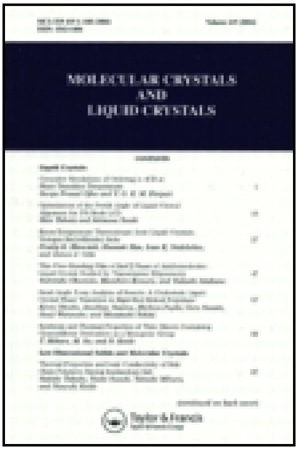

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Bowlic Liquid Crystalsl

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Bowlic Liquid Crystals†

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A new type of liquid crystals made up of bowl-like molecules was predicted by Lin in 1982 and was recently synthesized. In this paper, the experimental findings about these bowlic mesophases are briefly summarized. Possible mesophases (polar nematic, non-polar nematic, cholesteric, stringbean, donut, columnar, etc.) are proposed and discussed. The possible breakdown of the macroscopic symmetry $\mathbf{n} \rightarrow -\mathbf{n}$ ($\mathbf{n}$ is the director) in these mesophases is emphasized. Novel properties including phase transitions and other physical aspects (optical, elastic, flexoelectric and hydrodynamic, as well as defects) are presented. Molecular engineering to produce new compounds (e.g. anisotropic ferromagnetic fluid and bowlic polymers) is suggested. Possible instabilities and applications are discussed. The possibility of second harmonic generation and simple sub-microsecond electro-optical switching (without the complications encountered in ferroelectric smectic C*) in these bowlic mesophases are pointed out. These bowlic mesophases may be ferroelectric, antiferroelectric or paraelectric.

Keywords: bowlic liquid crystal, columnar mesophase, second harmonic generation, electro-optical switching, phase transition, instabilities

I. INTRODUCTION

Liquid crystals of rod-like molecules were first discovered by Reinitzer in 1888.[1] In 1977 mesophases of disc-like molecules were synthesized by Chandrasekhar *et al.*[2] which was preceded by theoretical predictions.[3,4]

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In the cases of rod-like and disc-like molecules the anisotropic properties of the mesophases come from the (*one- or two-dimensional*) asymmetric shape of the molecules. On the other hand, Halperin and Nelson[5] in 1978 considered a two-dimensional lattice of mass-point molecules and suggested that a hexatic liquid crystal phase may appear before the lattice melts into liquid. The mass-point molecules are *zero-dimensional* and it is the bonds connecting them that correspond to the rod-like molecules in the more traditional liquid crystal phases.

Rigorously speaking, all molecules in nature are of course three-dimensional. The "dimension" of molecules referred here really means the dimension of "molecules" in the physical model used in the description of the mesophases. In other words, it means the minimal (or important) character of the molecular shape when mesophases are formed.

Since one- and two-dimensional molecules have been proved to have liquid crystal phases and zero-dimensional molecules may also form liquid crystal phases, it is then natural to consider the case of *three-dimensional* molecules.

In 1982 liquid crystals of (three-dimensional) *bowl-like* molecules (Figure 1) were formally proposed by Lin.[6-7] It was predicted[6,7] that these new mesophases (i) may form columnar phase, (ii) nematic or cholesteric phases, or (iii) some intermediate phases such that among the spatially separate individual molecules as in nematics there exist short columns (of various length) of stacking molecules—called "stringbean" phase here. (iv) They may be ferroelectric in character. (v) The $\mathbf{n} \rightarrow -\mathbf{n}$ symmetry (where $\mathbf{n}$ is the director) valid in rod-like and disc-like cases may be broken here, resulting, in particular, (vi) the coupling of thermal gradient and molecular orientation in nematics of bowl-like molecules, and other novel properties.

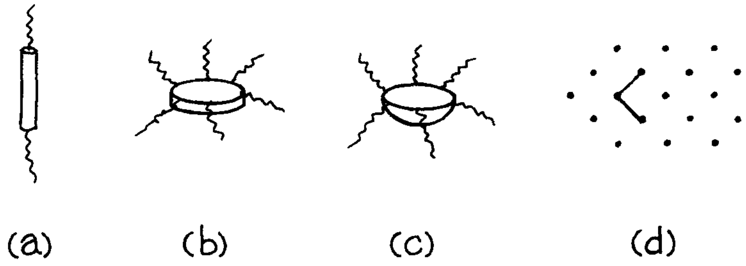

FIGURE 1 Shape of molecules that form liquid crystal phases.
(a) Rod-like (1D). (b) Disc-like (2D). (c) Bowl-like (3D). (d) Mass point (OD)—hexatic phase.

