

Interwoven hydrogen-bonded network assembly and supramolecular isomerism of *meso*-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin as its dimethylformamide solvate

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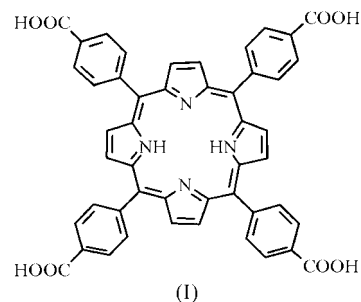
Molecules of the title compound, porphyrin-5⁴,10⁴,15⁴,20⁴-tetrabenzoic acid, C₄₈H₃₀N₄O₈, lie on sites of *2/m* symmetry in the space group *Cmca*. The crystals consist of doubly interwoven two-dimensional supramolecular arrays sustained by multiple (COOH)₂ cyclic dimeric hydrogen bonds, each molecule of the porphyrin-tetrabenzoic acid coordinating to four neighbouring species. This structure, which encloses substantial spaces occupied by disordered dimethylformamide solvent molecules, represents yet another supramolecular isomer of this porphyrin.

Comment

The supramolecular chemistry of the title compound, (I), has been widely studied in recent years in an effort to formulate network and framework solids (George & Goldberg, 2006; George *et al.*, 2006; Goldberg, 2005, and references therein; Diskin-Posner & Goldberg, 1999; Dastidar *et al.*, 1996). Compound (I) provides a classic example of an organic moiety with multiple complementary terminal functional groups directed in four diverging directions of the equatorial molecular plane that exhibit a high propensity for self-assembling into hydrogen-bonded two-dimensional nets. One of the possible interaction modes involves association of every porphyrin unit with four different neighbouring species *via* four head-to-head (COOH)₂ cyclic dimeric associations. This leads to the formation of quadrangular grid arrays with large pores and varying shapes, to be filled during the crystallization process either by occlusion of another guest/solvent component to avoid interweaving and allow a stacked organization of these arrays, or by their self-interpenetration.

The different modes of the self-assembly of (I) (George & Goldberg, 2006; George *et al.*, 2006; Diskin-Posner & Goldberg, 1999) represent a phenomenon known as supramolecular isomerism of the conformation and catenane types

(Moulton & Zaworotko, 2001). Fig. 1 shows the molecular structure of (I) (as observed in this study), which resides on a



special position of site symmetry *2/m*. The supramolecular assembly of (I) into flat grid arrays sustained by co-operative (COOH)₂-type four-point hydrogen bonding is illustrated in Fig. 2. Every molecule of the tetra-acid effectively connects to four neighbouring species, being involved in eight nearly linear O—H...O interactions at O...O = 2.626 (2) Å.

Within the two-dimensional supramolecular assembly there are nearly square spaces with dimensions *ca* 18 × 18 Å² between the van der Waals surfaces. The crystalline architecture involves double interpenetration of these networks partly to fill the empty space (Fig. 3). The remaining voids between these hydrogen-bonded networks are occupied by molecules of the dimethylformamide solvent, which could not, however, be modelled as discrete atoms.

This structure represents a catenane-type supramolecular isomer of other architectures of (I) observed earlier (George

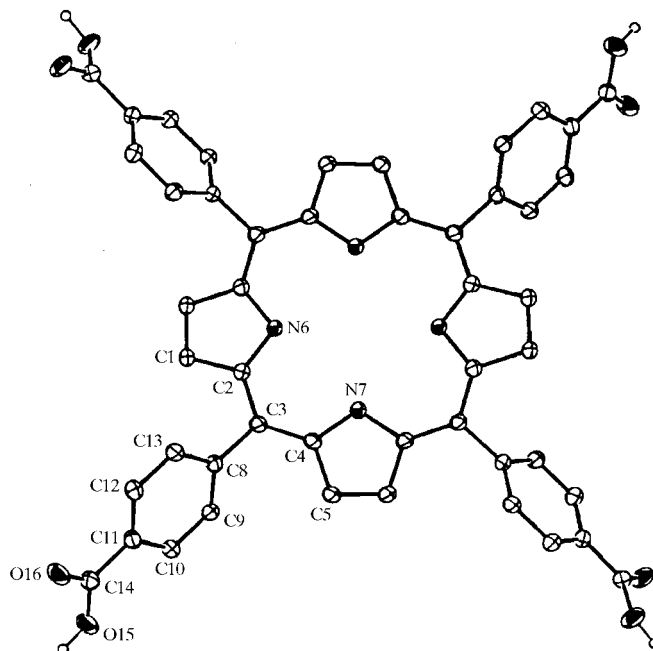


Figure 1

The molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K. The molecule resides on a special *2/m* position and the asymmetric unit consists of only one quarter of the molecule. H atoms have been omitted, except those of the carboxyl groups.

