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Liquid crystals of disc-like molecules

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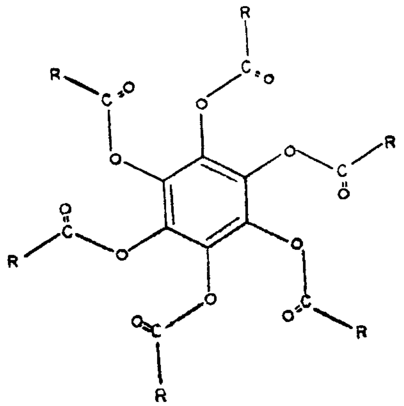
Abstract. Thermotropic mesomorphism has been observed in pure compounds consisting of simple disc-like molecules, viz., benzene-hexa-*n*-alkanoates. Thermodynamic, optical and x-ray studies indicate that the mesophase is a highly ordered lamellar type of liquid crystal. Based on the x-ray data, a structure is proposed in which the discs are stacked one on top of the other in columns that constitute a hexagonal arrangement, but the spacing between the discs in each column is irregular. Thus the structure has translational periodicity in two dimensions and liquid-like disorder in the third.

Keywords. Thermotropic liquid crystals; disc-like molecules; benzene-hexa-*n*-alkanoates; x-ray diffraction.

1. Introduction

It has long been recognized that the distinctive feature of thermotropic liquid crystals formed by pure compounds is the rod-like or lath-like shape of the molecule. Mesophases composed of large plate-like molecules are known to occur at high temperatures during the carbonization of graphitizable substances, such as petroleum and coal tar pitches (Brooks and Taylor 1965, Zimmer and White 1977), but these are rather complex materials and certainly cannot be regarded as single-component liquid crystalline systems. We report here what is probably the first observation of thermotropic mesomorphism in pure, single-component systems of relatively simple plate-like, or more appropriately disc-like, molecules.

The compounds investigated were benzene-hexa-*n*-alkanoates (abbreviated, for convenience, as BHn-alkanoates):



$R = n-C_4H_9$ to $n-C_9H_{19}$

They were synthesized according to the procedure of Neifert and Bartow (1943) and purified by chromatography and repeated crystallizations from absolute ethyl alcohol.

2. Thermodynamic data

The transitions were studied by differential scanning calorimetry using a Perkin-Elmer Model DSC2. Four homologues, BHn-hexanoate to nonanoate, show meso-