In Ref. 6, it is pointed out that the term "bowl-like" used there is only symbolic. Other three-dimensional molecules of, for example, pyramid or hemisphere shapes which are asymmetric in the up and down directions may also be considered.

In 1985 the experimental existence of these new mesophases are reported[8,9] (called pyramidic[8] or cone-shaped[9]). X-ray structural study of some of these mesophases has been carried out.[10] In addition to the classical columnar phases a new structure in which the external shell of each column (the paraffinic medium) assuming a helical structure is observed.[10]

In this paper, the experimental findings of these *bowlic* liquid crystals is briefly reviewed (in Sec. II). Their physical properties are then discussed from the theoretical point of view.

II. EXPERIMENTAL FINDINGS

A. *The Molecules*

Up to now molecules known to form bowlic mesophases are those consisting of a rigid bowl structure (with three benzene rings)[8,9] and six identical flexible side chains (Figure 2), or of a flexible bowl with four benzene rings and eight side chains.[11] Specifically, the former are hexaalkyloxytribenzocylononene (HETB), hexaalkanoyloxytribenzocyclononene (HATB) and hexaalkoxybenzoyloxytribenzocyclononene (HBTB) (see Figure 2 for the molecular formulas). The latter are octasubstituted tetrabenzocyclododecatetraene ethers and esters of sufficiently long chains.

B. *Mesophases*

All bowlic mesophases found *so far* are columnar. There are at least five of them. In analogy to the discotics we denote them as B_1–B_5

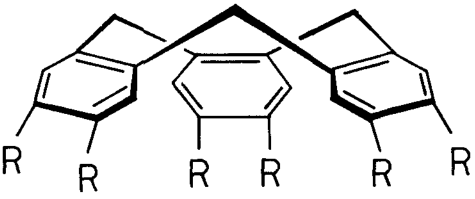

FIGURE 2 Bowlic molecules: Hexasubstituted tribenzocyclononane with $R = C_nH_{2n+1}$ O—, $n = 4 - 12$ (HETB, Ref. 8), $R = C_nH_{2n+1}$ COO—, $n = 7 - 14$ (HATB, Ref. 8), $n = 9, 11, 15$ (Ref. 9), $R = C_{12}H_{25}$ O—Ø—COO— (HBTB, Ref. 9).

(corresponding to $P_A, \ldots, P_E$ in Ref. 8). Structurally, B_{hd} and B_{rd} are found.[8-10] In addition, in the low temperature columnar phase of HBTB a helix structure presumably exists in each column[10] (which is not observed in discotics).

C. *Phase Transitions*

The sequence of phase transition observed[8-10] is:

$$\text{crystal} \rightarrow B \rightarrow \text{isotropic}$$

All phase transitions are first order. A typical case is given in Table I. Note that bowlic columnar phase does occur at room temperature (n = 7, 8 in Table I). Phase diagrams for both pure compounds[8-10] and binary systems[8] have been reported.

TABLE I

HATB: Temperatures and heats of transitions.[a]

n	K_2	K_1	B_5	B_4	B_3	I
7	● 5.2 (16.1)			● 153.1 (31.0)		●
8	● 23.9 (28.2)			● 152.6 (30.2)		●
9[b]	● 18.2 (22.1)	● 32.7 (14.8)		● 146.2 (29.2)		●
10	● 31.5 (22.0)		● 38.6 (17.3)	● 131.6 (3.7)	● 140.8 (18.8)	●
11[c]	● 58.1 (48.4)			● 118.8 (3.1)	● 140.6 (20.2)	●
12	● 67.4 (67.0)			● 99.5 (2.3)	● 139.2 (20.9)	●
13	● 73.4 (81.0)			● 81.4 (1.4)	● 136.2 (18.5)	●
14	● 80.5 (118.4)				● 134.6 (19.1)	●
15	● 80 (89.9)				● 129 (8.4)	●

[a] $n = 7 - 14$ from Zimmermann *et al.* (Ref. 8). n = 15 from Malthêle and Collet (Ref. 9). The phases exhibited by a compound are indicated by points in the appropriate columns. K_1, K_2 stands for crystals, B_3, B_4, B_5 (designated as P_C, P_D, P_E in Ref. 8) for mesophases, I for isotropic liquid. The transition temperatures are given in °C and the corresponding enthalpies in parenthesis in kJ/mole.