& Goldberg, 2006; Diskin-Posner & Goldberg, 1999). In the latter, the supramolecular networking of (I) exhibits the same interporphyrin connectivity *via* cyclic dimeric hydrogen-bond synthons, but the open networks form offset stacks one on top of the other. It also represents a conformation-type supramolecular isomer, with differently shaped grids within the individual layers. Thus, the networks in this study represent a regular nearly square grid with a van der Waals width of about 18 Å. In another structure with similarly doubly interpenetrating networks of (I), a rhomboid grid with van der Waals width of about only 16 Å was observed (George *et al.*, 2006). On the other hand, in yet another non-interpenetrating structure of network arrays of the porphyrin tetra-acid, the

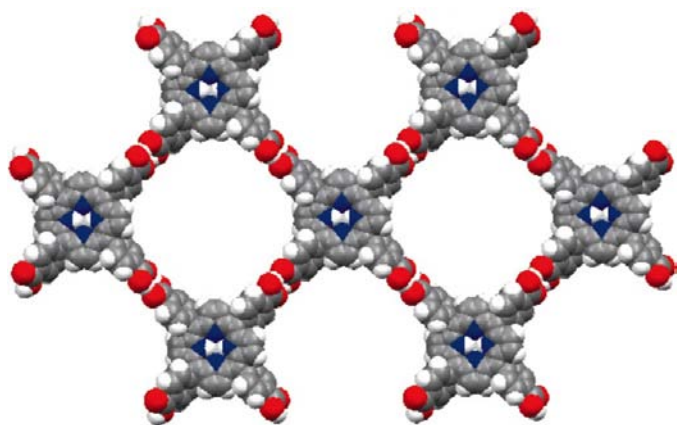


Figure 2
Space-filling illustration of the supramolecular assembly of (I) into two-dimensional networks by co-operative (COOH)₂ hydrogen bonding in the four lateral directions of the porphyrin unit.

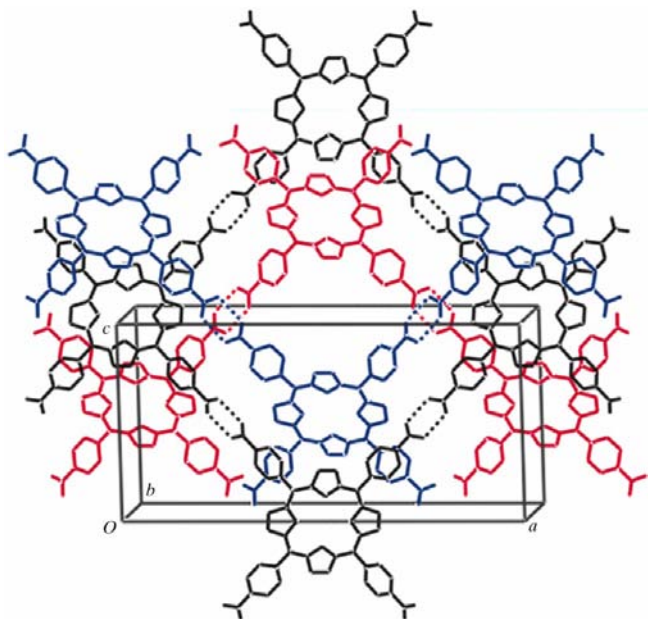


Figure 3
The crystalline architecture of (I), viewed approximately down the *b* axis, exhibiting the double interpenetration of the porphyrin networks (stick illustration; H atoms omitted for clarity). The cyclic dimeric (COOH)₂ hydrogen bonds are indicated by dotted lines.

