X-Ray Crystal Structures of Bridged Porphyrins

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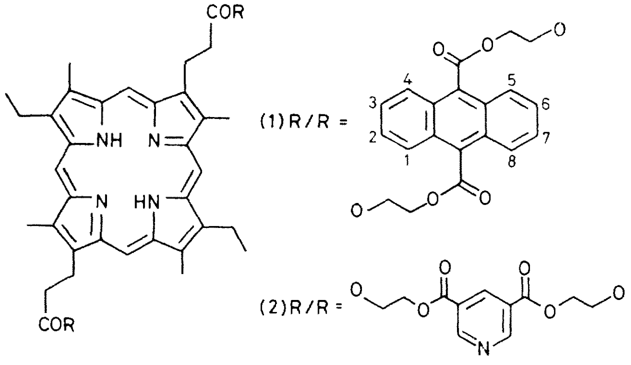
Summary *X*-Ray crystal structures of an anthracene-bridged porphyrin and of a pyridine-bridged analogue show 'off-set' conformations with close van der Waals stacking of the bridging groups on the porphyrin macrocycles.

THE synthesis of model systems has yielded important information which broadens chemical understanding of natural haem proteins such as haemoglobin and myoglobin [1–3] The aim of work in Cambridge is to synthesize a set of related models which differ in the size of the cavity over the porphyrin plane and in the nature and availability of the basic ligand [3] It is essential to know accurately the dimensions and shapes of the molecules so produced and *X*-ray analysis is thus a necessary parallel study We report here structure solutions for two porphyrins, one with an anthracene bridge (**1**) and one bridged by a pyridine ligand (**2**) The syntheses followed procedures outlined earlier[3,4] and the products were crystallized from dichloromethane–hexane



Crystal data anthracene-bridged porphyrin (**1**) $C_{54}H_{52}N_4O_8(0{\cdot}5\ CH_2Cl_2)$, monoclinic, space group $C2/c$, a = 21·283(3), b = 16 651(2), c = 27·450(4) Å, β = 106·71(1)°, Z = 8 Cell constants and intensities measured on a diffractometer The structure was solved by the direct methods (program SHELX) and refined using 3998 reflexions with $F>3\sigma(F)$ The R factor at the end of the anisotropic refinement, with the porphyrin nucleus isotropic, was 8% Values of the bond lengths and angles were as expected §

Pyridine-bridged porphyrin (**2**) $C_{45}H_{47}N_5O_8(1\ 5\ CH_2Cl_2)$, triclinic, space group $P\bar{1}$, a = 15·571(2), b = 16 987(2), c = 9 982(1) Å, α = 87 35(1), β = 97·80(1), γ = 117·32(1)°, Z = 2 (diffractometer data) The structure was solved, with difficulty, using direct methods Isotropic least squares refinement (anisotropic for Cl) of 5386 reflexions with $F>3\sigma(F)$ gave R = 15% Further refinement was not attempted since the difference map indicated severe disordering of the solvent molecule and the ester chains of the bridging ligand §

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§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW Any request should be accompanied by the full literature citation for this communication

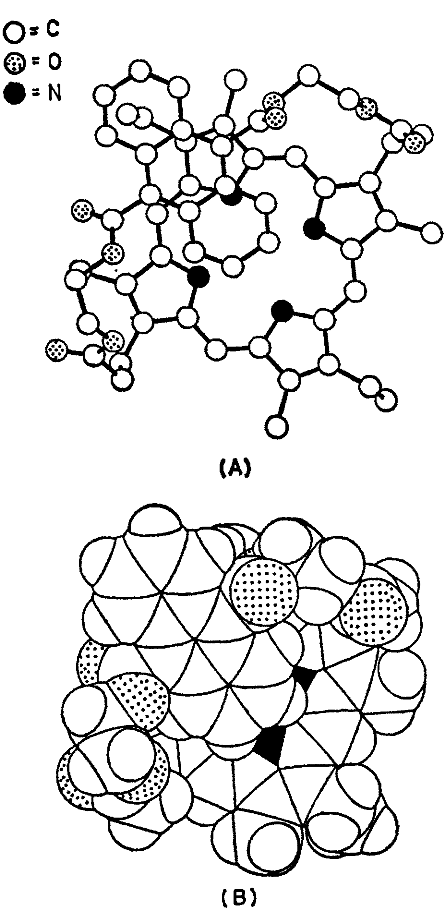

FIGURE 1. Structure of the anthracene-bridged porphyrin (**1**): (A) a view of the molecule perpendicular to the plane of the porphyrin nucleus; (B) space-filling diagram of the same view with the hydrogen atoms included.

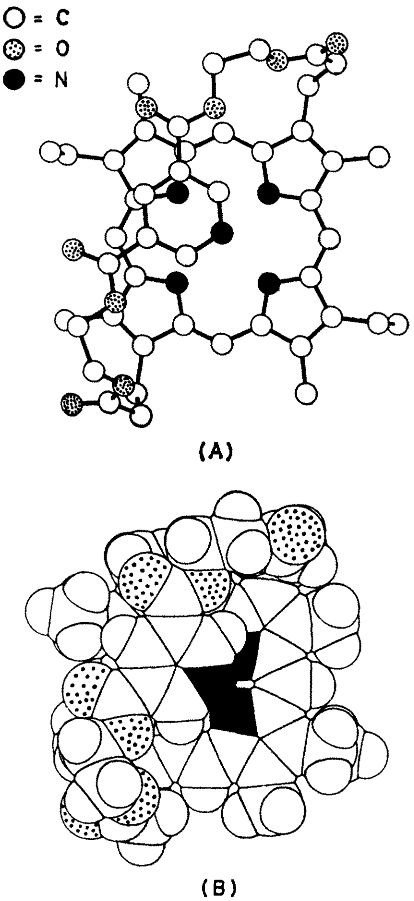

FIGURE 2. Structure of the pyridine-bridged porphyrin (**2**): (A) a view of the molecule perpendicular to the porphyrin nucleus; (B) space-filling diagram of the same view with the hydrogen atoms included.

The structure of (**1**) is shown in Figure 1. The anthracene ring is in an off-set position and inclined by 18·4(1)° to the mean plane of the porphyrin nucleus. The two carbon atoms at one end of the anthracene ring are in relatively close contact with the porphyrin at distances of 2·89(1) and 2·72(1) Å from the mean plane. The other end is within 3·4(1) Å of one ethyl group.

Figures 2 (A) and (B) illustrate structure (**2**). The pyridyl ligand is also displaced from the symmetric position, leaving the centre of the porphyrin ring partially exposed. The inclination of the pyridyl ring is 6·0(1)° and the distances of the atoms from the plane of the porphyrin range from 3·2 Å (for N) to 3·5 Å. There is thus, in both structures, close van der Waals stacking of the asymmetrically disposed bridging groups with no free cavity at the centre of the molecule. The two structures have additional interest in that they represent, in analogous form, the two 'halves' of the recently described doubly bridged oxygen carrier.[3]

N.m.r. spectroscopy shows that the 'off-set' conformation found in the crystal for (**1**) does not remain fixed in solution; only two sets of double doublets were observed for the anthracene protons.[3] The bridge is thus sufficiently mobile in solution for the anthracene protons at positions 1, 4, 5, and 8 to be equivalent and similarly for the protons at 2, 3, 6, and 7. It seems therefore that in solution the anthracene slides to and fro keeping one of its faces always near the upper face of the porphyrin.

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