[b] Ref. 9 gives $K \xrightarrow{-50(1.7)} B_4 \xrightarrow{144.5(28.5)} \text{I}$.

[c] Ref. 9 gives $K \xrightarrow{55(43.1)} B_4 \xrightarrow{115.5(2.9)} B_3 \xrightarrow{138(20.5)} \text{I}$.

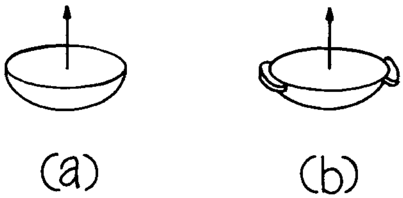

FIGURE 3 Two types of bowls. (a) Chinese bowl (uniaxial). (b) French bowl (biaxial). The direction of the arrow, representing the dipole, may actually be in the opposite direction in other cases.

III. POSSIBLE MESOPHASES

In bowl-like molecules the up-down symmetry is broken (which distinguishes them from the disc-like molecules). Depending on the structure of the molecule the molecule may or may not possess cylindrical symmetry (as exemplified by Chinese and French bowls, respectively) leading to either uniaxial or biaxial compounds (see Figure 3). The up-down asymmetry makes a net electric dipole possible.[6,7] Because of the peculiar shape of the molecules it may be possible to have two types of nematic phases—polar nematic and nonpolar nematic (see Secs. IV and V)—as sketched in Figure 4.

The columnar phases are similar to that of discotics except that the bowls in each column should be parallel to each other (unless there are defects). In other words, each column has a direction (or polarity). These polar columns may arrange into two-dimensional arrays of tetragonal or hexagonal symmetry.[8] As pointed out by Zimmermann *et al.*[8] both ferroelectric and antiferroelectric arrangements of the columns are possible for tetragonal lattice; for hexagonal lattice only ferroelectric case is possible, the antiferroelectric case is *frustrated.* It should be pointed out that there may be a random distribution of the polarity of the columns in the two-dimensional lattice. We then have a two-dimensional Ising model or a percolation problem.

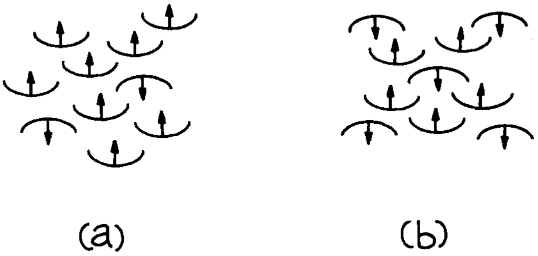

FIGURE 4 (a) Polar nematic, $\overline{N}_B$. (b) nonpolar nematic, N_B.

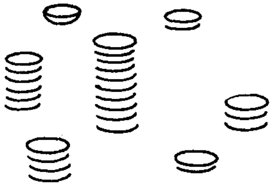

FIGURE 5 The "stringbean" phase.

An intermediate phase is the "stringbean" phase depicted in Figure 5.

Another interesting possibility is the "donut" phase (Figure 6). These are acturally hairy donuts—there are side chains above and below each donut. These hairy donuts may go on to form different structures such as three dimensional lattices, or they may form nematic (or even columnar) phase with the donuts acting like the discs in discotics. We may even have lyotropic systems when they are mixed with a second compound.

For the newly discovered bowlics with flexible central core (consisting of four benzene rings),[11] in addition to forming the donuts, they may even be able to form "onions," i.e., a spherical unit with the bowls more or less facing the center in layers (Figure 7). The onions may act as the units of more complicated structures. Lyotropic systems are also possible.

