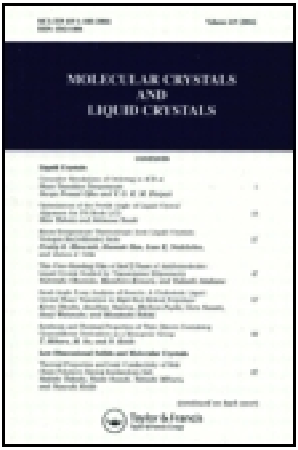

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Liquid Crystals of Disc-like Molecules

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Liquid Crystals of Disc-like Molecules†

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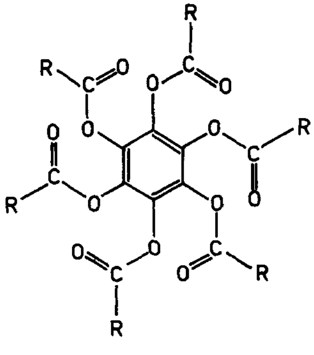
The paper deals with thermotropic mesomorphism in pure compounds composed of disc-like molecules. The disc-like mesogens known to date are reviewed and the present state of knowledge of the structures of the mesophases are described. A few brief remarks are made about the physics of these new systems.

INTRODUCTION

In 1977 we reported observations of a new type of thermotropic mesomorphism, i.e., liquid crystallinity in *pure* compounds composed of disc-like molecules.[1,2] The compounds that we investigated were the benzene-hexa-*n*-alkanoate series (hereafter abbreviated to BHA):



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† Invited lecture, presented at Eighth International Liquid Crystal Conference, Kyoto (Japan), June 30–July 4, 1980.

If at all these compounds did show mesomorphism, what we were expecting was a nematic type of behaviour, but what we found was in fact quite different. From thermodynamic, optical and x-ray studies we concluded that these compounds form an entirely new type of liquid crystal, quite unlike the classical nematic or smectic types that have been investigated for around 90 years. The structure that we proposed is illustrated schematically in Figure 1: the discs are aperiodically stacked in columns, the different columns forming a hexagonal array. The mesophase has been variously described as discotic,[7] canonic,[3,4,6] and columnar.[5,6]

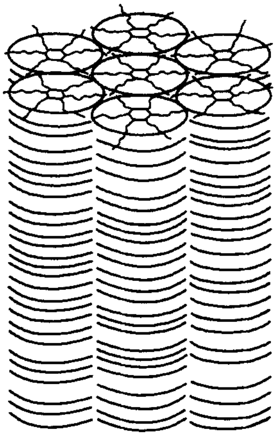


FIGURE 1 Schematic representation of the columnar structure proposed originally[1,2] for the mesophases of BHA.

Other disc-like mesogens have since been found,[7–15] the columnar structure has been confirmed by the excellent x-ray work of Levelut,[16,17] and, in particular, in the last year or so it has been established that these mesophases exhibit a rich polymorphism,[8–11,13,14] comparable to the polymorphism observed in rod-like systems. Thus a new and interesting area of research has opened up. The aim of this paper is to summarize the current situation in the field.

REVIEW OF RESULTS ON DIFFERENT COMPOUNDS

Only a few homologous series of disc-like mesogens have so far been discovered. Their molecular structures along with some relevant results are presented below.

We shall begin by describing some recent observations on BHA. Three homologues, heptanoate to nonanoate, are mesomorphic.[2] However the hexanoate compound shows pressure induced mesomorphism.[2] The mesophase-isotropic transition extrapolated to atmospheric pressure yields a virtual transition temperature of 89°C (Figure 2). Interestingly, this value is in excellent agreement with the results of miscibility studies[20] (Figure 3).

With benzene, BHA form lyotropic mesophases.[2,20] Goozner and Labes[21] have studied the effect of dissolving small non-mesogenic molecules such as xylene, toluene, etc., in these columnar phases and drawn some conclusions regarding specific solute–solvent interactions.

