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DISC-LIKE MESOGENS

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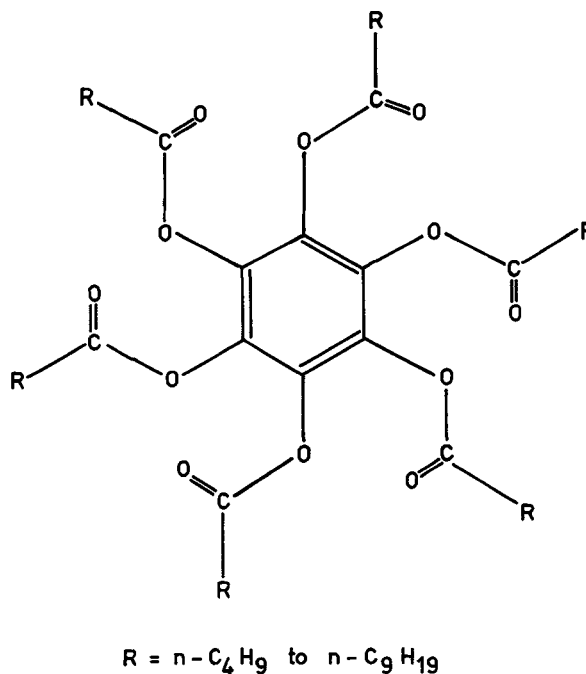
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Résumé. — Dans cet article, nous étudions des mésophases thermotropes observées dans des systèmes de molécules décortiqués : des benzène-hexa-*n*-alcanoates purs et leurs mélanges avec du benzène. Ces mésophases présentent des textures optiques typiques de phases lamellaires de cristaux liquides. Les données de rayons X pour les composés purs correspondent à une structure dans laquelle il existe un ordre lamellaire, avec une symétrie hexagonale dans le plan de la lamelle et un désordre de type liquide suivant la troisième dimension. Des résultats préliminaires de NMR indiquent que le degré d'ordre moléculaire dans la mésophase est intermédiaire entre ceux des phases solide et liquide isotropes. On présente des diagrammes de phase (*P*, *T*) pour deux homologues, les composés hexanoate et octanoate.

Abstract. — The paper deals with a study of the thermotropic mesophases observed in systems of disc-like molecules, viz., pure benzene-hexa-*n*-alkanoates and their mixtures with benzene. The mesophases exhibit optical textures that are typical of a lamellar type of liquid crystal. The X-ray data for the pure compounds are consistent with a structure in which there is lamellar order with hexagonal symmetry in two dimensions and liquid-like disorder in the third. Preliminary NMR results are described, which again indicate that the degree of molecular order in the mesophase is intermediate between those in the solid and isotropic phases. Pressure-temperature phase diagrams are presented for two of the homologues, the hexanoate and octanoate compounds.

1. **Introduction.** — Since the discovery of liquid crystals in 1888 several thousands of pure compounds have been found to exhibit thermotropic mesomorphism. The distinctive feature common to all of them is the rod-like or lath-like shape of the molecule. In 1965, Brooks and Taylor [1] described the formation of mesophases consisting of plate-like molecules at relatively high temperatures ($\sim 450^\circ\text{C}$) during the carbonization of certain graphitizable substances, such as petroleum and coal tar pitches. However, these *carbonaceous* mesophases are rather complex materials composed of large molecules of a range of molecular weights (typically around 2 000) and certainly cannot be regarded as single-component liquid crystalline systems. Recently, we reported the occurrence of thermotropic mesomorphism in pure compounds consisting of relatively simple disc-like molecules [2] and, based on optical and X-ray evidence, proposed a structure for the mesophase. Similar disc-like mesogens have been found by groups working in the laboratories of Thomson-CSF, Collège de France and Centre de Recherche Paul Pascal [3].

