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Branched chain discotics

Phase structure and orientation behaviour

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Studies show that branching the side chains of hexakis(acoyloxy)-benzenes (HAB) and -cyclohexanes (HAChx) does not modify the structure of the discotic mesophase formed. Shear fields appear to act on entire columns, not on individual discs, thereby causing alignment of columns in the shear direction. X-ray diffraction patterns of samples at temperatures between 30°C and 40°C above the clearing temperature provide evidence for the presence of mesophase order.

1. Introduction

The introduction of branches into the conformationally flexible side chains of discotic mesogens selectively depresses the melting temperature, thereby broadening the temperature range over which the mesophase is stable [1, 2]. Phase compatibility of branched and unbranched chain discotics, along with preliminary diffraction data, suggested that chain branching did not alter mesophase structure [1, 2]. We confirm this prediction in this contribution and report a study of isotropic phases just above the clearing temperature. Uniformly oriented samples were essential for our diffraction experiments. Low molecular mass discotics have been oriented in magnetic fields [3, 4], shear fields [5] and in uniaxial flow fields (drawn fibres) [6]. Homeotropic alignments on glass surfaces have been produced by surface pretreatment with highly polar materials like mellic acid [7] or polyamide films [8]. Sample alignment has been found in 20 to 80 Å films on gold surfaces [9]. We report here on alignment of discotics in magnetic fields and in shear fields.

2. Experimental

The synthesis of the discotic liquid crystalline samples used in this study has been described elsewhere in detail [2] (see figure 1). All samples have been kindly supplied by C. P. Lillya. X-ray diffraction data were obtained using a fine-focusing X-ray tube equipped with a graphite monochromator and a pinhole collimator (diameter 0·3 mm) or a collimator, compromising two pairs of crossed slits. The detection device used was a Xentronics area detector from Nicolet–Siemens, coupled with a PCS-system for collecting, storing and analysing X-ray images. Temperature control of the samples was maintained with a heating unit/temperature control unit from Huber. The temperature accuracy was 0·5 K. Oriented samples were prepared using a shear field between two beryllium plates. Oriented samples, sealed in Lindemann capillaries, have also been

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obtained using the support of a magnetic field of approximately 1 T by cooling down from 10 K above the clearing point into the mesophase with a rate of 1 K min^{-1}. Molecular modelling and simulation of X-ray diffraction data have been performed using a Silicon Graphics Personal Iris Workstation and CERIUS 3·1 software from Molecular Modelling, Cambridge.

3. Results and discussion

Samples studied were branched chain hexaesters of hexahydroxybenzene and all-*trans*-hexahydroxycyclohexane (*scyllo*-inositol) (see figure 1) [1, 2]. All samples were a mixture of 13 stereoisomers regarding the side chain substitution. However, no influence of the stereochemistry is observable with regard to the formation of different phase structures [2]. Phase transition temperatures are given in the table. The 5-methyl derivatives exist as thermodynamically stable mesophases at 25°C.

X-ray diffraction patterns for unoriented samples of the mesophases are consistent with hexagonal columnar order D_h, and results from oriented samples confirm a hexagonal packing of the columns (see below). Comparison of all small angle reflections revealed that disc spacing along the columns is irregular (weak, diffuse reflection at 4·6 Å) for the HAB's, but regular for the HAChx's (sharp, strong reflection

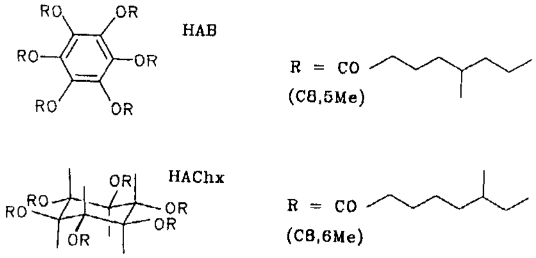

Figure 1. Structures of hexa-acoyloxybenzenes, HAB, and all *trans*-hexa-acoyloxy-cyclohexanes, HAChx, used in this study.

