JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2000; **13:** 382–387

Solid-state supramolecular chemistry of porphyrins. Hydrogen-bonded networks and porous crystals of *meso*-tetra[4-(3,5-diaminotriazino)phenyl]porphyrin

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Received 3 March 2000; revised 23 March 2000; accepted 24 March 2000

ABSTRACT: Tesselation of new porphyrin-based network motifs was demonstrated in crystals by incorporation of the diaminotriazine functions in the molecular building blocks. The title compound was synthesized and successfully applied in the construction of a uniquely structured solid which consists of flat multiporphyrin networks with very large voids, 2.2 × 2.2 nm^2. These assemblies mutually interpenetrate each other, yielding a spectacular concatenated arrangement sustained in three dimensions by cooperative hydrogen bonding. The resulting multiporphyrin architecture resembles a molecular-sieve material, having 0.6 nm wide channels which propagate through the crystal and are accessible to other molecules. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: crystal engineering; porphyrin networks; supramolecular chemistry; nanoporous solids

INTRODUCTION

Supramolecular synthesis has been widely used in recent years for the fabrication of new molecular devices, nano structures and porous solids.[1] The rigid and thermally stable tetraarylporphyrin building blocks have played a major role in this respect in view of their unique photoelectronic and catalytic features and the potential utility of multiporphyrin architectures as sieve materials, molecular sensors and heterogeneous catalysts (for recent reviews on non-covalent assembly of porphyrin arrays and their potential applications, see Ref. 2). The synthetic feasibility and the diverse molecular recognition features that can be readily incorporated into the porphyrin species make them very attractive in this type of chemistry. We have described recently several successful designs of porphyrin-based molecular sieve type structures by non-covalent bonds,[3] using well established principles of supramolecular self-assembly in solids.[4] As part of this extensive crystal engineering effort of porous multiporphyrin architectures, we focused in the present study on the *meso*-tetra[4-(3,5-diaminotriazino)phenyl]-porphyrin framework (Fig. 1). This compound has a rigid square geometry and contains symmetrically displaced polar recognition sites at the peripheral positions of the phenyl rings for lateral self-complementary intermolecular association through multiple hydrogen bonds. Yet it is considerably bulkier, and it contains more hydrogen bonding sites, than the previously studied tetra(4-amidophenyl)porphyrin and tetra(4-carboxyphenyl)porphyrin analogues.[3a–c] This may lead to more extended networked materials with larger interporphyrin void volumes than produced before.[3] The diaminotriazine element of molecular recognition has been previously utilized in the fabrication of porous hydrogen-bonded networks with remarkable structural integrity from simple building blocks.[5] In this work it was incorporated into the considerably wider tetraphenylporphyrin frameworks and successfully applied for the first time to the construction of porphyrin-based networks with intermolecular pores of nanometric dimensions.

RESULTS AND DISCUSSION

Synthesis

The free-base tetra(*p*-3,5-diaminotriazine) derivative of 5,10,15,20-tetraphenylporphyrin (*p*-triazine-TPP, **1**) was synthesized by treating the known nitrile tetra(4-cyanophenyl)porphyrin with dicyandiamide[6] (for related conversions of nitriles into 2,4-diaminotriazines, see ref. 7; limited solubility of tetra(*p*-cyanophenyl)porphyrin in most organic solvents necessitates the use of DMSO as solvent; excess use of dicyandiamide is essential for a successful and complete reaction). A 300 mg (0.42 mmol) amount of the latter was dissolved in 30 ml of

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Contract/grant sponsor: Israel Science Foundation.