2. **^{13}C -NMR spectra in isotropic solution.** — Our studies were on benzene-hexa-*n*-alkanoates :



In the paper published last year [2] we had stated that four homologues, hexanoate to nonanoate (hereafter abbreviated to BH_n , $n = 6 \dots 9$) show meso-

phases. We have now found by ^{13}C -NMR spectroscopy that the BH6 compound used in the earlier experiments has an impurity of a homologous type (which, we suspect, may have been present in the hexanoic acid used at that time). The impurity was not evident from the ^1H -NMR spectra recorded earlier. Pure BH6, prepared afresh and checked by ^{13}C -NMR, does not, in fact, show a mesophase but a solid-solid transition followed by the melting transition. However, the mesomorphic behaviour of the other three compounds, BH7...BH9, in the pure state has been confirmed.

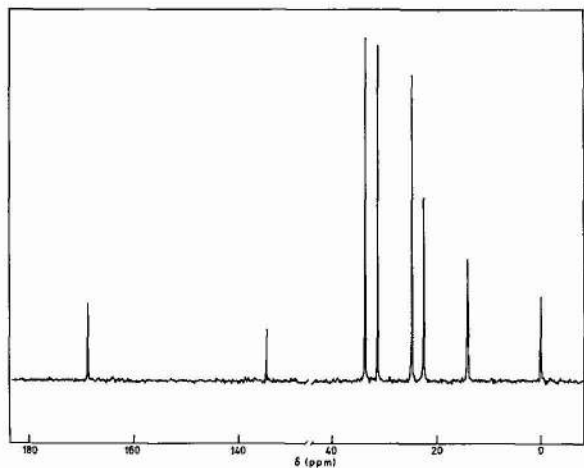


FIG. 1. — ^{13}C -NMR spectrum of an isotropic solution of BH6 in CDCl_3 with proton decoupling. Chemical shifts relative to TMS.

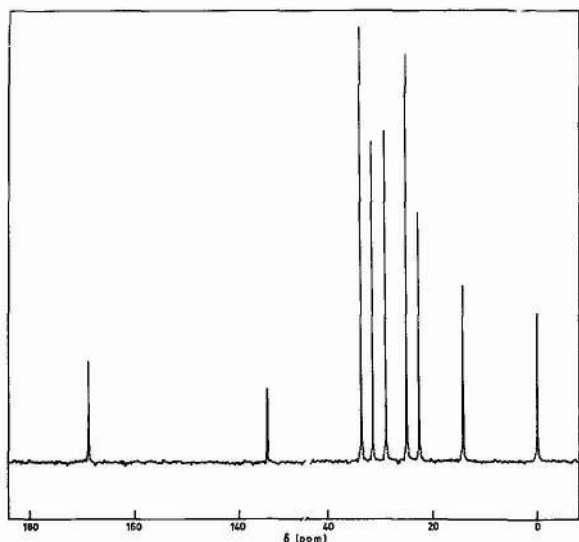


FIG. 2. — ^{13}C -NMR spectrum of an isotropic solution of BH7 in CDCl_3 with proton decoupling. Chemical shifts relative to TMS.

Figures 1 and 2 give the ^{13}C -NMR spectra (in natural abundance, with proton decoupling and TMS as internal standard) of isotropic solutions of pure

BH6 and BH7 in CDCl_3 , obtained on a Bruker WH-270 spectrometer. The lines arising from the chain carbons, aromatic carbons and carbonyl carbons are clearly seen in the spectra. Spectra of solutions of BH8 and BH9 were similarly recorded but are not reproduced here. These spectra establish the six-fold symmetry of the molecule and confirm the purity of the samples used in the present studies.

3. Optical, thermodynamic and X-ray studies. — Typical fan-shaped textures exhibited by the mesophase are shown in figure 3. They resemble the textures of some of the smectic phases and indicate a highly ordered stratified structure.

