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Studies of the thermotropic mesophase behaviour exhibited by a highly asymmetric tetrabenzotriazaporphyrin derivative

by E. A. CORSELLIS[†], H. J. COLES^{‡*}, N. B. MCKEOWN[§], P. WEBER[†],
D. GUILLON[†] and A. SKOULIOS[†]

[†]Groupe des Matériaux Organiques,
Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess,
67037 Strasbourg Cedex, France

[‡]Department of Physics and Astronomy, Southampton Liquid Crystal Institute,
University of Southampton, Highfield, Southampton SO17 1BJ, UK

[§]Polymer Research Group, Department of Chemistry, The University,
Manchester M13 9PL, UK

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The thermotropic mesophase behaviour of an asymmetrically shaped and highly substituted tetrabenzotriazaporphyrin (TBTAP) derivative has been studied by optical microscopy, DSC and X-ray diffraction. The TBTAP macrocycle differs from the more common phthalocyanine ring system by the substitution of a methine for a nitrogen at one meso-position. The TBTAP core was substituted with a single heptadecyl chain at this meso-position and four neopentyl groups were statistically distributed around the peripheral benzene rings. In contrast to an earlier study of this system which described the structure of the mesophase as discotic lamellar, detailed X-ray diffraction study indicates that the TBTAP derivative forms a disordered hexagonal columnar mesophase (Col_{hd}), with a weak tendency towards antiparallel orientation of neighbouring molecules observed in the form of a weak pseudo-centred rectangular packing.

1. Introduction

Phthalocyanine ring systems have been widely studied in the solid state due to the striking combination of physical properties that they exhibit [1]: extensive planar aromatic structures, high anisotropic polarizability and intense colour. Phthalocyanine derivatives are commonly used as commercial pigments and are renowned for their high thermal and chemical stability. The central cavity of the molecule presents a complexing site for over 70 species of transition metal atoms. Much interest has been expressed in the conductivity and optoelectronic properties of phthalocyanine-based materials: for example, as the photoconducting elements in photocopiers [2] and for use in fuel cells [3].

The first mesomorphic phthalocyanines were reported in the early eighties [4] and since then numerous liquid crystalline phthalocyanine derivatives have been synthesized with the aim of producing more easily controllable macroscopic structures. These derivatives have been predominantly alkyl and alkoxy octa-substituted mesogens with side chains substituted at the 2,3-positions on the benzene ring [5-8] or octa-alkyl compounds substituted at the 1,4-positions [9], but mesomorphic tetra-

substituted compounds have also been synthesized [10]. Hexagonal columnar phases are most commonly cited (both Col_{hd} and Col_{ho}), however, nematic [6] and rectangular columnar [9] structures have also been reported. Much work needs to be carried out to link unambiguously the phase structure to the anisotropic macroscopic properties, and one current interest is the possibility of using mesogenic metal-substituted aromatic ring systems as self-assembling, one-dimensional molecular semiconductors [11].

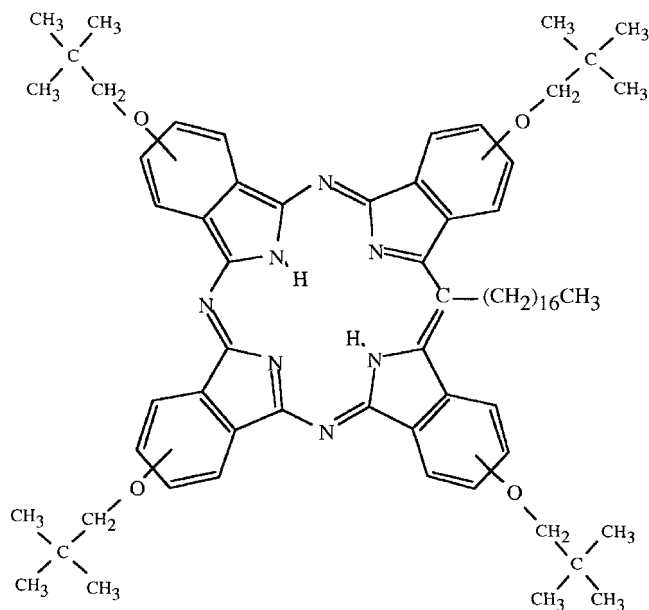
Asymmetrical substitution of the aromatic core is a rarely used method of varying the molecular architecture of a discotic mesogen. To date, asymmetry in phthalocyanine derivatives has been introduced by substitution to an outer benzene ring: mesophases have been reported for a phthalocyanine substituted at the 2,3-positions on the benzene rings with two cyano groups and six long alkyl chains $((CN)_2[CH_3(CH_2)_{11}OCH_2]_6PcH_2)$ [7] and for a phthalocyanine substituted at the 1,4-positions with either one or two hydroxy groups replacing alkyl chains $(HO(C_{10}H_{12})_7PcH_2)$ and $(HO)_2(C_{10}H_{12})_6PcH_2)$ [9]. The asymmetrical substitution of the macrocycles seems to have little effect on the structure of the resulting mesophases when compared with those of the analogous symmetrical compounds. However the temperature