The textures of the mesophases of BHA when the isotropic liquid is cooled *rapidly* are usually straight narrow fans (see Figure 3 of Ref. 1 and Figure 3(a) of Ref. 2) and quite often there is extinction when the polarizer or analyser direction is along the central radius of the fan. It was verified that the refractive index is greater for the electric vector parallel to the central radius, and accordingly it was concluded that the columns run transversely and that the planes of the discs are normal to the columnar axis. However, in subsequent observations with the pure compounds as well as with the benzene-mixtures, textures have been obtained (at a very slow rate of cooling) with the columnar

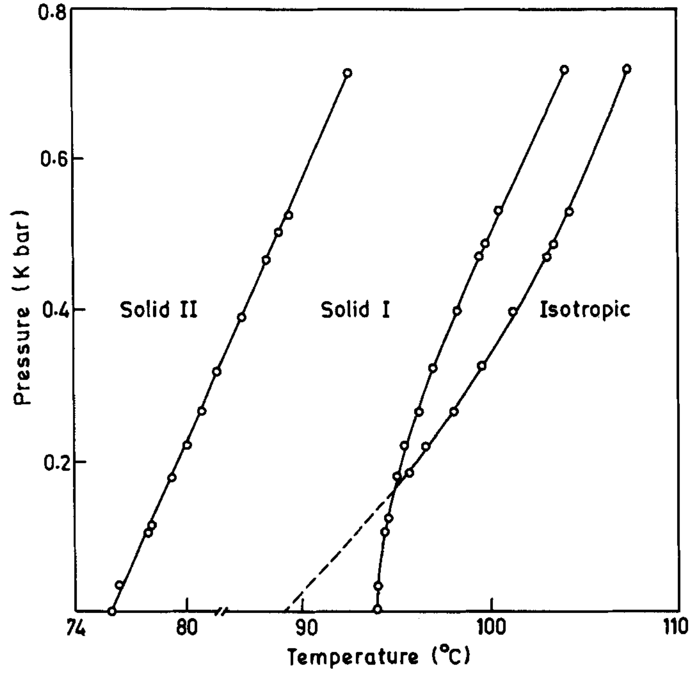


FIGURE 2 Experimental P–T diagram of BH-hexanoate.[2] The mesophase-isotropic transition line extrapolated to atmospheric pressure yields a virtual transition temperature of 89°C.

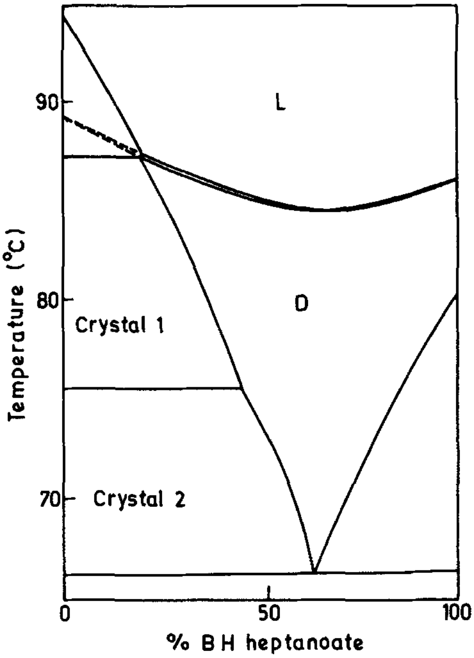
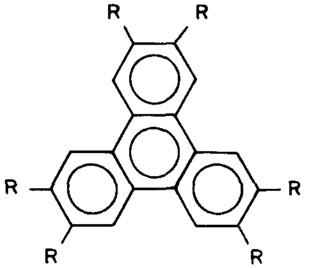


FIGURE 3 Miscibility diagram of BH-hexanoate and BH-heptanoate.[20] The virtual mesophase-isotropic transition temperature of the hexanoate = 89°C.