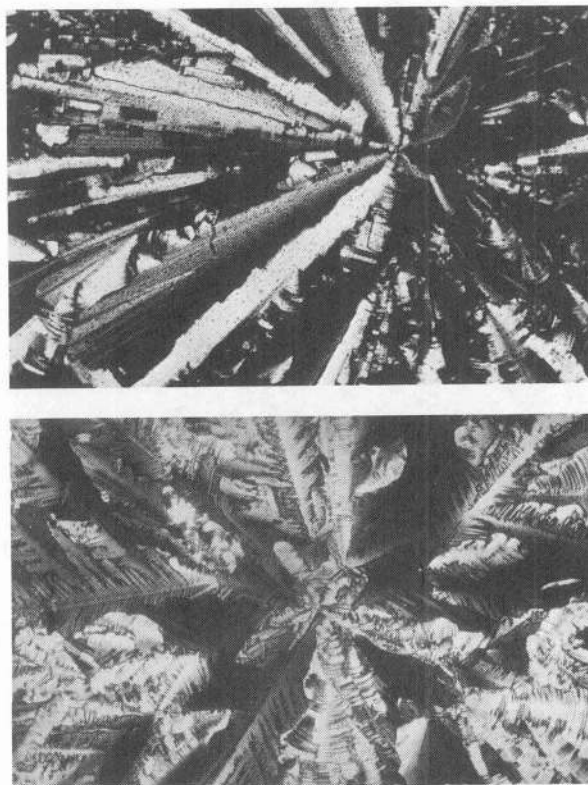


FIG. 3. — Typical fan-shaped textures of the mesophase of the pure material.

X-ray diffraction photographs of the liquid crystalline and isotropic phases of BH8 are presented in figure 4. The X-ray pattern from the mesophase consists of relatively sharp inner rings, and a diffuse, *liquid-like* outer ring whose appearance remains practically unchanged when the sample goes over to the isotropic phase. The Bragg spacings corresponding to the first 3 prominent inner rings are in the ratio $\sqrt{3} : 1 : \sqrt{3}/2$ (i.e., 1 : 0.5773 : 0.5), characteristic of a hexagonal lattice. Based on this evidence we proposed a structure in which the discs are stacked one on top of the other in columns which form a hexagonal arrangement, but the spacings between the discs in each column is irregular (Fig. 5).

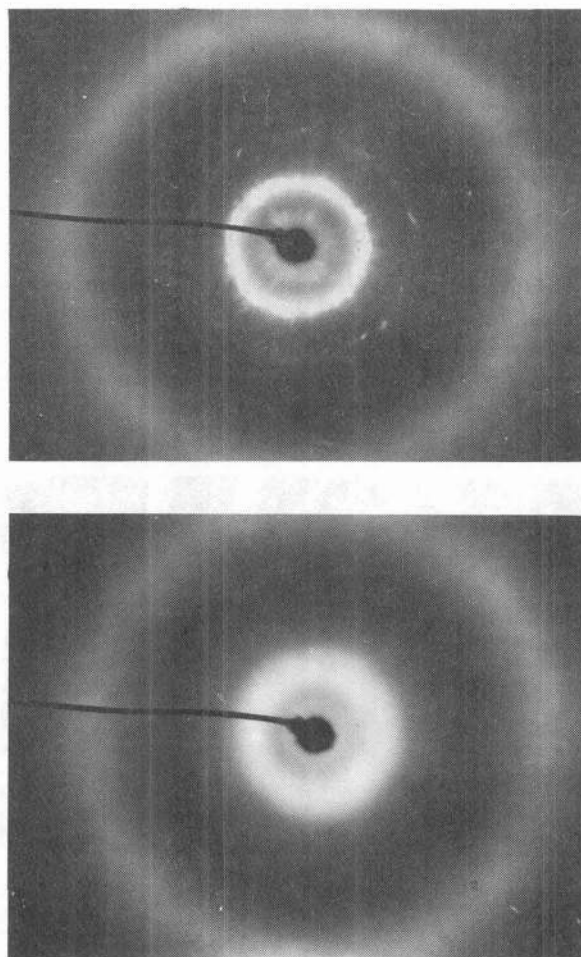


FIG. 4. — X-ray diffraction photographs of BH8 using Ni-filtered CuK_α radiation. Top : mesophase; bottom : isotropic liquid.