When the molecule is chiral (e.g. if the two tails attached to each benzene ring in Figure 2 are not the same[9]) then it is possible to have bowlic cholesterics. They may also give rise to some variations of those phases discussed above.

IV. BREAKDOWN OF THE $\mathbf{n} \rightarrow -\mathbf{n}$ SYMMETRY

Microscopically most of the rod-like molecules are asymmetric in their heads and tails. However, the shape of the molecules makes it easy for them to arrange in such a way so that the permanent dipoles of the molecules compensate each other on a macroscopic scale, re-

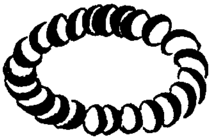

FIGURE 6 The "donut" phase.

FIGURE 7 A cross section of the "onion".

sulting in the $\mathbf{n} \rightarrow -\mathbf{n}$ symmetry observed in the corresponding mesophases.[12] The same symmetry appears in the discotics for similar reason.

The $\mathbf{n} \rightarrow -\mathbf{n}$ symmetry is thus a macroscopic symmetry (occurring on a scale much larger than the molecular dimension). It is valid in optical or light scattering experiments but may be invalid in x-ray experiments with short enough wavelengths.

In any case, the $\mathbf{n} \rightarrow -\mathbf{n}$ symmetry is not a basic symmetry such as the translational symmetry of space or time. (Note that the "basic" symmetry of parity can be and is indeed broken in weak interactions.) In the case of bowlic molecules the steric effect makes the compensation of the permanent dipoles of the molecules difficult and then the $\mathbf{n} \rightarrow -\mathbf{n}$ symmetry may break down in bowlic mesophases (see Figure 8).

In the rest of this paper the $\mathbf{n} \rightarrow -\mathbf{n}$ symmetry is assumed to be broken and the consequences discussed.

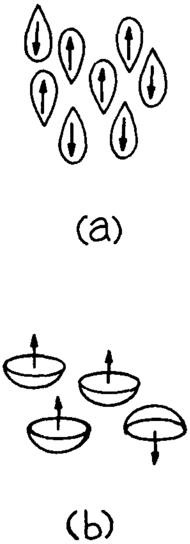

FIGURE 8 (a) Dipoles of the rod-like molecules easily compensate each other on the average. (b) Steric effect of bowlic molecules makes the compensation of dipoles difficult, resulting in the breakdown of the $\mathbf{n} \rightarrow -\mathbf{n}$ symmetry.

V. PHASE TRANSITIONS

For polar molecules (such as the bowlic ones) which are uniaxial the pairwise intermolecular interaction potential is given by

$$V_{ij} = -V_0(r_{ij}) - V_1(r_{ij})P_1(\cos\theta_{ij}) - V_2(r_{ij})P_2(\cos\theta_{ij}) \qquad (1)$$

where θ_{ij} and r_{ij} are the angle and distance between the orientations and centers of mass of the two molecules, respectively. For bowlic molecules the steric effect favors the parallel configuration over the antiparallel configuration (in contrary to the rod-like case) resulting in $V_1 > 0$.[13] $V_2 > 0$ as usual.

Phase diagram for the simple case of V_0, V_1 and V_2 being independent of r_{ij} has been given by Leung and Lin[13] and is sketched in Figure 9. Three phases (I-isotropic, N_B-nonpolar nematic and $\overline{N}_B$-