*Author for correspondence.

range of the phase is affected, being increased for the first example, while being decreased to the extent of the formation of a monotropic phase for the bis-hydroxy derivative. The rarely studied tetrabenzotriazaporphyrin (TBTAP) ring system [12] presents the possibility of substitution at one meso-position while maintaining the spectroscopic properties and chemical stability of the phthalocyanine parent material. The present compound, which is based on TBTAP, is unusual both for its asymmetric shape and for the use of short peripheral substituents. It was originally synthesized during research into the development of chemically modified electrodes and its mesomorphic properties were unexpected. From preliminary studies it was proposed that the material formed a lamellar phase [13], which would have been the first time such a structure was observed for a phthalocyanine-like core. In order to understand this proposed structure better, we decided to investigate further the mesomorphic behaviour of this compound, and in the present paper we report a detailed structural characterization of the mesophase based on optical microscopy, DSC, high resolution X-ray scattering and molecular modelling.

2. Experimental

The TBTAP derivative was synthesized and purified using an identical method to that previously described [14]. The TBTAP macrocycle differs from the more common phthalocyanine ring system by the substitution of a methine for a nitrogen at one meso-position. The TBTAP core was substituted with a single heptadecyl chain at this meso-position and four neopentyl groups statistically distributed around the peripheral benzene rings, as shown below:



Thin film samples of the material were prepared between two untreated glass cover slips and optical textures were observed using an Olympus BH-2 polarizing microscope with a Linkam hot stage and controller (accurate to $\pm 0.1^\circ\text{C}$). Thermographic data were obtained using a Perkin Elmer DSC-7 differential scanning calorimeter using a heating/cooling rate of $10^\circ\text{C min}^{-1}$. Powder X-ray diffraction patterns as a function of temperature were recorded using $\text{K}\alpha_1$ radiation from an INEL generator and a CPS 120 curved position-sensitive gas detector. For selected temperatures, patterns were recorded on film using a Phillips PW-1009 generator. Samples were studied in sealed, 1 mm diameter Lindeman glass capillaries. Molecular dimensions were estimated and structures visualized using Sybyl 5.5 software from Tripos run on a PS390 Evans and Sutherland graphics workstation managed by a MicroVax minicomputer.

3. Results

3.1. Optical studies

When observed using the microscope, the TBTAP derivative was seen to become a highly viscous, birefringent fluid above $\sim 100^\circ\text{C}$. The exact temperature of the transition from the solid to the mesophase was not optically observable due to the high viscosity of the material. On further heating, the birefringent texture was maintained and the sample became less viscous until the transition into the isotropic phase at $\sim 344^\circ\text{C}$. A small amount of decolouration was observed at the edges of the samples due to what was assumed to be an oxidation process. The transition was reversible and on slow cooling from the isotropic phase, the birefringent texture emerged in the form of 'petals' (figure 1(a)) which coalesced to produce a fan-like structure (figure 1(b)). This texture remained on cooling to room temperature.

3.2. Differential scanning calorimetry studies

The DSC trace of a fresh TBTAP sample on heating to 100°C exhibited a single, small, broad peak with an onset at 58°C and an enthalpy of 3.5 J g^{-1} . The sample was cooled from 100°C to -100°C , but no features were observed, and likewise on immediate reheating. When the measurements were repeated several days later, a similar behaviour was observed: a single peak on heating starting at 58°C (3.2 J g^{-1}) and no further features or peaks on subsequent cooling and immediate reheating. Decomposition was observed on taking the bulk sample above 250°C and so it was not feasible to record the transition into the isotropic phase. It is possible that this degradation also occurred throughout the sample during formation of the spontaneous optical textures on cooling from the isotropic phase. With this in mind, the main structural characterization was based on X-ray diffraction studies carried out at $< 200^\circ\text{C}$.

