

X-Ray Crystal Structure of 1,4,8,11,15,18,22,25-Octa-*iso*-pentyloxyphthalocyanine

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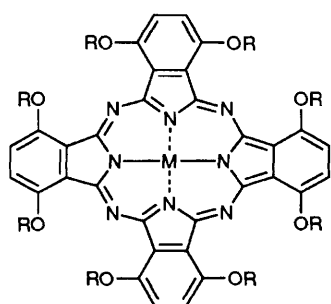
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Crystals of 1,4,8,11,15,18,22,25-octa-*iso*-pentyloxyphthalocyanine are comprised of tilted stacks of molecules, the individual molecules being well separated by the alkoxy chains.

Unsubstituted phthalocyanine, Pc, and its first row transition metal derivatives show a rich polymorphism which has been much studied,¹ not least because different molecular packings within the crystal state lead to variations in important properties such as the optical absorption envelope,² photoconductivity,³ and the modulation of conductivity on exposure to oxidants, *e.g.* NO₂ gas.⁴ Over the last ten years or so, considerable attention has centred on developing novel, multi-substituted derivatives.⁵ Substituents modify the properties of the ring system in a number of ways. They affect the energy of the visible region electronic transitions, can encourage liquid crystal behaviour,⁶ and may confer solubility in specified media. Importantly, they might lead to new molecular assemblies in the solid state which will themselves exhibit a new range of solid-state properties. As yet, little is known about the way these more complex molecules pack in the crystal state. Indeed, our recent X-ray structure determination of the molecular packing in a single crystal of 1,4,8,11,15,18,22,25-octahexylphthalocyanine appears to be the first for a heavily substituted derivative.⁷

In the present paper we have investigated the diffraction from crystals of three further octa-substituted derivatives in which the side chains are alkoxy groups. Measurements were

performed using a Siemens R3m/V diffractometer system. 1,4,8,11,15,18,22,25-Octapentyloxyphthalocyaninato nickel, **1**, contains the same number of linking atoms in the side chain as the compound examined previously. It recrystallises from MeOH-THF (tetrahydrofuran) to form cuboids. However, no diffraction is observed from these crystals implying that there is no long-range ordering within the solid state. The longer chain derivative, **2**, showed some diffraction but this was very weak. The third compound investigated, the octa-*iso*-pentyloxy derivative, **3**, was recrystallised from MeOH-THF to give dark-green needles, m.p. 201 °C. A full diffraction pattern was



- 1; R = (CH₂)₄Me, M = Ni
 2; R = (CH₂)₆Me, M = H,H
 3; R = (CH₂)₂CHMe₂, M = H,H

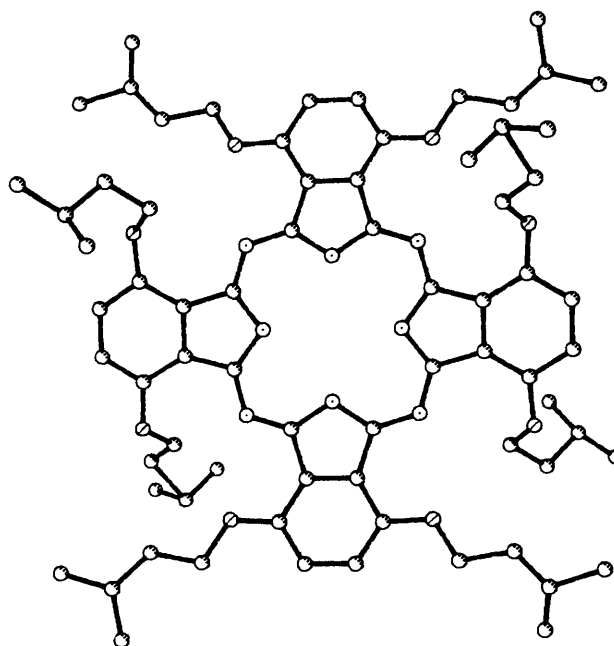


Fig. 1 Representation of the molecular structure of 1,4,8,11,15,18,22,25-octa-*iso*-pentyloxyphthalocyanine, **3**. ⊙ = C, ⊖ = N, ⊘ = O.