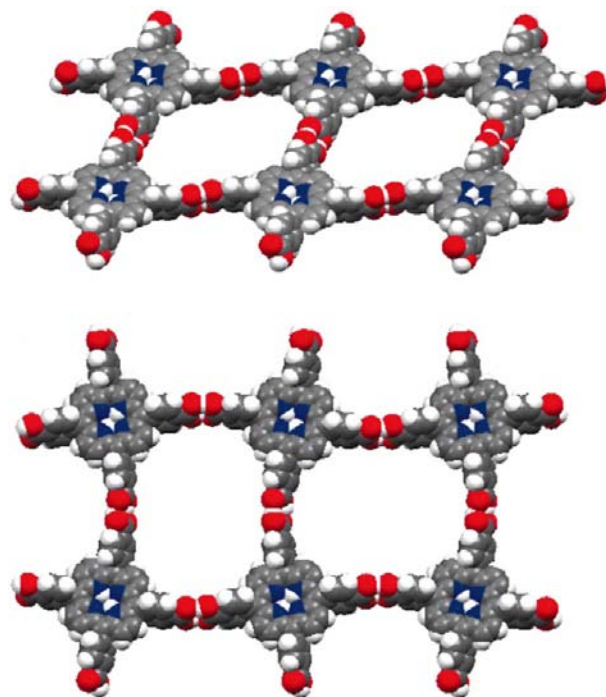


Figure 4
Two other conformational isomers of the network grid of the porphyrin tetra-acid, as observed in previous investigations (George & Goldberg, 2006; George *et al.*, 2006).

supramolecular networks were found to be characterized by a distorted grid with alternating spacing of about 15 and 20 Å (George & Goldberg, 2006). The previously observed conformational isomers of the grid networks are shown in Fig. 4.

The various distortions could be associated with the tendency to minimize the interporphyrin void space in such hydrogen-bonded networks. The supramolecular isomerism discussed above resembles to some extent the appearance of isomeric interwoven and non-interwoven supramolecular hexagonal networks in solids of benzene-1,3,5-tricarboxylic acid (Moulton & Zaworotko, 2001; Herbstein, 1987).

Experimental

Crystals of (I) were obtained accidentally while trying to react the free base porphyrin tetra-acid with Gd³⁺ ions in the presence of dimethylformamide in an effort to prepare the corresponding metal-organic framework material (all reactants are commercially available). Single crystals were obtained by recrystallization from dimethylformamide.

Crystal data

C ₄₈ H ₃₀ N ₄ O ₈	<i>V</i> = 4048.3 (5) Å ³
<i>M_r</i> = 790.76	<i>Z</i> = 4
Orthorhombic, <i>Cmca</i>	Mo <i>K</i> α radiation
<i>a</i> = 31.0164 (3) Å	<i>μ</i> = 0.09 mm ⁻¹
<i>b</i> = 8.5897 (11) Å	<i>T</i> = 110 (2) K
<i>c</i> = 15.1952 (6) Å	0.50 × 0.25 × 0.02 mm

Data collection

Nonius KappaCCD area-detector	2033 independent reflections
diffractometer	1653 reflections with <i>I</i> > 2σ(<i>I</i>)
15184 measured reflections	<i>R</i> _{int} = 0.072

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.138$	
$S = 1.13$	
2033 reflections	$\Delta\rho_{\max} = 0.61 \text{ e } \text{\AA}^{-3}$
141 parameters	$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O15-H15\cdots O16^i$	0.94 (3)	1.69 (3)	2.626 (2)	176 (3)

Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.

H atoms bound to C and N atoms were located in calculated positions and constrained to ride on their parent atoms, with $N-H = 0.88 \text{ \AA}$ and $C-H = 0.95 \text{ \AA}$, and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C,N)$. The inner pyrrole H atoms are disordered between the four N-atom sites. H atoms attached to O atoms were located in a difference Fourier map and their parameters were allowed to refine freely; $O-H = 0.94 (3) \text{ \AA}$. The porphyrin molecules reside on special positions of $2/m$ symmetry at $(0, 0, \frac{1}{2})$. The solvent molecule is disordered about a similar site at $(0, \frac{1}{2}, \frac{1}{2})$, but it could not be reliably modelled as discrete atoms. Correspondingly, the contribution of the solvent was subtracted from the diffraction data using the SQUEEZE procedure in PLATON (Spek, 2003). The solvent-accessible voids were estimated to be 487 \AA^3 , 12% of the unit-cell volume. The residual electron-density count was assessed as 132 electrons per unit cell, which is consistent with nearly four molecules of dimethylformamide solvent. The maximum residual electron density is located at the inversion centre in the porphyrin unit, 1.16 \AA from atom H6 and 1.23 \AA from atom H7.

Data collection: COLLECT (Nonius, 1999); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: DENZO; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPIII (Burnett & Johnson, 1996) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3109). Services for accessing these data are described at the back of the journal.

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