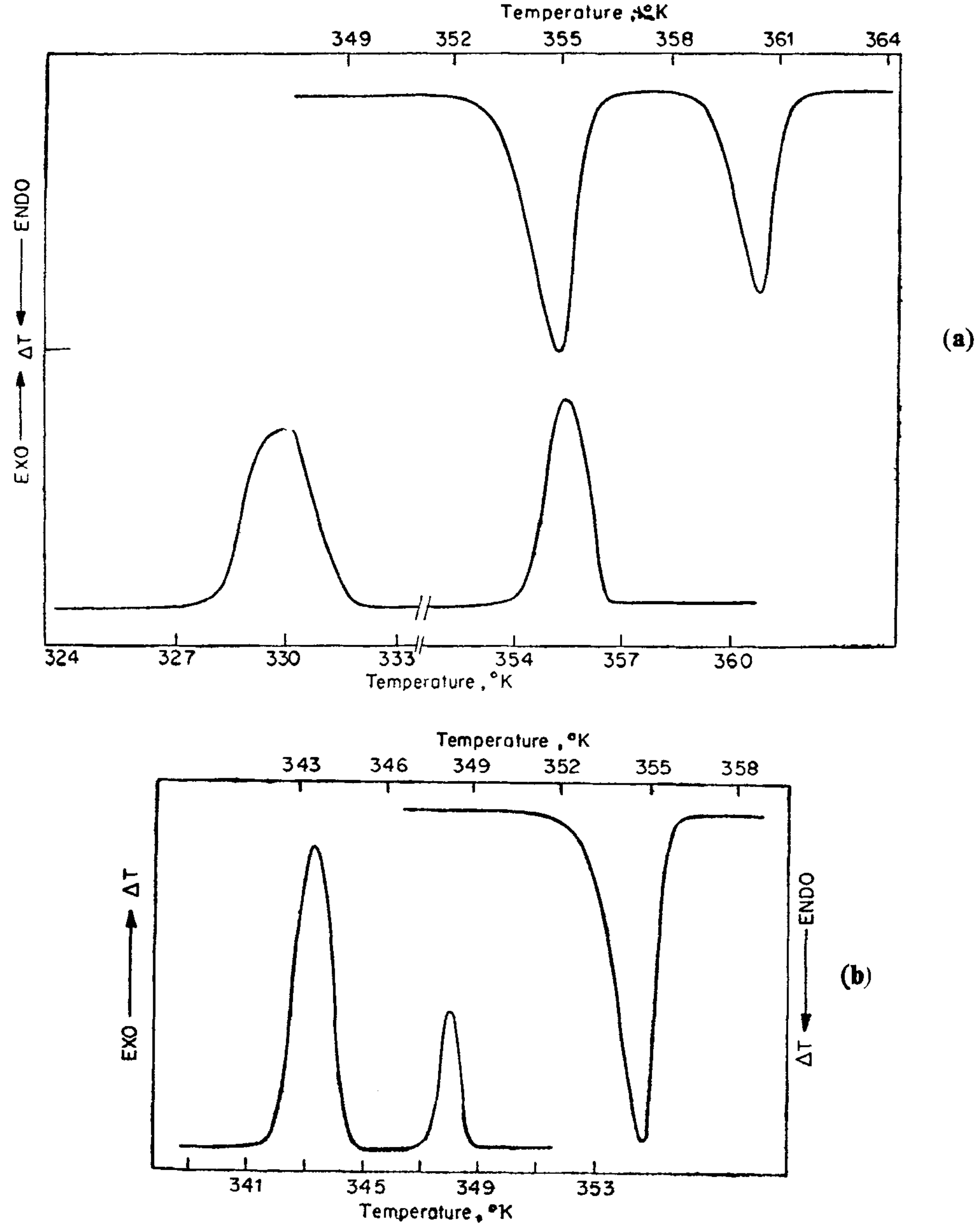


Figure 1. Differential scanning calorimetric curves for (a) BHn-heptanoate, (b) BHn-nonanoate.