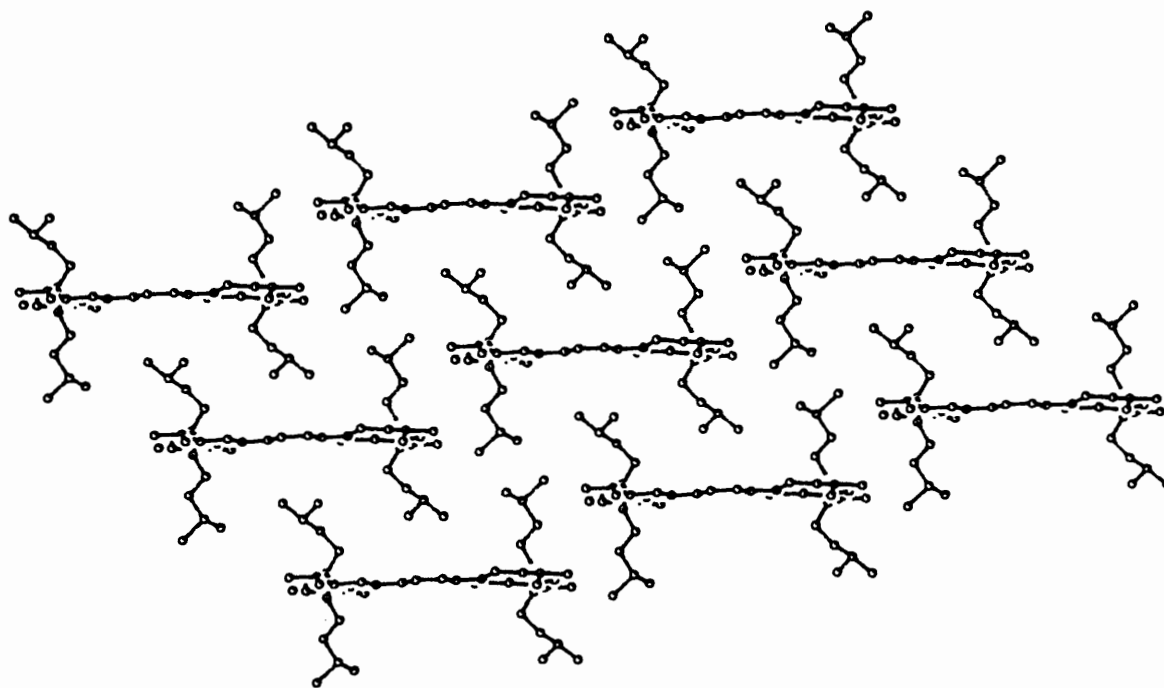


Fig. 2 The packing of the phthalocyanine molecules in crystals of 3

collected from a crystal of dimensions $0.18 \times 0.20 \times 0.60$ mm enabling the structure to be solved.[†]

Fig. 1 shows the molecule in the unit cell. Four chains are approximately in the plane of the ring and four approximately orthogonal to it. There is an inversion centre (at the centre of gravity of the molecule) relating the two halves of the molecule. The packing of the molecules in the lattice is shown in Fig. 2. The molecules are arranged in offset stacks with the sidechains acting as spacers between them. The shortest distance between planes of phthalocyanine molecules within a stack is *ca.* 8.5 Å and the distance between the centres of the molecules is 11.12 Å. The nearest approach of a terminal carbon of the spacer sidechain to the centre of the next ring in the stack is *ca.* 3.6 Å. The angle of tilt of the plane of the molecules from the column axis is of the order of 50°. The results contrast with structural data obtained for the common α and β forms of unsubstituted phthalocyanines where the molecules stack in 'herring bone' assemblies with an inter-ring distance of 3.4 Å.⁴ They also contrast with those obtained for 1,4,8,11,15,18,22,25-octahexylphthalocyanine.⁷ While the inter-ring spacings in the columns for the latter are also *ca.* 8.5 Å, the columns are less tilted, only two of the sidechains are out of the plane of the ring, and the aromatic cores of molecules in adjacent stacks are arranged in the same plane.

The lack of long-range order for the straight-chain derivatives 1 and 2 provides a further, and more dramatic,

demonstration that molecular packing in 1,4,8,11,15,18,22,25-octa-substituted phthalocyanines is critically dependent upon the nature of the substituent group. This dependence appears to be a consequence of the substituents forcing the aromatic cores far apart, so minimising ordering effects resulting from core-core interactions. Interestingly, the apparent beneficial effect of *iso*-pentyloxy groups on crystal state packing among alkoxy substituted Pcs appears to be mirrored in Langmuir-Blodgett film deposition of these compounds. *iso*-Pentyloxy derivatives show superior deposition and give more even films than the straight chain derivatives.⁸ However, it would be imprudent to pursue this relationship further at this stage because the details of the molecular organisation within the films has yet to be firmly established.

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References

- 1 F. H. Moser and A. L. Thomas, *The Phthalocyanines*, CRC Press Inc. Boca Raton, Florida, vol. 1, 1983.
- 2 M. J. Stillman and T. Nyokong, in *Phthalocyanines—Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989, p. 133.
- 3 P. Gregory, *High-Technology Applications of Organic Colorants*, Plenum Press, New York, 1991.
- 4 A. W. Snow and W. R. Barger, in *Phthalocyanines—Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989, p. 341.
- 5 C. C. Leznoff, in *Phthalocyanines—Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989, p. 1.
- 6 J. Simon, in *Phthalocyanines—Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, vol. 2, 1993.
- 7 I. Chambrier, M. J. Cook, M. Helliwell and A. K. Powell, *J. Chem. Spec. Chem., Commun.*, 1992, 444.
- 8 M. J. Cook, J. McMurdo, D. A. Miles, R. H. Poynter, J. M. Simmons and K. Welford, manuscript in preparation.

[†] Crystal data: $C_{72}H_{98}N_8O_8$, $M_r = 1203.6$, triclinic, space group, $P\bar{1}$, $a = 10.665(4)$, $b = 11.108(4)$, $c = 15.597(6)$ Å, $\alpha = 73.08(3)$, $\beta = 87.16(3)$, $\gamma = 87.93(3)^\circ$, $U = 1765.3(12)$ Å³, $Z = 1$, $D_c = 1.132$ g cm⁻³, Mo-K α radiation (graphite monochromator), $\lambda = 0.71073$ Å, $\mu = 0.069$ mm⁻¹, $F(000) = 650$, 2899 observed reflections with $F > 4\sigma(F)$, 6249 independent reflections were collected at 23 °C in an ω scan. No absorption correction was applied. The structure was solved by direct methods and refined with full matrix least-squares analysis using the SHELXTL PLUS programs. All but the hydrogen atom attached to N(1) were placed in calculated positions. This last hydrogen was located by difference Fourier and allowed to refine isotropically. Refinement converged with $R = 8.40$ and $wR = 11.77\%$. 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.