Thermodynamic and X-ray data have been redetermined with improved accuracy and are presented in tables I and II. The temperatures and heats of transition were obtained using a Perkin-Elmer differential scanning calorimeter, model DSC-2, and the X-ray measurements were made from photographs taken with Ni-filtered CuK_α radiation.

TABLE I
Temperatures and heats of transition

Compound	transition	Temperature (°C)	Heat of transition kcal/mole
BH6	crystal II → crystal I	75.7	3.8
	crystal I → isotropic	94.5	7.9
BH7	crystal → mesophase	81.2	7.6
	mesophase → isotropic	87.0	5.3
BH8	isotropic → mesophase	83.5	10.7
	crystal → mesophase	79.8	10.7
	mesophase → isotropic	83.4	4.5
	isotropic → mesophase	81.8	4.5
BH9	crystal → isotropic	80.4	16.7
	isotropic → mesophase	76.6	3.4
BH10	crystal II → crystal I	50.5	10.4
	crystal I → isotropic	85.5	20.7

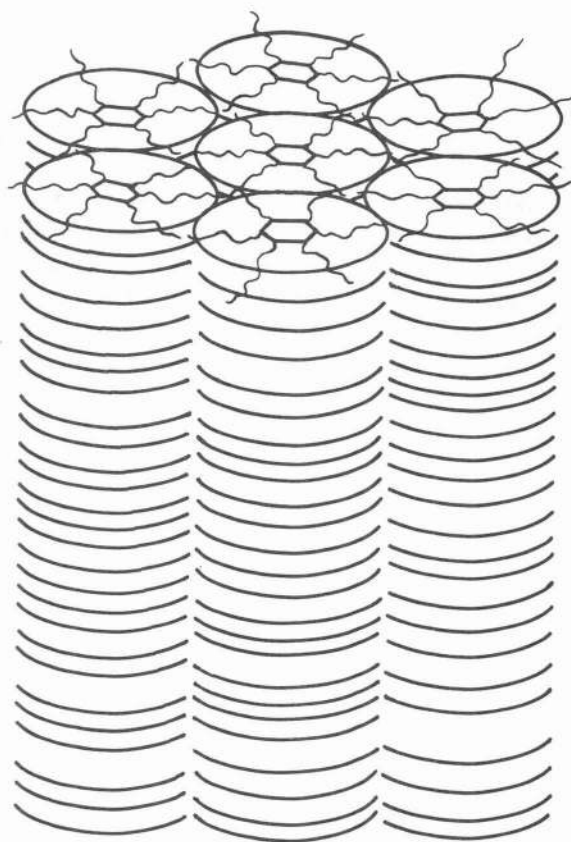


FIG. 5. — Schematic representation of the structure of the mesophase. The discs are irregularly spaced to form liquid-like columns.

TABLE II
Molecular spacings in the mesophase ()*

	BH7	BH8
d_{100} (Å)	15.0	15.9
d_{110} (Å)	8.7	9.1
d_{200} (Å)	7.6	8.0
$d_{100} : d_{110} : d_{200}$	1 : 0.58 : 0.51	1 : 0.57 : 0.50
Lattice constant (Å)	17.4	18.4
Mean intermolecular spacing along hexagonal axis (Å)	4.6	4.6

(*) X-ray photographs could not be taken of the mesophase of the monotropic BH9 compound as it tended to solidify in a short time.

The pure compounds mixed with a small quantity of benzene (up to about 10% w/w) also form mesophases. These mesophases are somewhat more mobile than the ones formed by the pure materials. They exhibit fan-shaped textures (Fig. 6) and often form spherulites, some of which show interesting growth spirals (Fig. 7). The X-ray photograph of the mesophase has a diffuse 4.6 Å outer ring and a 15 Å inner ring, the latter almost exactly corresponding to the innermost ring of the mesophases of the pure compounds, but not as sharp, suggesting that the mixture is not as highly ordered.