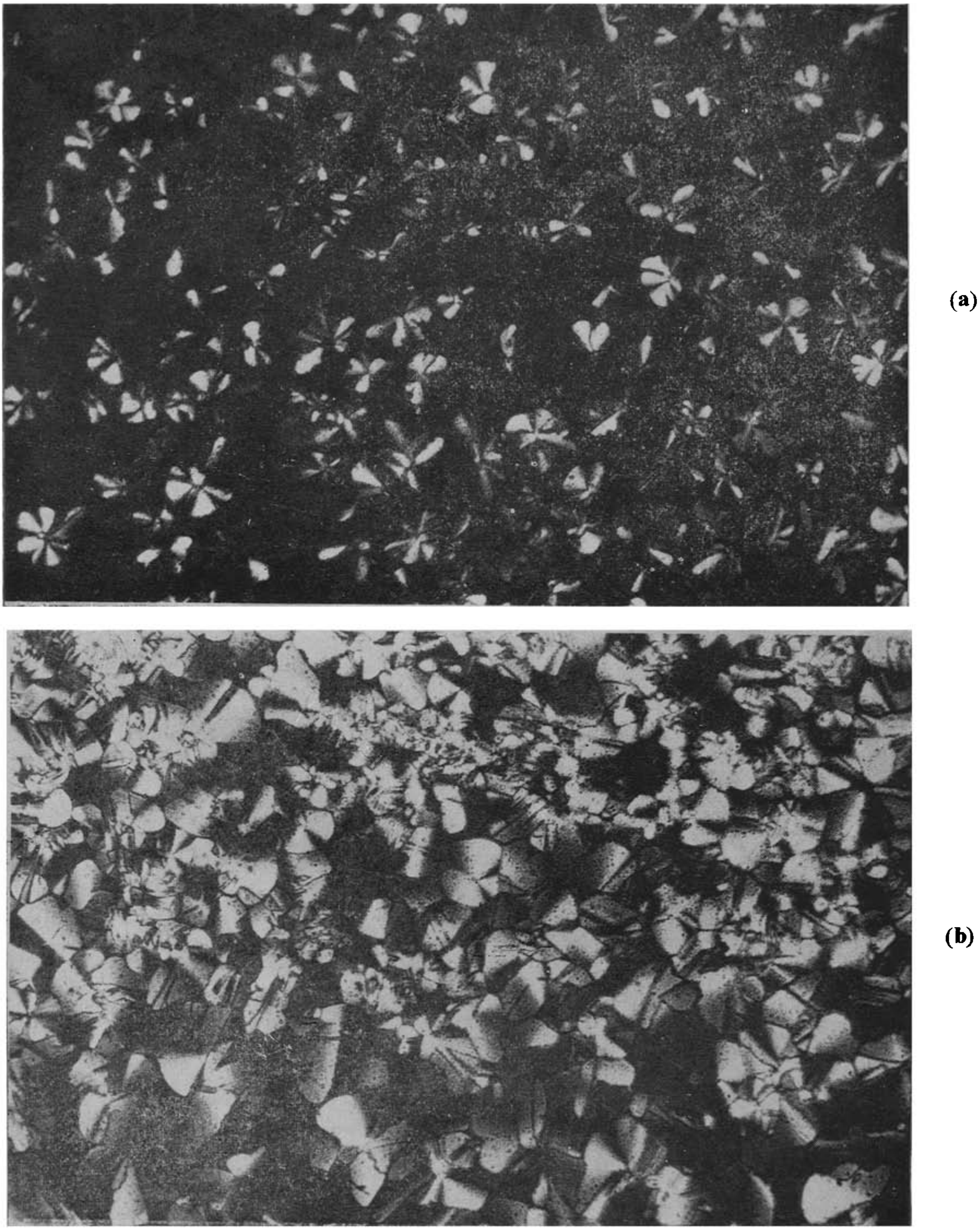


Figure 2. (a) The mesophase appearing as flower-like particles on cooling the isotropic liquid; (b) on further cooling, the particles grow and merge together to fill the entire field of view. Crossed polarizers, × 400.