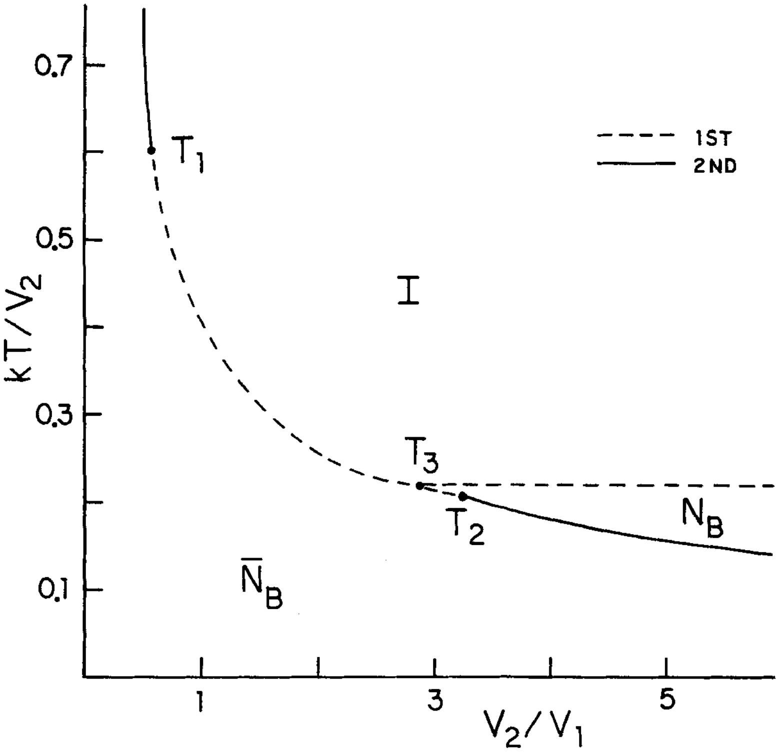

FIGURE 9 Phase diagram of bowlic nematic and isotropic phases. Two order parameters, $P \equiv \langle P_1\rangle$, $Q \equiv \langle P_2\rangle$. I–isotropic ($P = 0 = Q$), N_B-nonpolar nematic ($P = 0$, $Q \neq 0$), $\overline{N}_B$-polar nematic ($P \neq 0 \neq Q$). T_1, T_2-tricritical point, T_3-triple point.

polar nematic) are possible and there are two tricritical points and one triple point.

Several remarks are in order. (i) The steric effect is included to some extent already in V_1 and V_2 (when their signs are considered). (ii) Eq. (1) is equally good for polar rod-like or disc-like molecules. In the rod-like case $V_1 < 0$, $V_2 > 0$ and there is no polar nematic phase[14] ($P \equiv \langle P_1 \rangle = 0$). Figure 9 is inapplicable. However, one should expect that $V_1 > 0$, $V_2 > 0$ and Figure 9 is equally applicable in the disc-like case. If one has not observed polar nematics in discotics yet it is because that the up-down symmetry of the disc-like molecule renders $V_1 = 0$ and one is in the far-right end of Figure 9 for discotics. (iii) Even though bowlic nematics have not been observed yet (see Sec. II) we and others[15] are optimistic about their existence. In this regard one should note that in the case of discotics it takes two years for the nematics[16] to be discovered after the columnars, and only after disc-like molecules of large enough cores are synthesized and used. The development of bowlics is like that in the first year of discotics when molecules of the minimal core size are first synthesized.

(iv) Thin films of bowlic nematics should be a good candidate to test the two-dimensional XY model results of Lee and Grinstein.[17] (v) To include the columnar phase in the phase diagram the full Eq. (1) (with r_{ij} dependence) should be used. One may proceed similarly to the discotic case.[18,19]

VI. PHYSICAL PROPERTIES

A. *Electrical Properties*

The up-down asymmetry of the bowlic molecules makes them polar in nature, generally speaking. However, it should be emphasized that polarity of the molecule alone is insufficient to guarantee ferroelectricity in the mesophases (as witnessed in the rod-like case). The steric effect (or the molecular shape) is important. As pointed out in Sec. IV there is no complete cancellation of the molecular polarity in bowlic molecules and bowlic mesophases can be ferroelectric.[6,7] And for that matter, they can also be antiferroelectric or paraelectric (see Sec. III and Ref. 8).

Experimentally, ferroelectricity in domains have been observed.[15] In our opinion, to have full ferroelectricity in bowlics one should use an electric field to line up the molecules when cooling them from the isotropic phase (analogous to the use of magnetic field in the rod-like case) or use good surface treatment. This has not been tried yet.

B. *Optical Properties*

Optically some of the bowlic columnar phases have been found to be uniaxial (with negative optical anisotropy) and some apparently biaxial.[8]

Second harmonic generation (and other even-order nonlinear optical effects) should be possible in the bowlic mesophases. (For defects and textures see subsection E below.)

