

## X-Ray Crystal Structure of a Mesogenic Octa-substituted Phthalocyanine

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Crystals of 1,4,8,11,15,18,22,25-octahexylphthalocyanine are composed of tilted stacks of molecules with an unexpectedly large separation between the aromatic cores.

X-Ray diffraction studies of phthalocyanines have centred predominantly on the unsubstituted metal-free and metallated derivatives and have provided details of the differences between the more common polymorphic forms.<sup>1,2</sup> In contrast, little is known about the crystal packing for ring-substituted derivatives, especially those which bear six or eight long aliphatic chains. These compounds are of interest because many are thermotropic liquid crystals; on heating they undergo a transition from the crystal state into a discotic columnar mesophase.<sup>3,4</sup> Examples include a number of 1,4,8,11,15,18,22,25-octaalkylphthalocyanines **1**, where the alkyl groups are hexyl or longer.<sup>5,6</sup> This communication reports the crystal structure of the octahexyl compound of this series **1**, R = C<sub>6</sub>H<sub>13</sub>, and is part of an investigation into the molecular packing within crystal phases from which mesophases are formed. To our knowledge the present work constitutes the first X-ray crystal structure determination of a heavily substituted phthalocyanine.

A problem we have met with compounds of series **1** is that they tend to recrystallise as fibrous needles<sup>7</sup> which are difficult to handle for diffraction work. However, recrystallisation of **1**, R = C<sub>6</sub>H<sub>13</sub>, from tetrahydrofuran (THF) afforded small blue plates which proved to be single crystals of rather small dimensions. A preliminary diffraction study on one such crystal using a Siemens R3m/V diffractometer system revealed that the compound crystallises in the triclinic system with one molecule per unit cell. Although it was possible to locate the atoms of the aromatic core, the data were too weak to be of further help. A second crystal of dimensions 0.030 × 0.150 × 0.350 mm was measured on a Rigaku AFC5R diffractometer equipped with a 12 kW rotating anode generator which resulted in a data set consisting of enough observable reflections for complete determination of the structure.<sup>†</sup>

Each unit cell contains one phthalocyanine molecule with an inversion centre (at the centre of gravity of the molecule) relating the two halves, Fig. 1. The packing of these in the lattice is shown in Fig. 2. Six of the alkyl chains are approximately in the plane of the ring with four having their C–C bonds staggered in the plane and two staggered out of the plane. The remaining two alkyl chains act as spacers between molecules in the packing (stack). The shortest distance between planes of phthalocyanine molecules is 8.5 Å with the nearest distance between the centres of the molecules being

9.3 Å. The calculated density of the crystal is 1.121 g cm<sup>-3</sup>, intermediate between that of unsubstituted phthalocyanine, 1.44 g cm<sup>-3</sup>,<sup>9</sup> and long-chain hydrocarbons, ca. 0.78–0.80 g cm<sup>-3</sup>. Despite the apparent free space between the rings, there is no evidence of solvent incorporation; there are no features larger than 0.32 e Å<sup>-3</sup> in the final difference map and the formulation is in good agreement with the microanalytical data.

The tilted columnar stacks depicted in Fig. 2 are unlike those which occur in the α and the thermodynamically more stable β polymorphs of unsubstituted phthalocyanine and its metal(II) analogues.<sup>1,2</sup> Single crystal X-ray diffraction data show that these forms contain tilted stacks within herringbone arrangements. The distances between the planes of the molecules are ca. 3.4 Å. This is very much smaller than 8.5 Å found here and implies a rather weak core–core interaction in the present compound.

At 159 °C, the compound undergoes a transition into a discotic columnar mesophase which had earlier been identified as hexagonal, *i.e.* columnar stacks of cofacial molecules arranged such that a cross section shows a classical two-

