

Evidence of a Chiral Superstructure in the Discotic Mesophase of an Optically Active Phthalocyanine

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In the liquid crystalline phase of optically active phthalocyanine (*S*)-**1** the columns are helically distorted, as has been shown by circular dichroism experiments on a Langmuir–Blodgett film of (*S*)-**1** and by small angle X-ray diffraction studies, and confirmed by time-resolved microwave conductivity measurements.

Although chiral nematic (N*) and chiral smectic (*e.g.* S_C*) mesophases are well known, only a few reports have been published on compounds displaying a chiral discotic mesophase. Destrade *et al.* were the first to describe the synthesis of chiral esters of triphenylenes and truxenes exhibiting a discotic mesophase.¹ One of the former compounds was studied by X-ray diffraction on an aligned sample, which clearly indicated the presence of a helical distortion of the columns.² One example of an optically active phthalocyanine mesogen has been published so far.³ However, no evidence of chiral superstructures was reported in this case. Therefore, we investigated the mesophase structure of phthalocyanine (*S*)-**1** (Fig. 1) which bears eight (*S*)-3,7-dimethyloctoxy substituents.

The synthesis and characterisation of (*R,S*)-**1** with (*R,S*)-3,7-dimethyloctoxy substituents has been previously published by Schouten *et al.*⁴ Because of the presence of eight chiral carbon atoms in one molecule this compound actually is a mixture of 16 enantiomers and 11 meso compounds. The optically pure compound was synthesised following the published procedure⁴ starting from (*S*)-citronellol. The analytical data of the product were as expected.⁴ The optical rotation of (*S*)-**1** amounted to $[\alpha]_{546}^{20} - 1200$ (*c* 0.001, CHCl₃).

The phase transition temperatures of (*S*)-**1** were determined by differential scanning calorimetry (DSC) and optical microscopy (Table 1). When the material was slowly cooled down from the isotropic phase to the mesophase a mosaic texture appeared between crossed polarisers which is characteristic for a discotic mesophase. However, when the material was quickly cooled down from the isotropic phase to room temperature we observed a texture with spiralised concentric rings (Fig. 2). Spiral textures have also been reported for chiral triphenylenes.⁵

We investigated the structure of the mesophases of (*S*)-**1** by small angle X-ray scattering (SAXS) measurements at 80 and 180 °C. The higher temperature measurement only gave a few reflections, from which it was difficult to derive a structure. The reflections suggest a disordered discotic mesophase, which is in agreement with optical microscopy observations. The result of the measurement at 80 °C is given in Table 2 and compared to the data of (*R,S*)-**1** in its D_{ho} phase. Extra reflections are observed in addition to the reflections arising from the hexagonal arrangement of the columns. Very striking are the two weak reflections on both sides of the 3.4 Å reflection. The additional reflections can be indexed if an extra periodicity along the columnar axis is introduced. In this