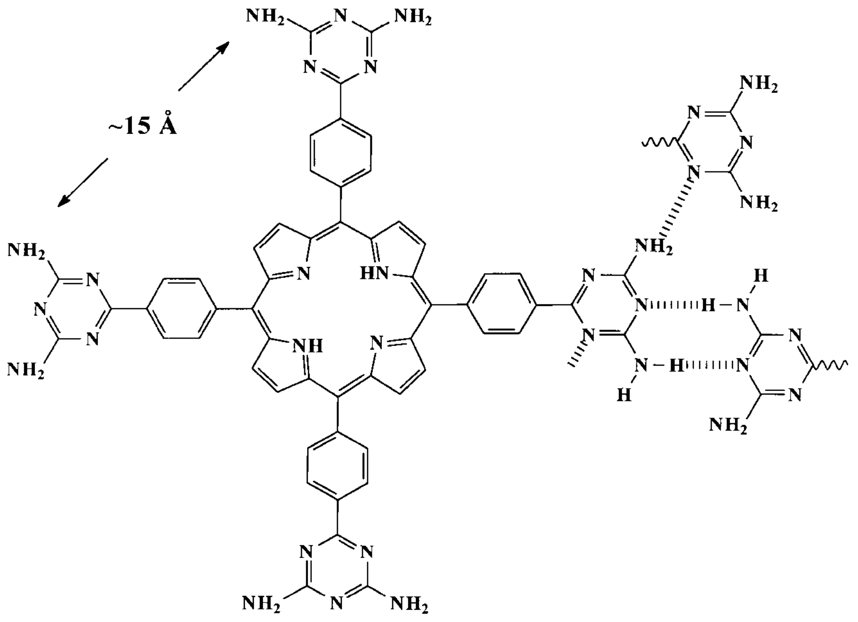

Figure 1. Schematic illustration of the square (approximately 15 × 15 Å^2) flat porphyrin building block **1**. The hydrogen bonding modes of the diaminotriazine substituents to neighboring porphyrin units in the present structure is marked as well by dashed lines

DMSO, then 353.1 mg (4.2 mmol) of dicyanamide were added, stirring the resulting solution at 75–80 °C. Next, 47 mg (0.84 mmol) of KOH dissolved in 10 ml of isopropyl alcohol were added slowly over a period of 15–20 min and the solution was refluxed for 48 h. The precipitate which formed after cooling to room temperature and adding cold water was filtered and thoroughly washed with water. The product was air dried and then dried under vaccum (the yield varied between the different batches within 85–90%). It was found to be only moderately soluble in DMF and DMSO.

UV (DMF): λ_{max} 421, 517, 551, 592, 647. ^{1}H NMR (DMSO-d_6, 298 K): δ 8.93 (s, 8H), 8.71 (d, 8H, ^3J = 8.03), 8.34 (d, 8H, ^3J = 7.83), 6.92 (br s, 16H, NH_2), 2.87 (br s, 2H, NH). MALDI TOF-MS: calculated for $C_{56}H_{42}N_{24}$ $[MH]^+$ 1052.12, observed 1053.98. The isolated product was treated with $Zn(OAc)_2 \cdot H_2O$ to yield the metallated porphyrin compound (Zn-**1**).

Crystal structure analysis

Efforts to obtain sizeable single crystals suitable for x-ray diffraction studies from either the free base or the metallated porphyrin were hampered by the low solubility of these compounds in most of common solvents, and also by the need to incorporate during crystallization a large amount of solvent into the

Table 1. Hydrogen bonding geometry[a]

Intermolecular donor ··· acceptor bonds within the porphyrin networks:			
N26···N37 (at $-x+1/2, y+1/2, z-1$)	3.004(4) Å	N—H···N	157°
N41···N23 ($-x+1/2, y-1/2, z+1$)	3.038(4) Å	N—H···N	164°
Intermolecular donor···acceptor bonds between porphyrin networks:			
N27···N35 ($x, y, z-1$)	3.004(5) Å	N—H···N	143°
N40···N25 ($x, y, z+1$)	3.081(5) Å	N—H···N	149°
Porphyrin–solvent and solvent–solvent donor···acceptor bonds:			
N26···O44 ($-x+1/2, y+1/2, z$)	2.930(5) Å	N—H···O	137°
N27···O43 ($x, y, z-1$)	2.845(4) Å	N—H···O	155°
N40···O44 ($x, y, z+1$)	2.997(5) Å	N—H···O	164°
N41···O49 ($-x+1/2, -y+1/2, z+1/2$)	3.124(7) Å	N—H···O	168°
O43···N21 ($x, 1-y, z+1/2$)	2.905(4) Å	O—H···N	179°
O43···O49 ($x, 1-y, z+1/2$)	2.605(6) Å	O—H···O	170°

[a] Labels N21, N23, N25 and N35, N37, N39 represent the sp^2 nitrogen sites in the two crystallographically independent triazine rings; N26, N27 and N40, N41 represent the corresponding—NH_2 substituents on each ring; O43 represents a molecule of water; O44, N46 and O49, N51 represent the H-binding sites of the two resolved molecules of DMF, respectively.