C. *Elasticity*

The curvature elasticity is described by the free energy density,

$$F = F_0 + K_0 \nabla \cdot \mathbf{n} + a\mathbf{n} \cdot \mathbf{E} - \frac{\epsilon_a}{8\pi} (\mathbf{n} \cdot \mathbf{E})^2 - \tfrac{1}{2}\chi_a (\mathbf{n} \cdot \mathbf{H})^2 \quad (2)$$

where the Frank energy[20] F_0 is given by

$$F_0 = \tfrac{1}{2}K_1 (\nabla \cdot \mathbf{n})^2 + \tfrac{1}{2}K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n} + q_0)^2 + \tfrac{1}{2}K_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2 \quad (3)$$

Eq. (2) is valid for both bowlic nematics and cholesterics (with $q_0 = 0$ for nematics). Here **E** and **H** are external electric and magnetic fields, respectively. The term $\mathbf{n} \cdot \mathbf{H}$ changes sign under time reversal and is thus precluded.

The K_0 term appears in Ref. 20. It is a total differential and will not appear in the Euler-Lagrange equation of motion. However, it will contribute to the surface energy and should show its effects in weak anchoring case, interfaces and droplets.

The a term is new and if it dominates over the dielectric term then there will be no Frederiks transition if electric field is used (there is no threshold and the transition is continuous[21]). But Frederiks transition still exists when magnetic field is used.

D. *Flexoelectricity*

Flexoelectricity comes from additional terms in the free energy density. To the F of Eq. (2) one should add

$$F_x = F_1 + d_1 (\mathbf{n} \cdot \mathbf{E}) (\nabla \cdot \mathbf{E}) + d_2 (\mathbf{E} \cdot \nabla) (\mathbf{n} \cdot \mathbf{E})$$
$$+ d_3\mathbf{E} \cdot (\mathbf{n} \cdot \nabla)\mathbf{E} - \tfrac{1}{2}(d_1 + d_2 + d_3) (\mathbf{n} \cdot \nabla) (\mathbf{n} \cdot \mathbf{E})^2 + \ldots \quad (4)$$

where

$$F_1 = -e_1 (\mathbf{n} \cdot \mathbf{E}) (\nabla \cdot \mathbf{n}) - e_3\mathbf{E} \cdot (\mathbf{n} \cdot \nabla) \mathbf{n} + e_0\mathbf{n} \cdot (\mathbf{n} \cdot \nabla)\mathbf{E} \quad (5)$$

Eq. (4) is valid for bowlic nematics (while $F_x = F_1$ for the rod-like case). The e_1 and e_3 terms are given by Meyer[12] and the e_0 term by Lin.[22]

E. *Defects and Textures*

For bowlic nematics all the disclinations (in the Schlieren textures) will be of integer strength, i.e., $s = \pm 1, \pm 2, \pm 3, \ldots$ (see Ref. 14). The half-integer strength ones are excluded resulting, in particular, the disappearence of textures with only two dark brushes.

In bowlic columnars textures similar to that in the discotic columnars have been observed.[8,9]

F. *Hydrodynamics*

For bowlic nematics the dissipation function describing the irreversible processes is given by[23]

$$D = D_0 + b_3 T_i d_{ij} n_j + b_4 T_i d_{jk} n_i n_k + b_5 T_i N_i \tag{6}$$

where $T_i \equiv \partial T/\partial x_i$ is the temperature gradient (see Ref. 23 for definition of the notations), D_0 is the part for the rod-like case. For bowlic cholesterics one more term $c_3\, \epsilon_{kij} d_{ip} N_j n_k n_p$ should be added to the right-hand side of Eq. (6) (while there are two more terms in D_0).[23]

The b_5 term couples molecular orientation and temperature gradient *even* in bowlic nematics. In the rod-like case this happens in cholesterics but not in nematics. We therefore expect something like the Lehmann rotation phenomenon[24] in bowlic *nematics*.

VII. MOLECULAR ENGINEERING

We propose that bowlic molecules with stronger dipole moments (e.g. by adding cyano —CN— parts to the tails) should be synthesized so that the ferroelectricity will be more pronounced. Bowlic molecules with larger central core (or shorter tails) should be made so that one may have bowlic nematics (see Sec. V).