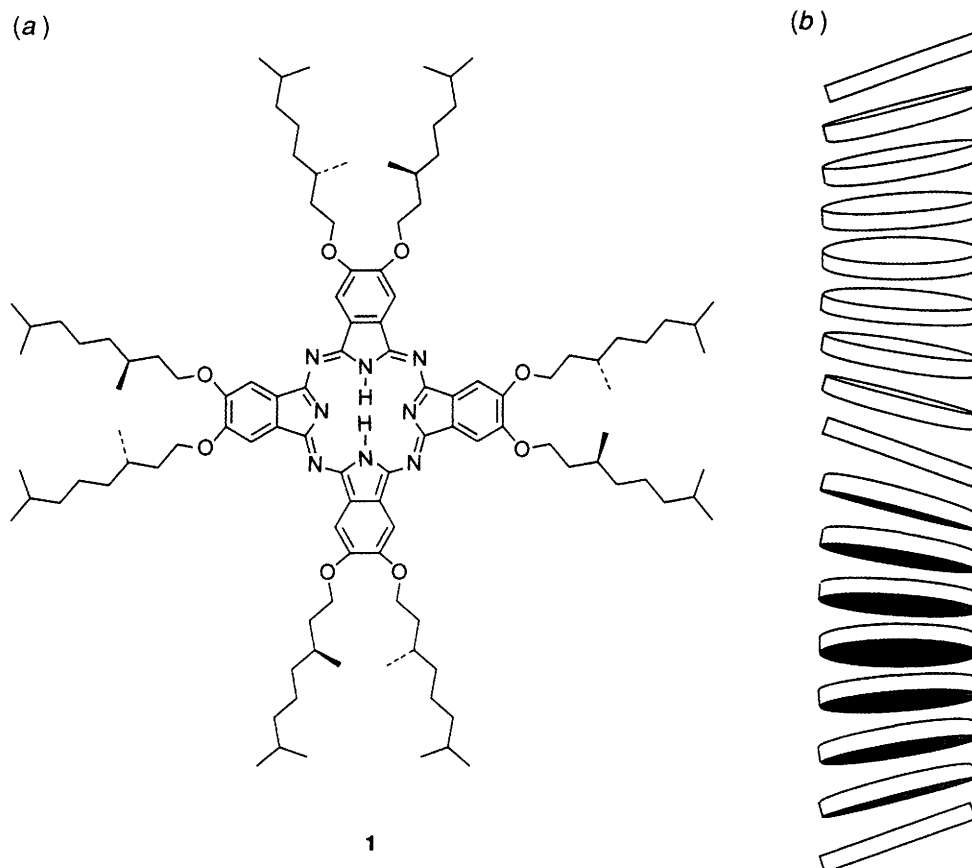


Fig. 1 (a) Molecular structure of (S)-1 and (b) drawing of a column in the D_{ho}^* mesophase of this compound

Table 1 Phase transition temperatures and enthalpies of (S)-1

| Phase transition ^a | $T/^\circ\text{C}^b$ | $\Delta H/\text{kJ mol}^{-1}$ |
|-------------------------------|----------------------|-------------------------------|
| $X \leftrightarrow D_{ho}^*$ | 16 | 6.4 |
| $D_{ho}^* \leftrightarrow D$ | 111 (95) | 3.1 |
| $D \leftrightarrow I$ | 295 (295) | 10.9 |

^a X: unknown phase, D: discotic mesophases, I: isotropic phase.

^b Heating run (cooling run).

Table 2 Spacings from X-ray diffraction data (\AA) and assigned Miller indices ($hklm$) of phthalocyanines (S)-1 and (R,S)-1 in their D_{ho} phases

| ($hklm$) | (S)-1 | (R,S)-1 ^a |
|------------|-------|----------------------|
| 0002 | 27.44 | — |
| 1000 | 24.01 | 24.64 |
| 0003 | 18.76 | — |
| 1100 | 15.32 | 15.59 |
| 2000 | — | 13.87 |
| 2100 | 10.16 | 10.44 |
| 3000 | 9.59 | 9.47 |
| 0011 | 3.63 | — |
| 0010 | 3.43 | 3.39 |
| 001-1 | 3.22 | — |

^a Data taken from ref. 4.

way the structure can be described by using the superspace notation of de Wolff, Janner and Janssen.⁶ In the superspace approach one mathematically describes a periodic structure in a higher dimensional Euclidean space. In the case of a single modulation, ($hklm$) expresses the components of a reciprocal wave vector \mathbf{K} in terms of four fundamental periodicities. In three dimensions one then has $\mathbf{K} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$,

where \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* are the reciprocal vectors of the basic structure and \mathbf{q} is the wave vector of the modulation.

From our X-ray results the mesophase of (S)-1 at 80 °C can be described as a D_{ho}^* phase, in which a helical superstructure is present with a periodicity of about 55 Å. Each period includes about 16 molecules. We propose a structure, schematically depicted in Fig. 1, in which the molecules are slightly tilted and the normal of the phthalocyanine planes rotates around the columnar axis. Because of the symmetry of the modulation the (0001) reflection appears to be extinguished. The structure of the phase below 16 °C is not yet clear, but conductivity measurements (*vide infra*) and solid-state NMR studies indicate that this phase probably is another mesophase or a glassy state.