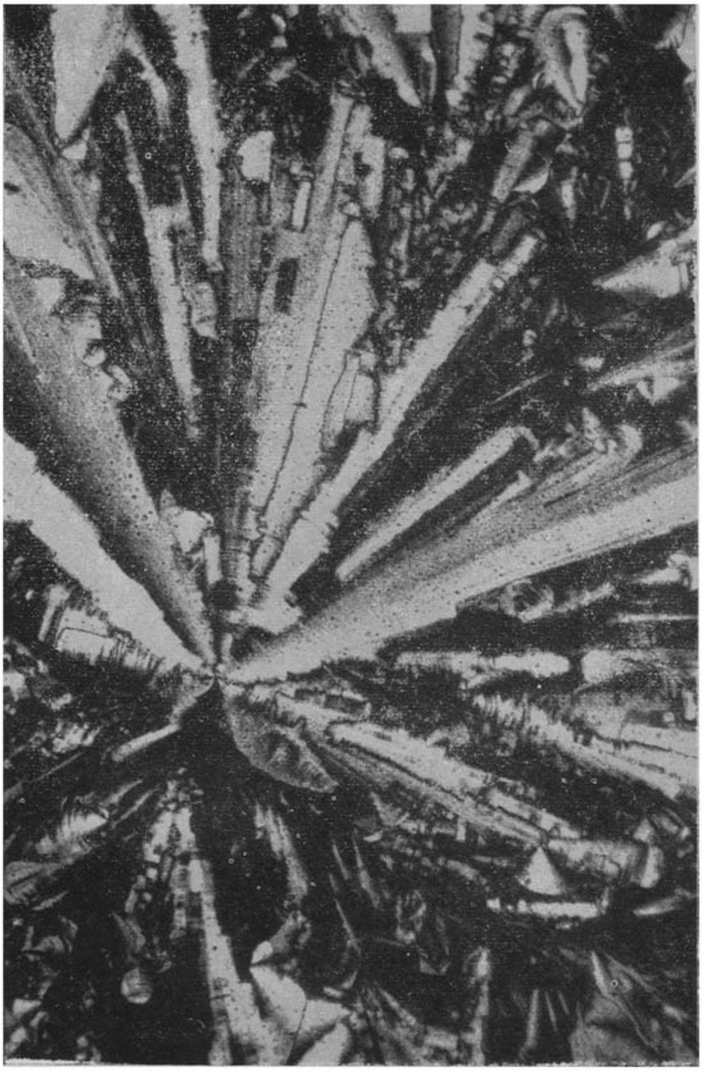


Figure 3. Broken-fan texture of the mesophase. Crossed polarizers, × 500.

Table 1. Transition temperatures and heats of transitions

Compound	Transition	Temperature (°C)	Heat of transition kcals/mole
BHn-pentanoate	crystal → isotropic (non-mesomorphic)	106	6·07
BHn-hexanoate	crystal → mesophase	68·3	4·78
	mesophase → isotropic	86·0	4·77
	isotropic → mesophase	83·25	
BHn-heptanoate	crystal → mesophase	80·2	6·97
	mesophase → isotropic	86·2	4·68
	isotropic → mesophase	83·6	
BHn-octanoate	crystal → mesophase	79·4	9·67
	mesophase → isotropic	83·6	3·79
	isotropic → mesophase	81·5	
BHn-nonanoate	crystal → isotropic	79·6	16·28
	isotropic → mesophase	74·7	3·38
BHn-decanoate	crystal → isotropic (non-mesomorphic)	85·35	18·24

phases. The DSC curves for two of them are reproduced in figure 1. The temperatures and the heats of transitions determined from the curves are given in table 1.

In the three enantiotropic compounds, hexanoate to octanoate, there is supercooling of both the isotropic liquid and the mesophase. Supercooling of the isotropic liquid is not surprising in these cases, since the heat of the isotropic-mesophase transition is quite large—indeed in one compound, BHn-hexanoate, equal to that of the mesophase-solid transition. This suggests a very highly ordered mesophase, probably smectic-like in character.

Though the molecule is by no means globular, we did consider the possibility of the mesophase being a *birefringent* plastic crystal—somewhat analogous to that exhibited by norbornylene and its homologues (Folland *et al* 1975)—with rotational disorder about an axis normal to the disc. However, from the optical and x-ray evidence, which we shall describe presently, we are inclined to think that this is a true liquid crystalline phase in the accepted sense of the term.

3. Optical textures

The transitions could be seen very clearly through the polarizing microscope when the sample was cooled from the isotropic phase. Typical textures are illustrated in figures 2 and 3. Sometimes, the mesophase made its appearance as flower-like particles (figure 2a), which on further cooling grew in size and finally merged together to fill the entire field of view (figure 2b). However, most often the mesophase adopted a ' broken-fan ' texture similar to that of smectic C (figure 3), occasionally with striations running across the fans as in smectics E and F (see Sackmann and Demus 1973). Optical observations with the aid of a phase retardation plate confirmed that the disc-like molecules are oriented with their long molecular axes (i.e., the diameters of the discs) aligned radially in the fan and their short axes (or the normals to the discs) lying in the plane of the sample. Also, like the smectic phases, the material is highly viscous.