X-ray diffraction data of discotic liquid crystalline substances.

			d-spacing/Å‖					
Sample	T_m/°C†	T_{cl}/°C†	Hexagonal lattice			Core–Core‡	Phase	T_0/°C§
HAB-C8(5-Me)	—	102	16·6	9·6	8·3	4·64	D_{hd}	70
HAB-C8(6-Me)	6	187	16·6	9·4	8·3	4·63	D_{hd}	70
HAChx-C8(5-Me)	—	187	18·5	10·0	—	4·72	D_{ho}	70
HAChx-C8(6-Me)	54	197	17·6	9·8	—	4·77	D_{ho}	70
HAB-C8(5-Me)	—	102	16·2	—	—	5·20		130
HAChx-C8(5-Me)	—	187	18·4	—	—	5·50		230

† From [1] and [2], T_m, T_{cl} refer to melting and clearing temperatures, respectively.

‡ Core–distance.

§ D_{hd} discotic hexagonal disordered phase, D_{ho} discotic hexagonal ordered phase, T_0 temperature of observation.

‖ All recorded lattice parameters were obtained directly from the diffraction pattern of non-oriented samples; the accuracy for the lattice parameters is 0·2 Å and for the core–core distances 0·05 Å.

at 4·7 Å) [10, 11]. The difference from the rectangular packing found for the unbranched HAB's may arise because of better space filling by the branched side chains and therefore stabilization of the hexagonal arrangement of the columns. The HAB disordering has been attributed to a difference in the preferred core–core and side–side chain stacking distances [5]. Adjacent cyclohexane cores are in van der Waals contact, in contrast to the benzene cores; this factor contributes to the higher clearing temperatures for the HAChx series [2]. Similar results have been found using the CERIUS software package for building up columnar arrangements of cores of HAB's and HAChx's. For the modelling, only one stereoisomer was used. After crystal packing, reasonable densities of about 1·05 g cm^{-3} were obtained. The *c*-parameter from the hexagonal cell obtained was reasonably well in agreement with the experimental results for the HAB's 4·63 Å and for the HAChx's 4·78 Å (see figure 2).

X-ray diffraction using oriented samples in capillaries allowed direct observation of the hexagonal lattice when beam and column directions were parallel, for example, see figure 3. The experiments with non-oriented samples have been the direct sources of the lattice parameters for the hexagonal cell.

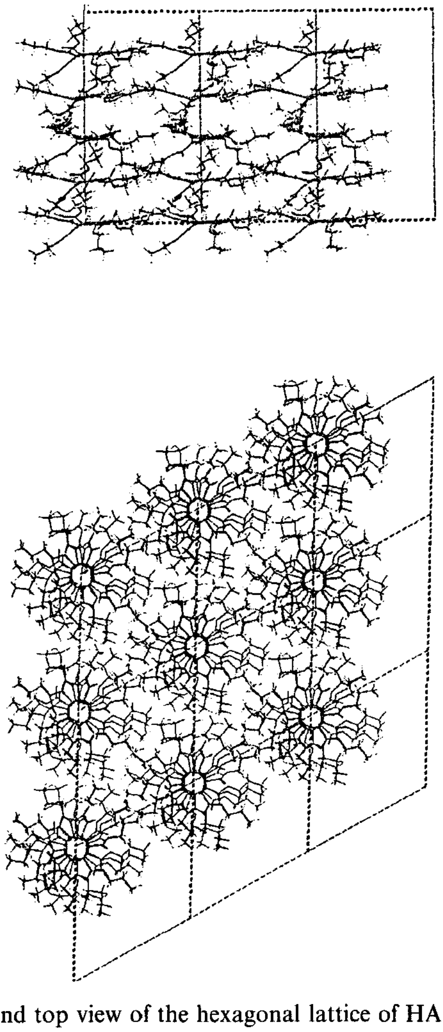

Figure 2. Side view and top view of the hexagonal lattice of HAChx-C3; CERIUS software.

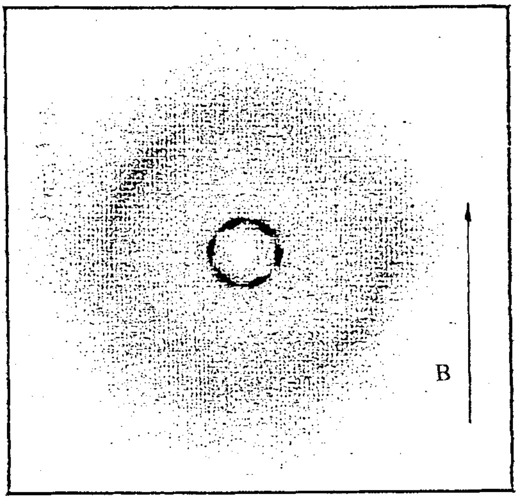

Figure 3. X-ray diffraction pattern of HAChx-C8(5-Me); hexagonal ordered mesophase, D_{ho}, 125°C, magnetic field direction indicated by the arrow.