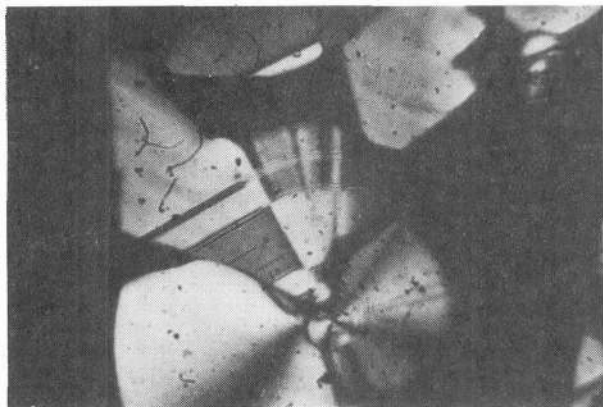


FIG. 6. — Mixture of BH6 + benzene : fan-shaped textures.

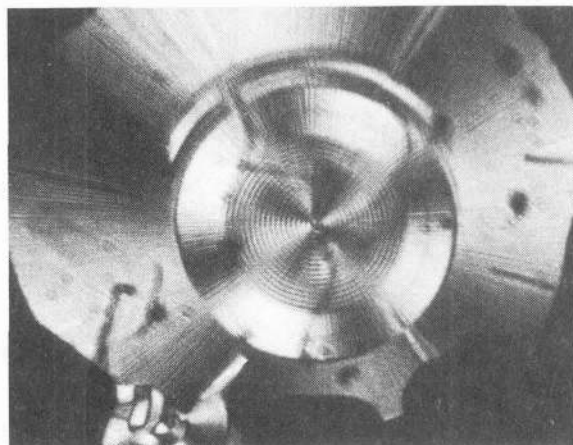
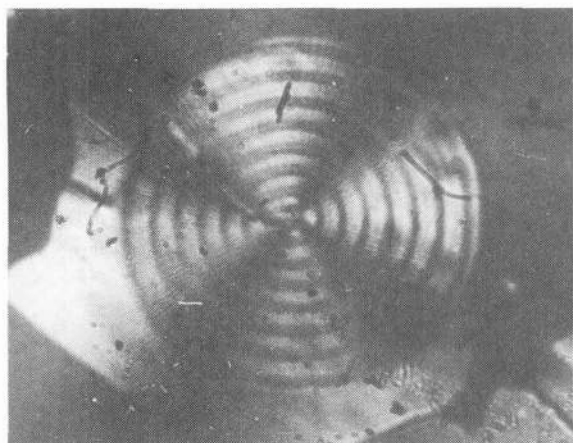


FIG. 7. — Mixture of BH6 + benzene : spherulites with growth spirals.

4. Preliminary NMR studies of the mesophases. —

We have carried out some preliminary NMR studies on the pure compounds as well as their mixtures with benzene.

In the isotropic phase, the $^1\text{H-NMR}$ spectra of the pure compounds show peaks due to the chain protons. In the mesophase, the peaks merge to form a broad maximum, while in the solid phase even this maximum

disappears completely. This clearly indicates that the chain ordering in the mesophase is intermediate between those in the solid and isotropic phases.

The $^1\text{H-NMR}$ spectrum of benzene in the mesophase of the BHn + benzene mixture shows a splitting due to direct dipolar coupling. A determination of the order parameter of the benzene molecules is under way. It is also proposed to carry out a detailed $^{13}\text{C-NMR}$ study of the mesophases of the pure materials.