The bowlic molecule is like a bowl; it can hold things. Let us put something into the bowl. Specifically, for example, we propose to put some transition element in the middle of the core to make bowlic molecule with permanent *magnetic* dipole—magnetic bowlic molecules. These magnetic bowlic molecules in the nematic phase will be an *anisotropic* ferromagnetic fluid. This is in contrast to the isotropic magnetic fluid.[25] The prinicpal type is colloidal ferrofluid which is composed of small particles of solid, magnetic particles coated with a molecular layer of a dispersant and suspended in a liquid carrier. In our case the tails of the bowlic molecules should be able to keep the molecules apart and form a fluid (without colloids). Of course, in the isotropic phase our magnetic bowlics are isotropic and should share many of the properties of the ordinary magnetic fluids.[25] (See also Sec. VIII.)

One can also make bowlic polymers from the bowlic molecules (such as that sketched in Figure 10).

VIII. INSTABILITIES, PATTERN FORMATION AND FRACTALS

In the isotropic phase (which is already available[8,9]) the bowlic mesophase should act like the isotropic ferrofluid[25] if electric field is used in place of the magnetic field in controlling it. Those instabilities and patterns found in magnetic fluid (Kelvin-Helmholtz instability, normal-field instability, labyrinthine instability, fingering instability, thermoconvective instability, etc.)[25] should also occur in the bowlic isotropic phase and can be tested immediately with the now available bowlic compounds.[8,9]

In the bowlic nematic phase, similar but different instabilities and patterns can be expected. One may even be able to form fractal structures[26] in either case.

IX. APPLICATIONS

Bowlic mesophases are *real* ferroelectric compounds. In contrast, in the ferroelectric smectic C* of rod-like molecules the polarization forms a helix and cancels out on a macroscopic scale. To make an electro-optical device out of it one has to use very thin samples to

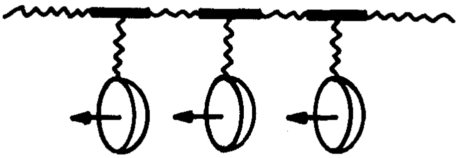

FIGURE 10 Sketch of a bowlic polymer.

prevent the helix from forming[27] and this causes many complications. For bowlic mesophases thick samples can be used and are much simple. They should have a response time (like that in the smectic C* case),

$$\tau \sim \frac{\eta}{\mathbf{p} \cdot \mathbf{E}} \tag{7}$$

where the viscosity η may be one to two order of magnitude larger than in the rod-like case and one expects τ to be in the sub-microsecond range. It is still pretty quick! (Here we are not talking about the bowlic columnars but rather the other phases.)

It should be pointed out that if one puts bowlic nematic in a twisted cell one still has a display device except that there is no threshold phenomenon any more.[21] The molecules rotates continuously with the electric field (similar to the Frederiks transition case discussed in Sec. VIC).

X. CONCLUSION

Bowlic liquid crystal is a new type of material. It is physically very interesting and has potentially very important applications. New bowlic molecules with strong dipoles should be constructed and ferroelectricity should be checked (see Sec. VIA). The possible breakdown of the $\mathbf{n} \rightarrow -\mathbf{n}$ symmetry should be checked too (by looking in the textures (Sec. VIE) and second harmonic generation experiments).

Finally, it should be pointed out that the magnetic bowlics discussed in Sec. VII are simple compounds (with one type of molecules) while the ferronematics[28] are binary systems.

Mesophase with rod-like molecules may be called "rodic".

Note added: During this Conference Dr. A. G. Petrov kindly brought to the author's attention the paper by A. Derzhanski and A. G. Petrov, *Mol. Cryst. Liq. Cryst.*, **89**, 339 (1982), in which "three-dimensional" molecules are discussed. It should be emphasized that what distinguish the bowlic molecules from all the others are two-fold: (i) The up-down asymmetry (in comparison with the discotic molecules). (ii) The bowlic molecules encompass some empty space in their geometry (as in a bowl). Alternative to the name "bowlic" is "bowlous" or "bowloid". English translation of Ref. 6 is available from the author upon request. Ref. 22 is in English.

Acknowledgments

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