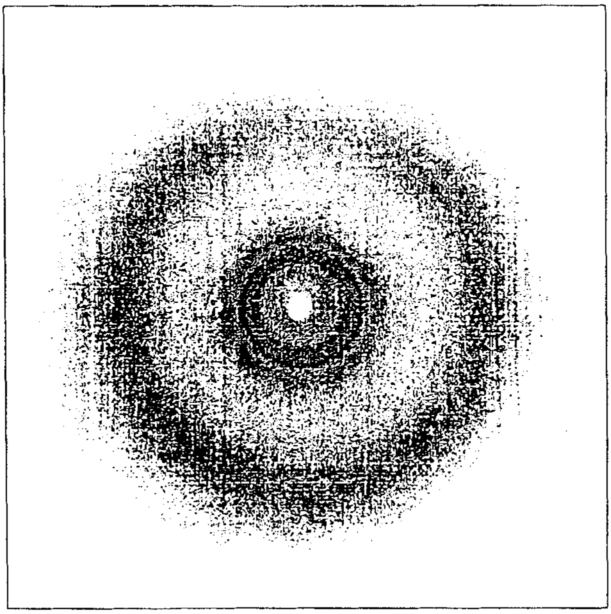

Figure 4. X-ray diffraction of HAChx-C8(5-Me); isotropic phase, 230°C. The wide angle reflection is diffuse, indicating disorder in the column axis.

Coherent reflections were also evident when the temperature of these samples exceeded their clearing temperatures as defined by DSC and POM observations. Figure 4 shows the diffraction pattern for HAChx-C8(5-Me) at 230°C, 43° above T_{cl}. The small and wide angle reflections are more diffuse then those exhibited by the mesophase. Observation of a reflection that corresponds to an intercolumnar distance is particularly significant in that it requires, at a minimum, some net local columnar organization [12]. The observed *d*-spacings are slightly smaller than those observed for

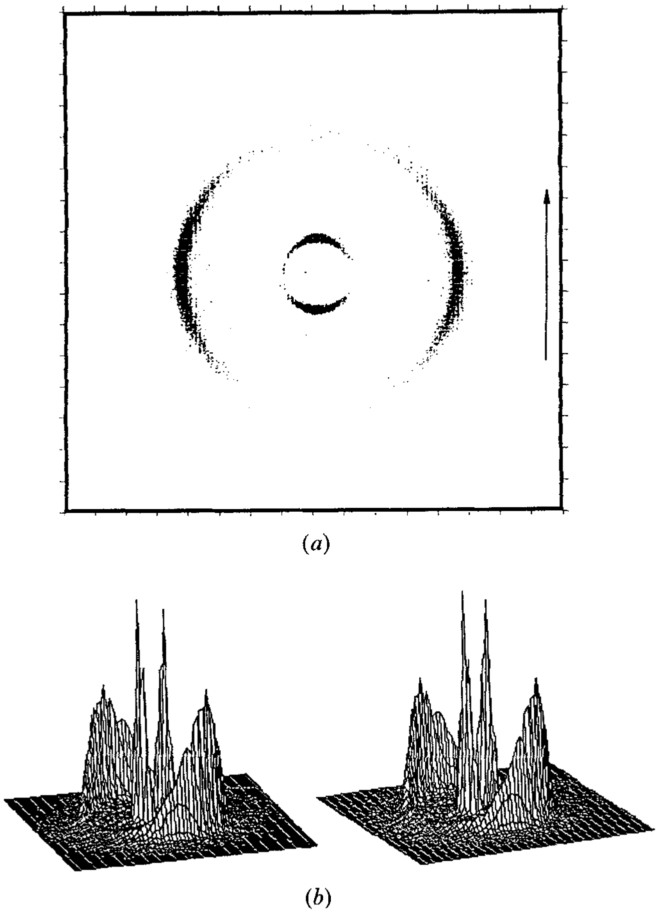

Figure 5. X-ray diffraction data for HAChx-C8(5-Me); hexagonal ordered mesophase, D_{ho}, 25°C, showing shear orientation of the columns in the shear direction; (*a*) 2D plot; (*b*) 3D plot, stereo view.

the mesophase and decrease as the temperature increases. The increase in population of *gauche* side chain conformations with temperature [13] is responsible for a decreasing column diameter and in turn accounts for an observed increase in core–core distances with temperature. The wide angle reflection for the HAChx samples, which is sharp in the mesophase, becomes diffuse in the isotropic state (see figure 4), the change indicating an increase in disorder along the column axis.