The transition to the solid phase on cooling the sample was also quite distinctly observable. However, the change in texture attending the reverse transition, i.e., when the solid transformed to the mesophase on heating, was so slight that it was practically undetectable, but the DSC curves proved that the three compounds hexanoate to octanoate, are in fact enantiotropic.

4. X-ray studies

X-ray diffraction photographs of the three phases of BHn-octanoate using filtered CuK_α radiation are shown in figure 4. Essentially similar patterns were obtained with the hexanoate and heptanoate compounds also. X-ray photographs could not be taken of the mesophase of the monotropic nonanoate compound as it tended to crystallize into the solid phase in a short time.

The crystalline phase gives a large number of sharp maxima as is to be expected of a regular three-dimensional lattice (figure 4a). There is a marked change when the sample goes over to the mesophase (figure 4b) and the pattern now closely resembles that from some of the smectic phases (see de Vries 1973). The outermost ring, which corresponds to a mean intermolecular spacing of about 6 Å, is quite faint and diffuse, and is characteristic of liquid-like disorder. On the other hand, the three inner rings are made up of a large number of fairly sharp spots, which clearly suggests a highly ordered lamellar structure. The Bragg spacings (d) corresponding to these three rings are 20·1, 11·7 and 10·1 Å. (In some photographs, there were one or two weak spots in between the 20·1 and 11·7 Å rings with $d \sim 15$ Å; however, even assuming that these were not due to some spurious effect, it appeared reasonable to ignore them in comparison with the three prominent diffraction rings, at least in a preliminary interpretation of the x-ray data.)

Both the 6 and 20 Å rings are present in the diffraction pattern from the isotropic phase (figure 4c); the intensity and the width of the inner ring shows that smectic-like (cybotactic) ordering persists in this phase also.

From the nature of the diffraction pattern, it seems safe to conclude that the mesophase is not a plastic crystal. For one thing, a large number of fairly clear sharp reflexions is not generally characteristic of the plastic phase (see e.g. Winsor 1974). But more significantly, the presence of the diffuse 6 Å ring in the mesophase pattern and the fact that its appearance hardly changes when the sample goes over to the isotropic phase is a clear indication that long range translational order is absent in the mesophase in at least one dimension. This again favours a liquid crystalline structure for, by definition, a plastic crystal should have an appreciable degree of three-dimensional order.

Now the fact that the thickness and the diameter of the disc-like molecule are respectively of the order of 6 and 20 Å gives a clue to a possible structure of the mesophase. This is illustrated schematically in figure 6. The discs are stacked one on top of the other in columns that constitute a hexagonal arrangement. The discs in each column are irregularly spaced with a mean separation of 6 Å. Such a structure would explain the diffuse ring as well as the sharp reflexions in the x-ray diffraction pattern. Direct evidence of the hexagonal symmetry of the structure is presented in figure 5. This is an x-ray photograph of a nearly monodomain specimen of the mesophase of BHn-hexanoate, with the incident beam almost exactly along the six-fold axis.