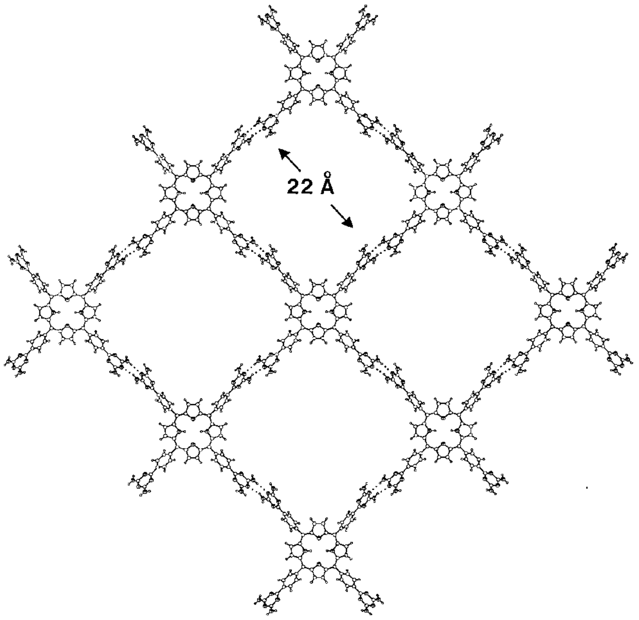

Figure 2. Supramolecular networks of **1** sustained by multiple hydrogen bonds (dotted lines), which extend equatorially, parallel to the porphyrin plane. The porphyrin units located across the square voids relate to each other by lattice translation either along *a* or along $b + 2c$. The distance between opposite van der Waals walls of the interporphyrin void space is about 22 Å

interporphyrin voids of the crystal lattice. As a result, crystals could be grown only from a mixture of DMF and THF, and most of them exhibited large mosaicity and diffracted poorly. Crystals of **1**, Zn-**1** and a mixture of **1** and Zn-**1** were found to be isomorphous by showing nearly identical unit cell and space symmetry. The least mosaic and best diffracting crystals were subjected to a detailed crystallographic analysis. The diffraction data were collected on a KappaCCD diffractometer system, using Mo Kα ($\lambda = 0.7107$ Å) radiation.

Crystal data. $[(C_{56}H_{42}N_{24}Zn_{0.36})\cdot 2(H_2O)\cdot(C_3H_7NO)_x]$: orthorhombic, space group $Cmc2_1$, $a = 38.559(1)$, $b = 15.807(2)$, $c = 16.842(1)$ Å, $V = 10265(1)$ Å^3, $Z = 4$, $T = 120$ K, 8806 unique reflections ($2\theta_{\max} = 51.2°$). For $x = 7$ (see below), formula weight 1622.4, $D_{\text{calc}} = 1.050$ g cm^{-3}, μ(Mo Kα) = 0.15 mm^{-1}. This crystallographic refinement converged at $R1 = 0.142$ for 6713 reflections with $F > 4\sigma(F)$, $R1 = 0.16$ and $wR2 = 0.38$ for all the data. The porphyrin molecules are located on, and are oriented perpendicular to, mirror planes of crystallographic symmetry. Two molecules of DMF and one molecule of water H-bonded to the 3,5-diaminotriazine groups were well resolved. The remaining solvent molecules included within the channel voids of the crystal lattice were found to be heavily disordered. Correspondingly, their structure could not be modeled and could not be properly accounted for in the structure factor calculations. Moreover, the resulting thermal displacement parameters of some atoms are relatively large, partly owing to the loose packing and partly because the atomic positions represent an average between the molecular structures of **1** and Zn-**1** (it appeared from the crystallographic refinement that about 36% of the porphyrin sites in the analyzed crystal are metallated by zinc ions). The contribution of the disordered solvent was thus subtracted from the diffraction pattern by the 'Bypass' method[8] (the 'Bypass' method is widely used in the crystallographic analysis of compounds containing substantial amounts of disordered solvent which cannot be located precisely from diffraction data). This refinement converged smoothly at final $R1 = 0.078$ for 6582 observations with $F_o > 4\sigma(F_o)$, $R1 = 0.096$ ($wR2 = 0.231$) for all unique data, $|\Delta\rho| \leq 0.38$ e Å^{-3}. The residual electron density diffused within the interporphyrin channel voids (with peaks ≤ 1.1 e Å^{-3}) accounted for the presence of at least five additional molecules of DMF (or a corresponding combination of DMF and water) in the asymmetric unit of this structure. A sufficient amount of the crystalline material with uniform solvent content for reliable elemental and thermal analyses of this material could not be obtained. All hydrogen atoms were placed in calculated positions and added as fixed contributions to the structure factors. CCDC-140981.