Experiments in which the mesophases were sheared between two beryllium plates were uniformly successful. X-ray diffraction revealed that individual discs are not oriented, but that entire columns respond to the shear field, aligning in this shear direction (see figure 5). A simulation of the X-ray pattern with CERIUS using cell dimensions of $a = b = 250$ Å and $c = 300$ Å and an orientating distribution half-width of 5° gave a quite similar picture (see figure 6). Rotation of the beryllium plates by 90° afforded a view in the columnar direction (see figure 7).

The resulting diffraction patterns exhibit little wider angle intensity (core to core), but higher intensity at small angles. A hexagonal arrangement of the columns, however, was not observable.

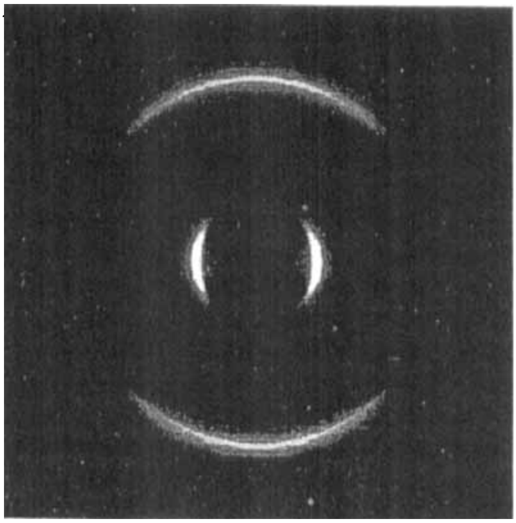

Figure 6. Simulation of the X-ray diffraction pattern of HAChx-C8(5-Me) in the hexagonal ordered mesophase, D_{ho}; CERIUS software.

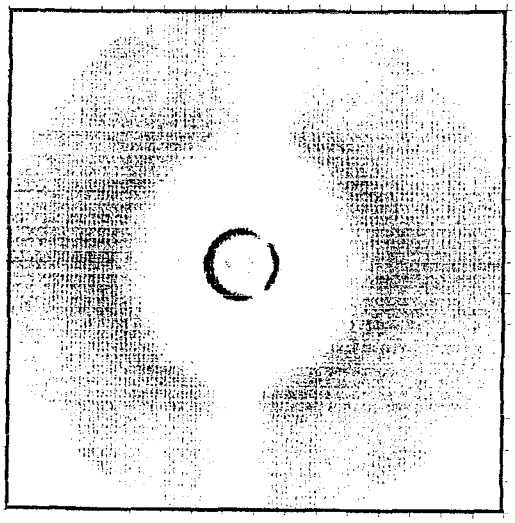

Figure 7. X-ray diffraction pattern of HAChx-C8(5-Me); hexagonal ordered mesophase, D_{ho}, 25°C, viewed in the columnar direction.

An investigation of the mesophase scattering at lower angles revealed no additional reflections in the range up to 200 Å. This can be interpreted in two different ways. The observation of a distinct reflection would hint at either a somewhat uniform size of the columns and a length of the columns larger than 200 Å, i.e., that a column is built up from 40 or more cores, or that the length of the columns is not very well defined, which would only give a constant level of background scattering. The column correlation length has previously been estimated for the hexagonal mesophase D_{ho} of hexakis(pentyloxy) triphenylene [14]. A value for the persistence length of the columns, based upon the column curvature constant is large, 0·2 μm. X-ray diffraction gave a smaller value of approximately 300 Å [15].

4. Conclusions

We may conclude that the incorporation of branches into the side chains of HAB and HAChx has no effect on mesophase structure. In the mesophases, entire columns respond to a shear field, aligning them in the shear direction. The columns act themselves rather as single mesomorphic particles, an interesting example of a spontaneous formation of a supermolecular structure of low molecular weight substances. Evidence for the persistence of some mesophase order well above the clearing temperature was observed for these samples. As temperature increases, individual discs contract in diameter and increase in thickness as a result of an increasing population of *gauche* side chain conformations. No evidence for a coherent column <200 Å was found.

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