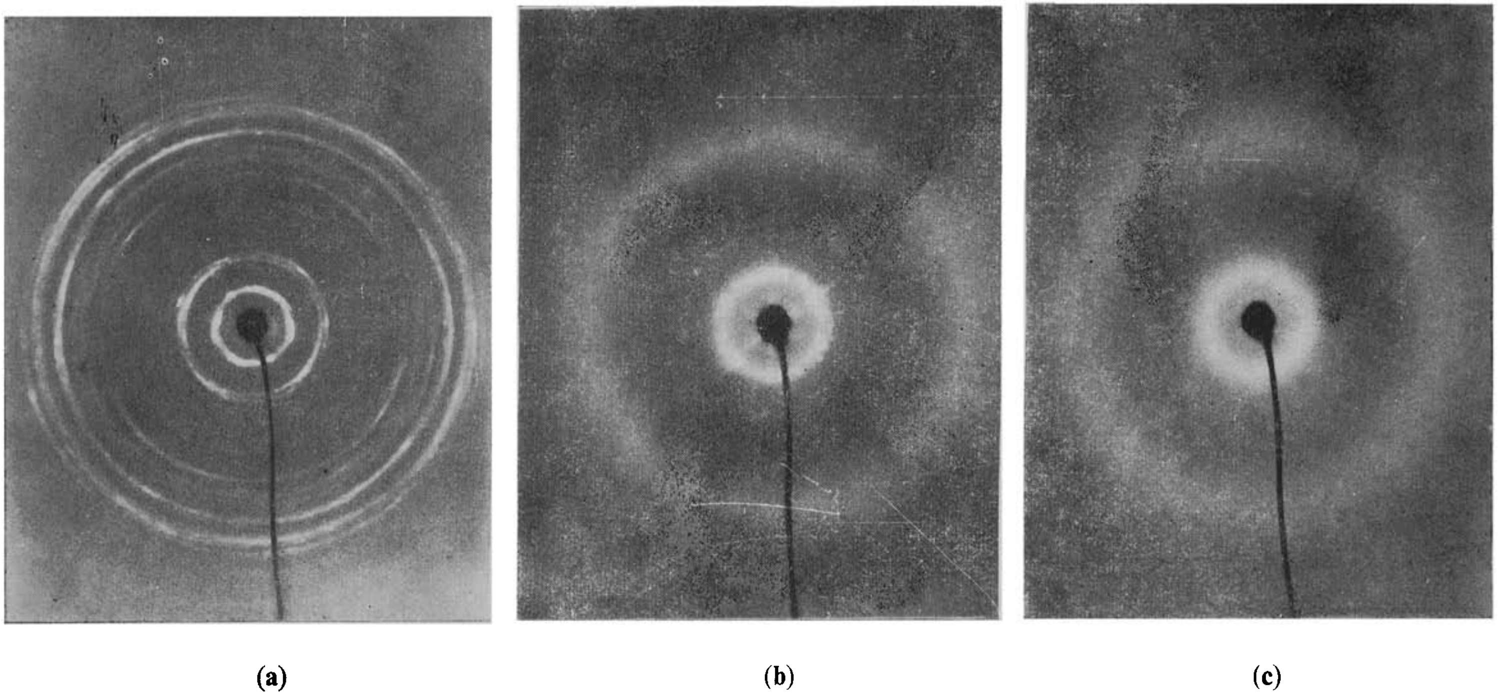


Figure 4. X-ray diffraction photographs of BHn-octanoate. Filtered CuK$_\alpha$ radiation. Specimen to film distance 9·6 cm. (a) crystalline phase, (b) mesophase, (c) isotropic liquid.

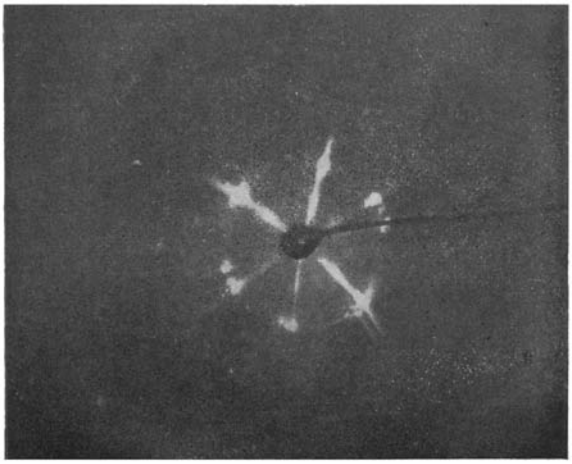


Figure 5. X-ray diffraction photograph of a nearly monodomain specimen of the mesophase of BHn-hexanoate. Specimen to film distance 12·5 cm. Incident beam almost exactly along the six-fold axis.

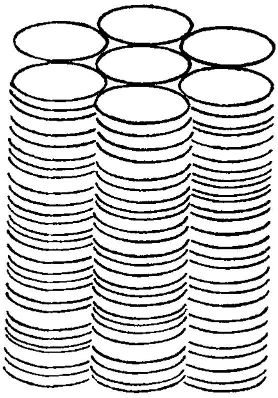


Figure 6. Schematic representation of the structure of the mesophase. The discs are spaced irregularly to form liquid-like columns.