Molecular structure

Compound **1** (and also Zn-**1**) is shaped as a flat ~15 Å square and contains self-complementary molecular recognition sites directed at the four corners of the square (Fig. 1). The molecular structure of the analyzed material is characterized by standard covalent parameters. The central porphyrin core is nearly planar, the random deviations of the various atoms from the mean plane of the four pyrrole nitrogens not exceeding 0.15 Å. The dihedral angles between the phenyl rings and the plane of the porphyrin core are 60.0° and 65.6°. The triazine fragments are coplanar with the phenyl rings to which they are bound in order to optimize electron delocalization, the corresponding torsion angles between them being only 1.7° and 4.2°. Correspondingly, framework **1** has limited conformational flexibility. The zinc ion, which is present only in about 36% of the porphyrin units, deviates 0.42 Å from the porphyrin plane and coordinates at these sites to a molecule of water as an axial ligand.

Supramolecular porphyrin networks

The uniquely defined geometric (square shape and rigidity) and functional (high potential for cooperative hydrogen bonding with 16 NH protons and 12 proton-acceptor N-sites in a single molecule) properties of **1**

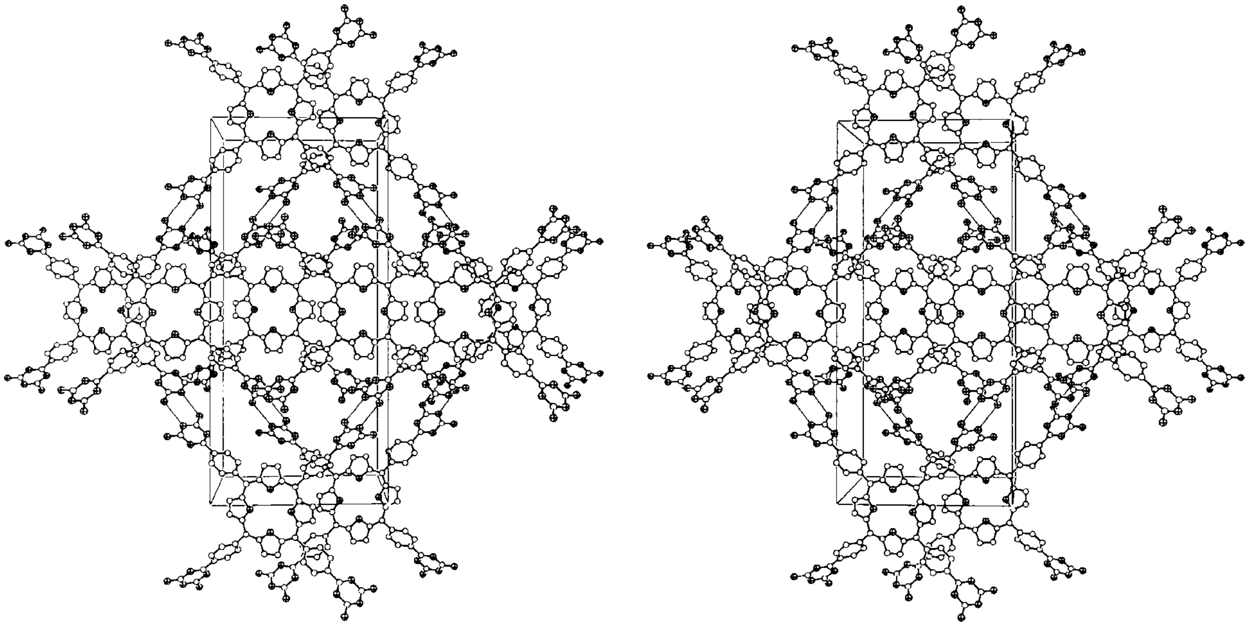

Figure 3. Stereoview of the crystal structure approximately down the *b*-axis of the crystal (*c* is horizontal), showing interweaving of the planar networks into one another. The N and O heteroatoms are marked by dark circles; hydrogens are omitted for clarity. Thin lines between the heteroatoms denote hydrogen bonds (see Table 1 for details). Wide channels propagate in the crystal along *c*, between segments of the porphyrin moieties (see Fig. 4). For illustrative purposes, the indicated frame of the unit cell has been shifted by $x = -1/2$ from its actual position

dictate the formation of planar and rigid hollow networks sustained by hydrogen bonds. In the observed conformation, effective association through multiple hydrogen bonds between two porphyrin species requires coplanarity and head-to-head orientation of the interacting 3,5-diaminotriazine functions, thus forcing each molecule to interact with four other species along the equatorial molecular axes. One of the amino groups (as a proton donor) and the sp^2 4-nitrogen (as a proton acceptor) of each diaminotriazine moiety are involved in these interactions (Fig. 1). Every porphyrin molecule is effectively connected to the neighboring units