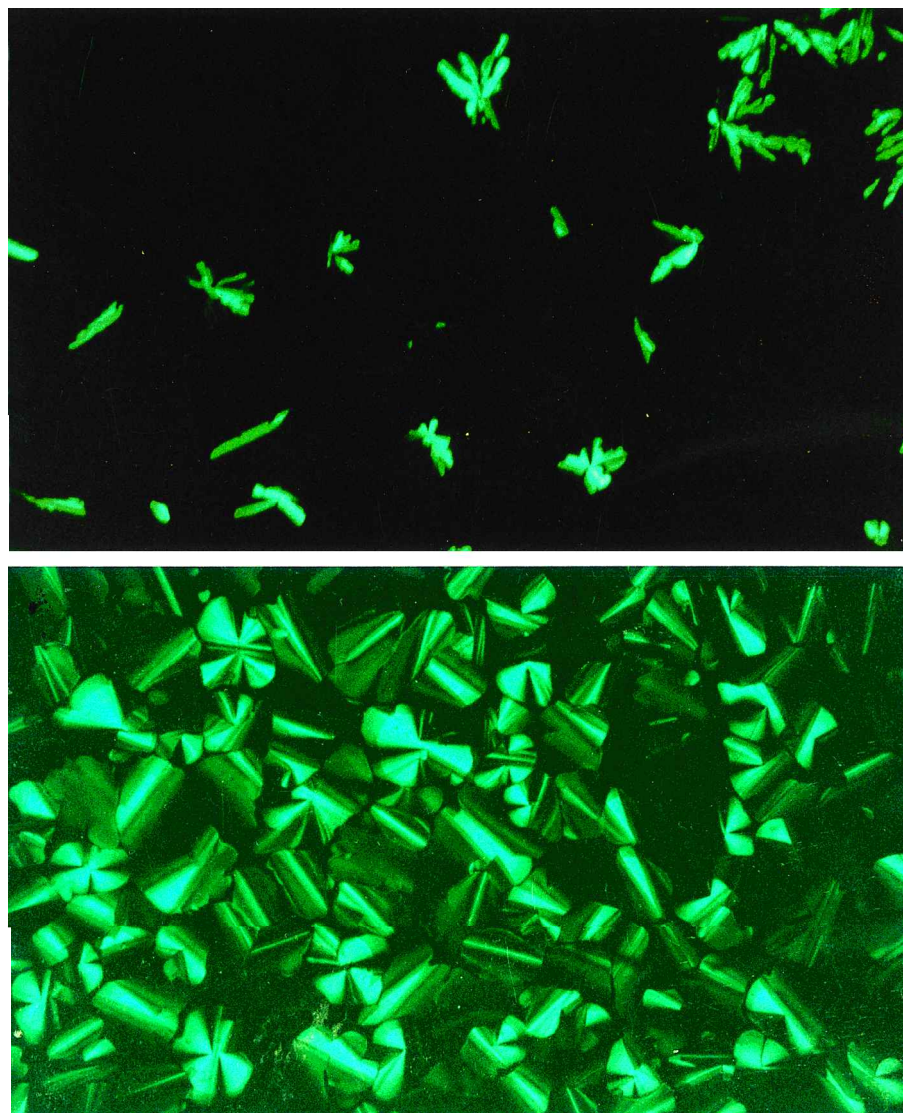


Figure 1. Optical textures of the TBTAP derivative observed between crossed polarizers ($\times 100$): (a) mesophase emerging on cooling from the isotropic phase; (b) birefringent texture maintained to room temperature.

3.3. X-ray studies

X-ray diffraction patterns were recorded at 10°C intervals on cooling from 160°C to 40°C using the Guinier-type camera with gas detector. The pattern obtained at 160°C is shown in figure 2: a sharp Bragg peak is observed at 21.0 \AA and two diffuse bands are seen centred at 5.1 and 3.5 \AA . On cooling, the small angle repeat distance demonstrated a weak temperature dependence down to $\sim 90^\circ\text{C}$ (plotted in figure 3 as calculated hexagonal lattice constant versus temperature). The general outline of the diffraction pattern remained unchanged down to 40°C . In order to obtain greater detail, patterns were recorded using photographic film and longer exposure times. Diffraction patterns were taken on heating at 35 , 55 , 65 , 75 and 90°C . All of the patterns were similar, and a

typical example is shown in figure 4 (75°C). An intense, sharp peak was observed at 20.6 \AA accompanied by faint peaks at 40.5 and 11.9 \AA . In the wide angle region two diffuse bands were seen centred at 5.3 and 3.8 \AA . An additional extremely faint diffuse band centred at $\sim 8.3\text{ \AA}$ was observable below 65°C . Computer modelling gave an estimated molecular diameter of 23 \AA , discounting the contribution from the heptadecyl chain, and the TBTAP core diameter was 13 \AA .