We may now proceed to interpret the x-ray data on the basis of this structure. If *a* is the lattice constant (which in this case is equal to the diameter of the disc), the Bragg spacings of the first three orders of reflexion from such a lattice should be

$$d_{100} = \frac{\sqrt{3}a}{2},\ d_{110} = a/2 \text{ and } d_{200} = \frac{\sqrt{3}a}{4}$$

or

$$d_{100} : d_{110} : d_{200} = 1 : 0{\cdot}5773 : 0{\cdot}5$$

The experimental results for the 3 compounds are given in table 2.

Table 2. Molecular spacings for the three compounds

	BHn-hexanoate	BHn-heptanoate	BHn-octanoate
Mean inter-molecular spacing along hexagonal axis Å (expt.)	6	6	6
d_{100} Å (expt.)	18·1	18·9	20·1
d_{110} Å (expt.)	10·6	11·1	11·7
d_{200} Å (expt.)	9·1	9·7	10·1
$d_{100} : d_{110} : d_{200}$ (expt.)	1 : 0·59 : 0·50	1 : 0·59 : 0·51	1 : 0·58 : 0·50
Lattice constant Å (expt.)	21·0	22·2	23·3
Approximate molecular diameter assuming fully extended chains Å	21·5	24·0	26·5

It is seen that the experimental ratios of the Bragg spacings are in reasonable accord with the values for a hexagonal lattice. Also, as is to be expected, the lattice constant a increases systematically from the hexanoate to the octanoate. The experimental value of a is in fair agreement with the calculated diameter of the idealized molecule with *fully* extended end-chains; there is a small discrepancy which increases with increasing chain length, but this is not surprising in view of the fact that the chains become more flexible as they get longer. Thus, on the whole, the proposed structure appears to be essentially correct.

In principle, there is an alternative structure which can give rise to exactly the same type of x-ray diffraction pattern. This structure consists of sheets which are regularly spaced at intervals of 6 Å. Each sheet contains a hexagonal close-packed arrangement of discs, but the different sheets are displaced parallel to themselves in an irregular fashion. A 'planar' disorder of this type should also result in a diffuse 6 Å diffraction maximum in addition to sharp reflexions from the hexagonal lattice (see Guinier 1963). However, such a disorder is probably more easily realized when the intermolecular attraction within each sheet is much greater than that between sheets. With these disc-like molecules, the opposite will be true, and the type of disorder depicted in figure 5 is likely to be more favourable. Moreover, by analogy with smectic A (see Chandrasekhar 1977) one may expect a structure consisting of liquid-like columns to be readily deformed to give the radiating or fan-like arrangement of molecules that is observed in the optical textures.

Further studies are in progress to test the validity of the structure and to investigate other properties of the mesophase.

Acknowledgements

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References

Brooks J D and Taylor G H 1965 *Carbon* **3** 185

Chandrasekhar S 1977 *Liquid Crystals* (Cambridge: Cambridge Univ. Press) p. 285

de Vries A 1973 *Proc. Int. Liquid Crystals Conf., Bangalore—Pramana Supplement* **1** 93

Folland R, Jackson D A and Rajagopal S 1975 *Mol. Physics* **30** 1053

Guinier A 1963 *X-ray Diffraction* (London: W H Freeman & Co.) p. 169

Neifert I E and Bartow E 1943 *J. Am. Chem. Soc.* **65** 1770

Sackmann H and Demus D 1973 *Mol. Cryst. Liq. Cryst.* **21** 239

Winsor P A 1974 in *Liquid Crystals and Plastic Crystals* eds. G W Gray and P A Winsor (Chichester: Ellis Horwood Ltd., Vol. 1, p. 51)

Zimmer J E and White J L 1977 *Mol. Cryst. Liq. Cryst.* **38** 177