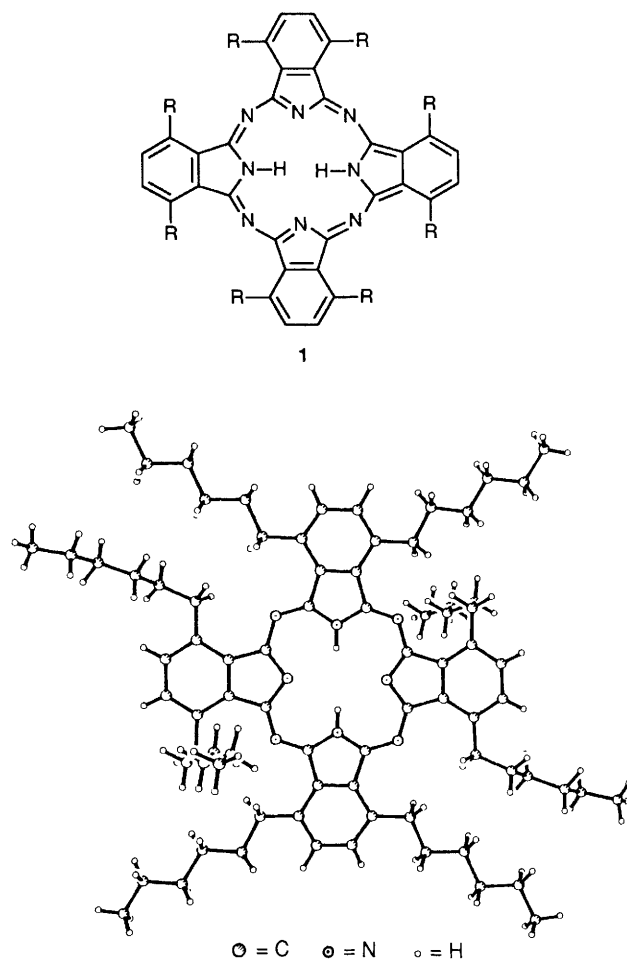
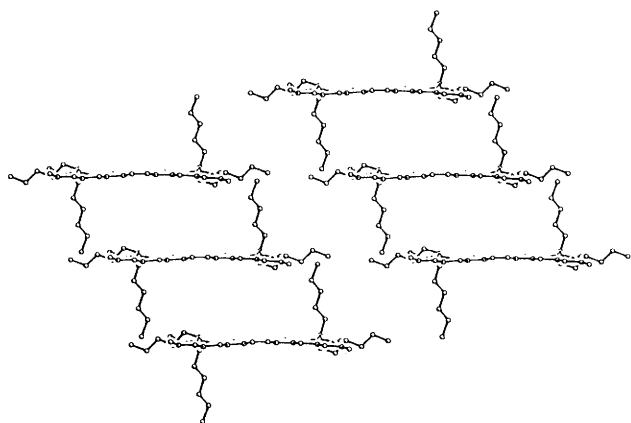


Fig. 1 Representation of the molecular structure of compound **1**, R = C<sub>6</sub>H<sub>13</sub>

<sup>†</sup> Crystal data: C<sub>30</sub>H<sub>114</sub>N<sub>8</sub>, M<sub>r</sub> = 1187.83, triclinic, space group  $P\bar{1}$ ,  $a = 9.2668(9)$ ,  $b = 9.7323(8)$ ,  $c = 19.991(2)$  Å,  $\alpha = 100.964(7)$ ,  $\beta = 91.166(7)$ ,  $\gamma = 95.899(7)^\circ$ ,  $U = 1759.2(8)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.121$  g cm<sup>-3</sup>, Cu-Kα radiation (graphite monochromator),  $\lambda = 1.54178$  Å,  $\mu = 4.62$  cm<sup>-1</sup>,  $F(000) = 650$ , 3105 observed reflections with  $F > 6.0\sigma(F)$ , 5218 independent reflections were collected at 22 °C in an  $\omega$ -2 $\theta$  scan. A semiempirical absorption correction was applied. The structure was solved by direct methods and refined with full-matrix least-squares using the programs in ref. 8. All but the hydrogen atom attached to N(1) were placed in calculated positions. This last hydrogen was located in a difference Fourier map and allowed to refine isotropically. Refinement converged with  $R = 0.089$  and  $R_w = 0.108$ . Max/min peaks in final difference map +0.32/-0.25 e Å<sup>-3</sup>. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Fig. 2** The packing of the phthalocyanine molecules in crystals of **1**,  $R = C_6H_{13}$ , showing the spacing effect of the alkyl chains

dimensional hexagonal lattice symmetry.<sup>5,6</sup> An X-ray diffraction study of the corresponding mesophase exhibited by the octaoctyl homologue **1**,  $R = C_8H_{17}$ , suggested that the distance between molecules within a column is *ca.* 4.4 Å.<sup>6</sup> A similar distance is likely for the present compound. The implication is that upon transition from the crystal into the liquid crystal phase there is a significant increase in core–core interactions which becomes possible once the alkyl groups become mobile and no longer act as spacers. This presumed change in spacing which occurs during the transition can be expected to have a significant effect on properties such as the semiconductivity of the system.

While the present results provide insight into the mechanics of the transition from crystal to the mesophase for the octahexyl compound, they clearly do not preclude other types of packing within crystals of other members of series **1**. Indeed, a preliminary spectroscopic comparison of crystals of the present compound with those of its homologues suggests that there may be at least two types of crystal packing within the series.<sup>10</sup>

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