axes bent in circles or spirals. These give well defined extinction brushes, 90° apart, but not in the "standard" directions parallel to the polarizer and analyser directions; rather they are inclined to the right or left of the polarizer-analyser directions.[2,4,22,23] The angle of inclination varies from specimen to specimen, the maximum angle being about 35°. Sometimes complex textures are seen with curved brushes connecting a radial brush at $+\sim 35°$ in one zone to one at $-\sim 35°$ in a zone of larger radius and zig-zag brushes alternating between these two extreme orientations (see Figure 7 of Ref. 2 and Figure 1 of Ref. 4). The explanation put forward recently[4] is that the direction of minimum polarizability is not parallel to the columns but inclined to it at angle of about 35°. Now, the molecule consists of a rigid core with a flexible aliphatic fringe, the diameter of the rigid core being only about a third of that of the whole molecule. The anisotropy of polarizability lies mainly in the rigid aromatic core and if this tilts more than the molecule as a whole one can account for the optical observations without requiring an unacceptably large lattice distortion. Such a configuration would allow more space for the aliphatic chains to gain entropy from their flexibility. The conclusion is, therefore, that the mesophases of BHA form a tilted columnar structure with the columns forming a pseudo-hexagonal lattice, i.e., a rectangular lattice with an axial ratio b/a differing by 5–10% from the ideal hexagonal value of $\sqrt{3}$. The possible structures compatible with this evidence have been discussed in Ref. 4. If it is assumed that the columns can be bent in any direction, then the extinction brush obliquity, viewed along the axis of bend, can take any value from 0° to the maximum value of about 35°, as is indeed observed to be the case. However, the avoidance of zero obliquity except in some very narrow fans suggests the existence of tilt-bend coupling, i.e., a preference for the axis of molecular tilt to be parallel to the axis of bend of the columns. A further complication is that with such a pseudo-hexagonal structure, twinning is likely to be an easy process. Several different twinning modes are possible and these allow most of the optical features to be interpreted. With the high probability of twinning and other processes and the difficulty of obtaining well aligned specimens, a precise x-ray determination of the departure of the axial ratio b/a from the ideal hexagonal value of $\sqrt{3}$ is not an easy task, but an attempt is being made to see if this is possible and to verify some of the above conclusions.

Very precise calorimetric and infrared studies of BHA have been carried out by Sorai *et al.*[24] Their data will no doubt be useful in assessing the role of the melting of the chains in promoting these phase transitions.

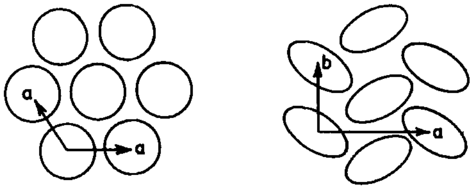
The next series of compounds that we shall consider are the hexa-substituted ethers[7,8] and esters[8,9] of triphenylene:



R = OC_nH_{2n+1}
or
$COOC_nH_{2n+1}$

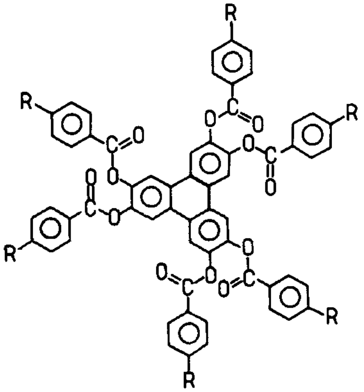
Levelut[16,17] has established that both these series form columnar phases. In the case of the ethers, the triphenylene cores are regularly stacked in each column, but there is no positional correlation between the centres of the molecules in neighbouring columns. The higher homologues of the esters show three mesophases. [This was the first instance of polymorphism in the columnar phases.[8,9]] Two of these phases have been clearly characterized:[17] in one the columns form a hexagonal lattice and in the other they form a rectangular lattice (Figure 4). In both structures, the molecules are stacked in an irregular fashion in each column, as in the case of BHA.

The hexa-*n*-alkoxy or alkyl benzoates of triphenylene,[10,11]



(a) (b)

FIGURE 4 (a) Hexagonal and (b) rectangular modifications of the columnar structure.



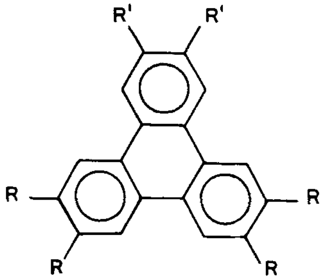
$R = C_nH_{2n+1}$

or

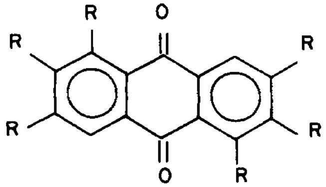
OC_nH_{2n+1}

show a most interesting type of polymorphism. A transition occurs from a columnar phase to a nematic-like phase. In one of the homologues ($R = C_6H_{13}O$), the columnar phase is believed to be tilted[11] (Figure 5). The nematic-like phase of these compounds is closely similar to the so-called carbonaceous mesophase formed during the carbonization of graphitizable materials.[25,26] It has been shown very recently that this nematic-like phase can be twisted by the addition of disc-like molecules with chiral substituents.[19]

So far we have dealt with molecules having 6-fold or 3-fold symmetry. Mesogenic disc-like molecules having lower symmetry have also been found. Examples are the dissymmetrically substituted ethers of triphenylene,[12]



and rufigallol-hexa-*n*-octanoate[13]



The latter shows two mesophases, one of which is totally miscible with the mesophases of three hexa-substituted esters of triphenylene.

