles or spirals, Sir Charles Frank showed that the lattice should be pseudohexagonal (Frank & Chandrasekhar 1980). This has recently been confirmed by Madame A. M. Levelut (to be published in *J. Chim. phys.*), who found that the lattice is rectangular with an axial ratio departing by about 3% from the true hexagonal value of $\sqrt{3}$.

LIN LEI (*Institute of Physics, Chinese Academy of Sciences, Beijing, China*). We have modified the McMillan hamiltonian so that in the two-particle interaction $W_{ij} = W_0(r_{ij}) + W_2(r_{ij}) P_2(\cos\theta_{ij})$, both W_0 and W_2 are functions of the molecular length d. For $W_0 = F(d) V_0(r_{ij})$, $W_2 = F(d) V_2(r_{ij})$ and $F(d) = d^\lambda$, our results for the I–N–A phase diagrams of long molecules reduce essentially to those of McMillan (1971) and Lee *et al.* (1973) when $\lambda = 1$ and 0 respectively (corresponding to T_{IN} being constant or decreasing with n, the number of carbon atoms in the end-chain of the molecule). For $\lambda = 2$, we find T_{IN} increasing with n; for more general $F(d)$, it is possible to have a minimum in T_{IN} (Shu Changqing & Lin Lei, *Acta phys. sin.* **31**, 915 (1982)). This simple method of obtaining different types of $T_{\text{IN}}(n)$ curve should also be applicable in Professor Chandrasekhar's theory in which disc-like molecules are treated.