in the network by eight N—H···N hydrogen bonds (see Table 1 for geometric details), imparting a considerable enthalpic stability to these arrays. This leads to the formation of layered multiporphyrin networks with unprecedently large cavities of approximate van der Waals dimensions of about 22×22 Å^2 (Fig. 2). The molecules located across these voids are displaced by *a* in one direction and by $b + 2c$ in the other direction of the crystal lattice.

Porous three-dimensional structure

As in other relevant examples related to self-assembly of conformationally rigid polyfunctional species, in the absence of a sufficiently sizeable guest component which could fill effectively the large intermolecular voids, these networks interpenetrate in the solid to fill the empty space. Representative examples published earlier include the intermolecular organization in crystal structures of the trigonally shaped benzene-1,3,5-tricarboxylic acid,[9] the tetrahedral adamantanetetracarboxylic acid[10] and one crystalline polymorph of the square-planar tetra(4-carboxphenyl)porphyrin tetraacid.[11] In the present case, the crystal structure is composed of two sets of differently oriented multiporphyrin networks related to one another by the screw axis and glide plane elements of symmetry (Fig. 3). Two adjacent molecular layers of one such set penetrate through the large interporphyrin voids of the second set, yielding a rigid concatenated lattice of the porphyrin building blocks. This lattice is further enforced by extensive hydrogen bonding between parallel molecular networks displaced along *c* with an interlayer distance of 5.48 Å. The latter involve the second amino substituent of every diaminetriazino moiety as proton donors, and the 2-nitrogen of neighboring molecules as proton acceptors (Table 1). The remaining hydrogen bonding sites in **1** are solvated in the crystal by molecules of water and DMF (Fig. 4, Table 1). Inspection of the resulting structure reveals that it occupies only 65% of the crystal volume, and still contains wide oval channel voids which propagate along the *c*-axis of the crystal (Fig. 4). These channels are centered at (0, 0, *z*) and (1/2, 1/2, *z*), have van der Waals width of approximately 6 Å, and are partly filled in the crystal by additional molecules of diffused (unresolved by diffraction) solvent. Identification of a suitable templating agent which may prevent the above described interpenetration of the porphyrin networks and thus yield a porous solid with much wider