4. Discussion

The TBTAP derivative is a blend of ten regio-isomers due to the statistical distribution of the four peripheral neopentyl groups and thus does not form a perfectly ordered crystalline solid. The small peak in the DSC trace

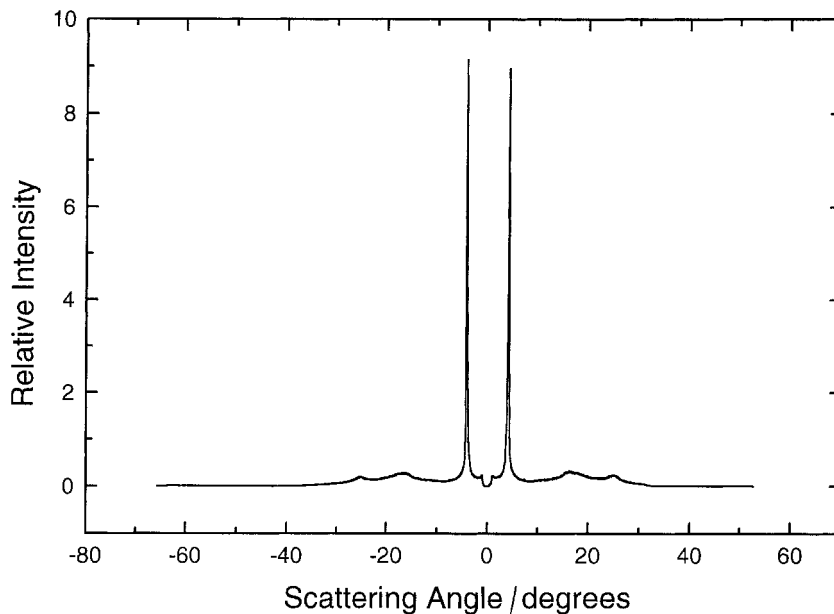


Figure 2. Typical X-ray diffraction pattern obtained for the TBTAP derivative recorded by a position-sensitive gas detector (160°C).

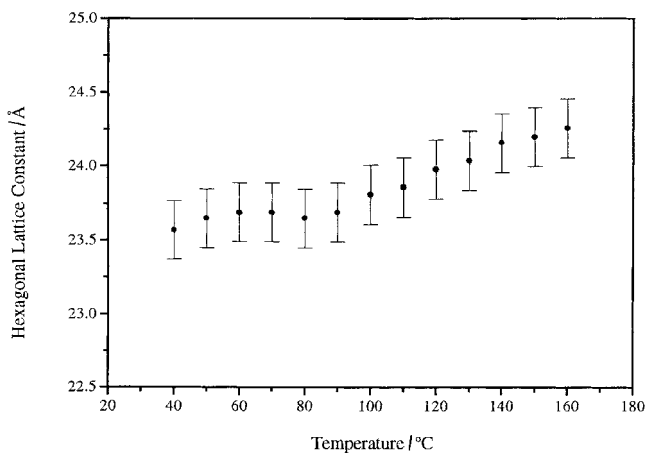


Figure 3. Temperature dependence of the hexagonal lattice parameter of the TBTAP derivative.

at 58°C arises as the result of minimal rearrangement within the material as it moves from the solid into the liquid crystalline phase, and is broadened due to the mixture of isomers present in the sample. The absence of

further features until the re-emergence of the peak demonstrates the existence of extensive supercooling and that the small amount of ordering in the solid phase needed a relaxation period on the time scale of days to develop.

The X-ray diffraction patterns are typical of those observed for columnar phases: the discotic molecules stack coaxially one upon another to form columns of indefinite length, which in turn pack to form a two-dimensional lattice. The 3.5 \AA band arises from the face-to-face packing of the aromatic cores and the 5.0 \AA band from the neopentyl group intermolecular correlation spacing. The diffuse nature of these bands indicates a liquid-like arrangement of the molecules within the columns. The very faint band at 8.3 \AA could be tentatively explained by the development at lower temperatures of locally alkyl rich areas with a correlation distance incommensurate with the spacing of the phthalocyanine cores.

