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

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Received, 26th March 1993; Com. 3/01752D

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. De Vosert al. were the first to describe the synthesis of chiral esters of triphenylenes and truxenes exhibiting a discotic mesophase. 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. One example of an optically active phthalocyanine mesogen has been published so far. 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-dimethyloctyloxy substituents.

The synthesis and characterisation of (R,S)-1 with (R,S)-3,7-dimethyloctyloxy substituents has been previously published by Schouten et al. 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 procedure starting from (S)-citronellol. The analytical data of the product were as expected. The optical rotation of (S)-1 amounted to [α]^20_546 = −1200 (c 0.001, CHCl_3).


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_{mes} 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
(a)

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. 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.

Pulse radiolysis time-resolved microwave conductivity measurements revealed that 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.
Fig. 2 Texture of (S)-1 in the Dho phase observed between crossed polarisers after quickly cooling from the isotropic phase to room temp.

(1) Measurement revealed that the end-of-pulse conductivity per unit dose, $\Delta \sigma_{\text{end}}/D$, 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 $\Delta \sigma_{\text{end}}/D$ 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.

This research was financially supported by the Dutch Innovation Oriented Research Programme (IOP) of the Ministry of Economic Affairs. The assistance of Rob van Puijenbroek (AKZO) for performing the SAXS measurements is gratefully acknowledged.

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Anti-organic Fouling Properties of Composite Membranes Prepared from Anion Exchange Membranes and Polypyrrole

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The composite membrane prepared from commercial anion exchange membranes and polypyrrole showed excellent anti-organic fouling properties in electrodialysis.

One unsolved problem in electrodialysis is organic fouling of ion exchange membranes, especially anion exchange membranes. Namely, when electrodialysis is carried out in the presence of large organic ions, the electric resistance of the membrane increased markedly during the electrodialysis. There have been various attempts to solve this problem: formation of a layer of opposite charge to that of the ion exchange groups of the membrane on the membrane surface to prevent permeation of the foulant ions,1 making the structure of the membrane loose so that ions could permeate...