The hexa-*n*-alkanoates of truxene[14]

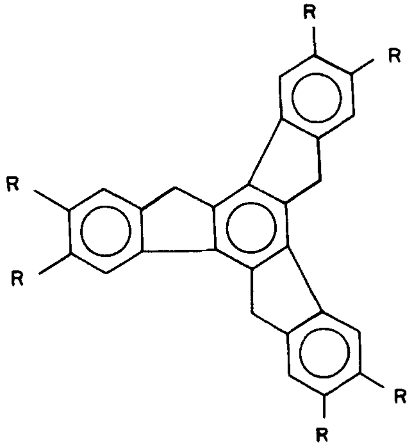
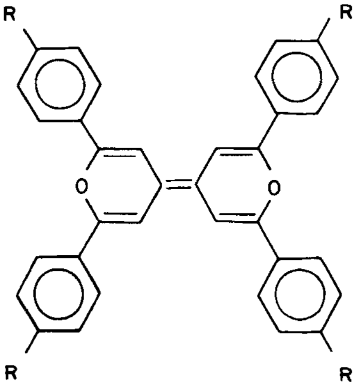


exhibit a remarkable type of polymorphism, somewhat reminiscent of (though not identical to) the re-entrant nematic phase observed in rod-like systems.[30] These compounds show columnar and "nematic" phases, but the latter occurs at lower temperatures.

Another series of mesogens synthesized very recently is the 2,2′,6,6′-tetraarylbipyran-4-ylidenes:[15]



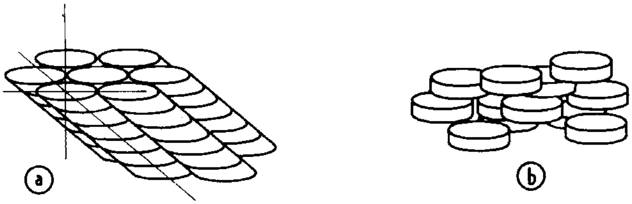


FIGURE 5 Schematic representations of (a) the tilted columnar structure, (b) the 'nematic' phase of disc-like molecules.

Next, we refer to an interesting observation of Bunning *et al.*[18] The mesophase di-isobutylsilanediol (DIISB) is found to be totally miscible with that of BH-heptanoate. How the molecules of DIISB are arranged to form a columnar structure still remains to be elucidated.

Billard[27] has proposed a nomenclature for the different types of mesophases of discotic molecules; an alternative scheme has been suggested by Destrade[11] based on x-ray structural evidence. It is hoped that a unified scheme will be evolved in due course.

CONCLUDING REMARKS

The columnar phase represents a distinctly new class of thermotropic liquid crystal: in its simplest form, it has translational order in two dimensions but not in the third. Helfrich[6] has described the three classes—columnar, smectic and nematic, representing singly, doubly and triply melted phases—in terms of their fluidity and defects.

The hydrodynamic properties of the columnar phase will of course be quite different from that of the lamellar liquid crystal (e.g., smectic A). For example, permeation can take place in two dimensions, whereas in smectic A it occurs in only one dimension. Prost and Clark[28] have made some preliminary calculations in terms of the general theory of Martin, Parodi and Pershan.[29] A prediction of the theory is that there should exist, in addition to the second sound found in smectic A, a third sound associated with the shearing of the columns relative to one another.

Defects in the columnar phases have been investigated in some detail by Kleman[31] and by Bouligand.[32] One of structures predicted by Kleman is a spiral arrangement of the columns, and such a structure has indeed been observed by us (see Figure 7 of Ref. 2).

The nematic phase of discotic systems, though resembling the classical nematic of rod-like systems, may be expected to show marked differences in its elastic, viscous and other properties. A detailed study of this phase is clearly of the utmost interest from the fundamental point of view and also in elucidating the structure and characteristics of the carbonaceous mesophase, which is of great practical importance.

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