The relative spacings of the small angle Bragg peaks dictate the nature of the 2-D lattice formed by the columns. The reciprocal spacings of the two outer sharp peaks fall in a ratio of $1:3^{1/2}$ demonstrating the existence

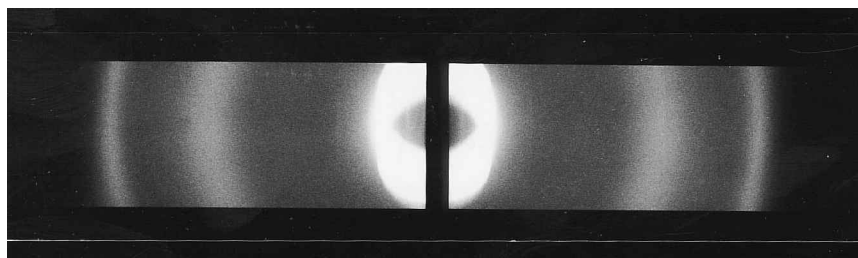


Figure 4. Typical X-ray diffraction pattern obtained for the TBTAP derivative recorded on film (75°C).

of hexagonal packing. The secondary peak is very weak due to the disruption introduced into the structures by the range of regio-isomers and the long alkyl chains present in the material. The hexagonal lattice parameter, a , corresponding to the diffraction repeat distance, d , given by $a = (2/3^{1/2})d$, is 24.3 Å at 160°C. This intercolumnar distance is reasonable when compared with the theoretical molecular diameter calculated for the neopentyl substituted TBTAP (23 Å), and the intercolumnar distance reported (21.4 Å) for a phthalocyanine mesogen peripherally substituted with eight pentoxyalkyl chains [8]. The octapentoxy substitution consists of a slightly larger number of peripheral carbon atoms than the combined tetraneopentyl and heptadecyl chain of the TBTAP derivative, indicating that accommodation of the volume occupied by the unusual substituents of the current compound is feasible in the proposed hexagonal structure.

The faint Bragg peak at 40.5 Å is at approximately twice the spacing of the intense small angle peak, which could have arisen due to diffraction of a $\lambda/2$ component in the X-ray beam, reflected by the monochromator and potentially visible because of the long exposure times necessary to obtain the faint $3^{1/2}$ peak discussed above. To ensure that this was not the case, the measurement was repeated with an aluminium filter ($\sim 100 \mu\text{m}$ thick) which absorbs the λ component more strongly than the $\lambda/2$. The relative intensity of the 40.5 Å peak with respect to the 21.0 Å reflection was preserved, indicating a slight tendency for neighbouring TBTAP molecules to orient themselves in opposite directions (figure 5) in order to allow for the packing of the heptadecyl chain, and resulting in a very weak pseudo-centred rectangular packing.

5. Conclusions

The thermotropic mesophase behaviour of an asymmetrically shaped and highly substituted tetrabenzotriazaporphyrin compound was not expected and most probably occurs due to the existence of numerous regio-isomers within the material which introduce a sufficient degree of disorder to prevent the formation of a crystalline structure. The mesophase formed is not lamellar as initially suspected, but is typical of phthalocyanine derivatives, being stable over a wide temperature range and exhibiting a disordered hexagonal columnar (Col_{hd}) structure. In addition, a tendency towards antiparallel orientation of neighbouring molecules was observed in the form of a weak pseudo-centred rectangular packing.

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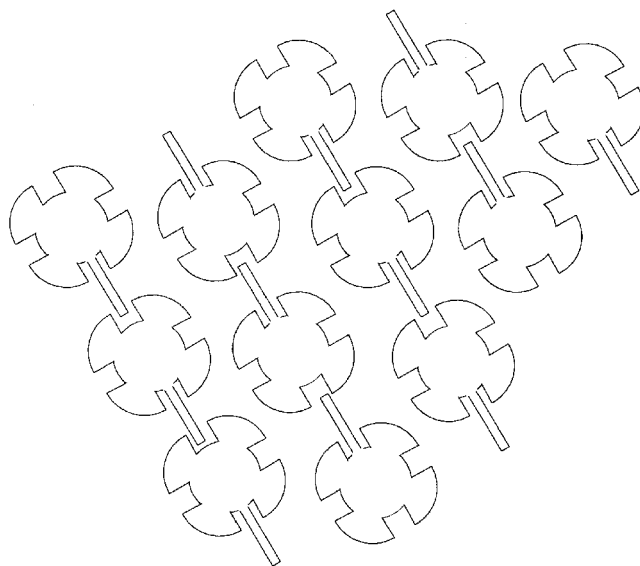


Figure 5. Schematic representation of proposed packing structure with antiparallel orientation of neighbouring molecules. (In reality the packing structure will show a large degree of disorder with only a *weak* tendency to this schematic antiparallel arrangement.)

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