5. **Pressure studies.** — Pressure studies were carried out on 2 homologues, BH6 and BH8. (For a descrip-

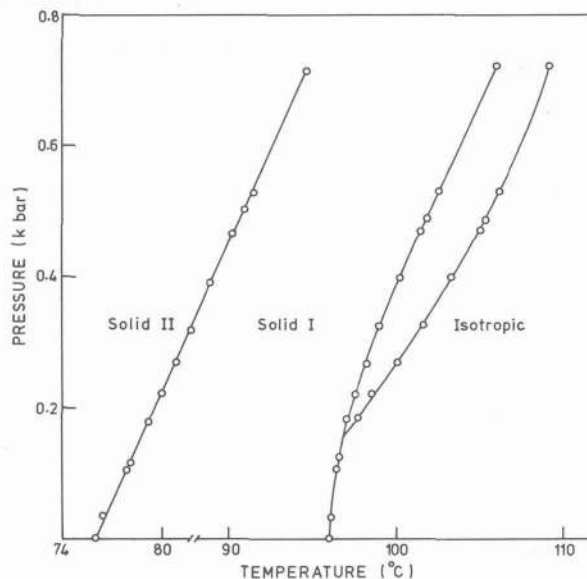


FIG. 8. — Experimental phase diagram for BH6. All data points have been obtained in the heating mode only.

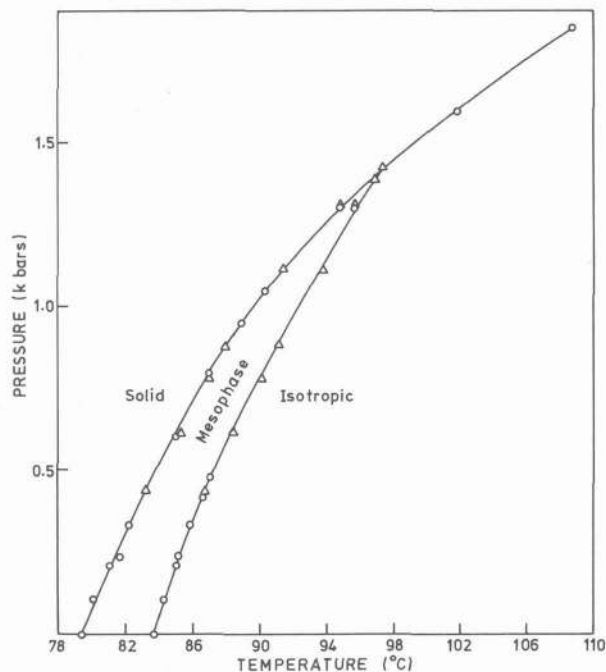


FIG. 9. — Experimental phase diagram for BH8. The data points have been obtained in the heating mode only.

tion of the experimental set up, see [4]). As expected, each compound appears to simulate the behaviour of a higher homologue on application of pressure. Thus, BH6 shows an additional phase above 160 bars (Fig. 8), while BH8 become non-mesomorphic above 1.4 kbar (Fig. 9). From the experimental values of dT/dP and ΔH at atmospheric pressure, ΔV for the

two transitions of BH8 turn out to be 12.3 and $3.5 \text{ cm}^3 \text{ mole}^{-1}$ for the solid-mesophase and mesophase-isotropic transitions respectively.

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References

- [1] BROOKS, J. D. and TAYLOR, G. H., *Carbon* **3** (1965) 185.
See also ZIMMER, J. E. and WHITE, J. L., *Mol. Cryst. Liq. Cryst.* **38** (1977) 177.
- [2] CHANDRASEKHAR, S., SADASHIVA, B. K. and SURESH, K. A., *Pramana* **9** (1977) 471.
- [3] BEGUIN, A., BILLARD, J., DUBOIS, J. C., NGUYEN HUU TINH and ZANN, A., this conference; DESTRADE, C., MONDON, M. C. and MALTHETE, J., this conference; FUG, G., ROUILLON, J. C. and GASPAROUX, H., this conference.
- [4] SHASHIDHAR, R., *Mol. Cryst. Liq. Cryst.* **43** (1977) 71.