When a helical superstructure is present, this should result in a circular dichroism (CD) activity.⁷ Therefore, we prepared a thin film of (S)-1 with the help of the Langmuir-Blodgett (LB) technique. This was possible because (S)-1 forms a stable monolayer at the air-water interface, which can be transferred to a hydrophobic glass slide. From the calculated area per molecule of the monolayer (78 Å²) it was concluded that the molecules are oriented edge-on with respect to the water surface. 20 Layers were deposited with X-type transfer. In this way a uniform thin layer was obtained. SAXS measurements revealed a single layer thickness of 26 Å. From polarised absorption spectra [Fig. 3(a)] it was concluded that the molecules are oriented with the columnar axis parallel to the transfer direction.

The LB film displayed a CD spectrum at ambient temperature as shown in [Fig. 3(b)]. However, a chloroform solution of (S)-1 (7.8 μmol dm⁻³) did not show any CD activity. Therefore, we may conclude that the CD activity of the LB film must result from the chiral stacking of the molecules.

Pulse radiolysis time-resolved microwave conductivity

Fig. 2 Texture of (*S*)-1 in the D_{ho}^* phase observed between crossed polarisers after quickly cooling from the isotropic phase to room temp.

(TRMC) measurements^{8,9} revealed that the end-of-pulse conductivity per unit dose, $\Delta\sigma_{\text{eop}}/D$, of (*S*)-1 has no sharp decrease in conductivity at elevated temperatures, as was found for (*R,S*)-1 at its solid to mesophase transition. This result is in agreement with the DSC data, which indicate that no crystalline solid phase is formed for (*S*)-1. The values of $\Delta\sigma_{\text{eop}}/D$ for (*S*)-1 are lower than those found in the mesophase of (*R,S*)-1. This interesting result suggests that the helical distortion of the macrocycles in (*S*)-1 is unfavourable for one-dimensional charge migration in the columnar stacks.

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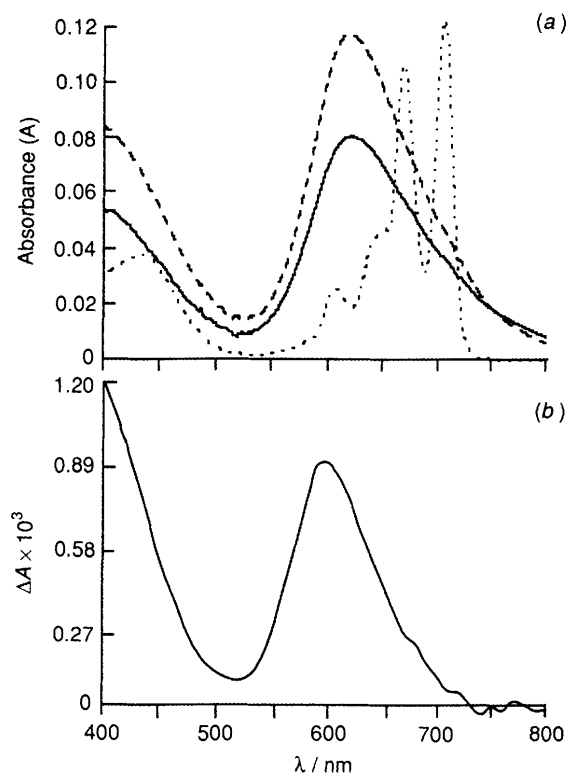


Fig. 3 (a) Visible absorption spectra of (*S*)-1: chloroform solution (....), 20 layer LB film with the electromagnetic field vector **E** parallel to the transfer direction **T** (—) and with **E** perpendicular to **T** (- - -); (b) CD spectrum of the same LB film

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