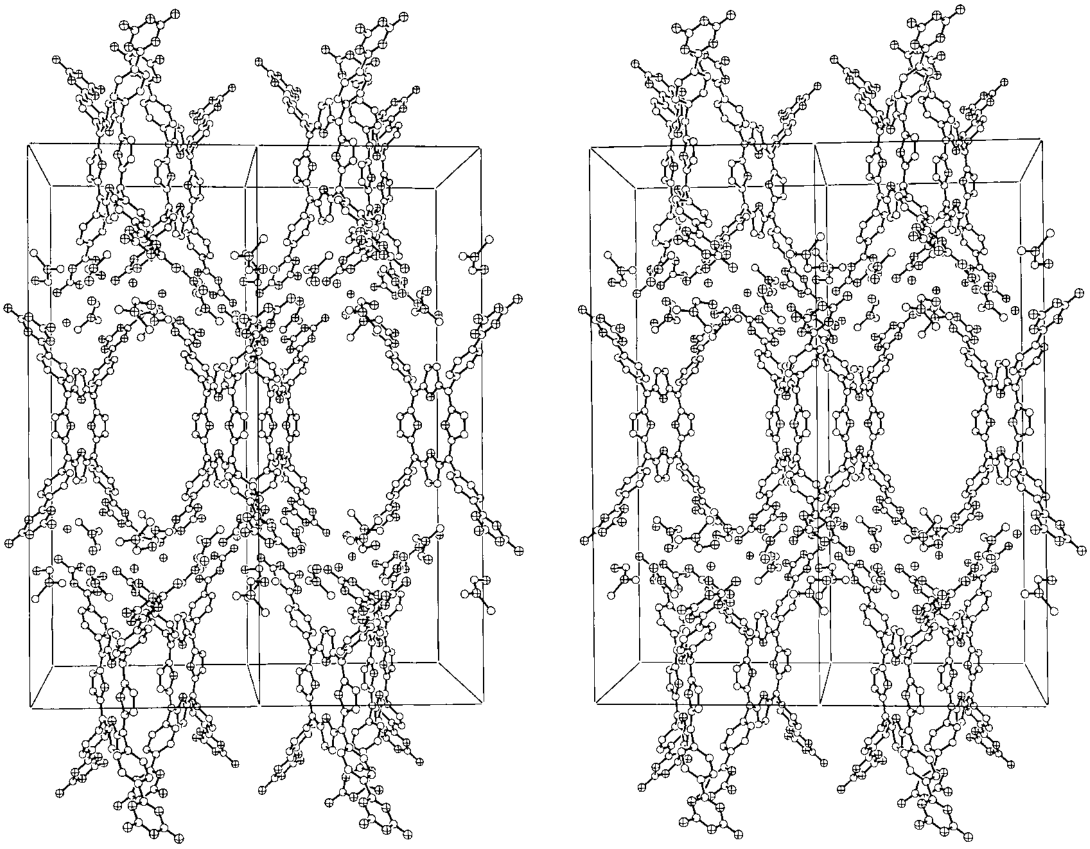

Figure 4. Stereoview of the crystal structure approximately down the *c*-axis of the crystal (*b* is horizontal; two unit cells), illustrating the 6 Å wide channels running through the crystal and centered at (0, 0, *z*) and (1/2, 1/2, *z*). It shows also the resolved water and DMF molecules which provide a solvation layer to those functional substituents which are not used in the interporphyrin binding. These solvent layers center at $x = 1/4$ and $x = 3/4$. The N and O heteroatoms are marked by crossed circles; hydrogens are omitted for clarity

channels presents an exciting challenge for further investigation.

CONCLUSION

Hydrogen bonding interactions provide a powerful organizing force in molecular crystals, a phenomenon which is even more pronounced in polyfunctional materials owing to a cooperative effect of these interactions. Although the enthalpies of such interactions when considered alone are relatively small, ≤ 20 kJ mol^{-1},[12] their cooperative effect (every porphyrin molecule takes part in 16 hydrogen bonds!) approaches the strength of a covalent bond and appears to be adequate to stabilize the open network structure. Along with earlier observations related to the assembly of other porphyrin network structures,[3] these results represent further progress towards the successful formulations of stable and rigid three-dimensional architectures by non-covalent synthesis, and provides a promising perspective for new molecular sieve materials with nanosized cavities of tunable dimensions.

Acknowledgements

This research was supported in part by the Israel Science Foundation founded by the Academy of Sciences and Humanities.

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