Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Borylated porphyrins: 5,10,15,20-tetrakis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)porphyrin nitrobenzene disolvate

Sankar Muniappan, Sophia Lipstman and Israel Goldberg*

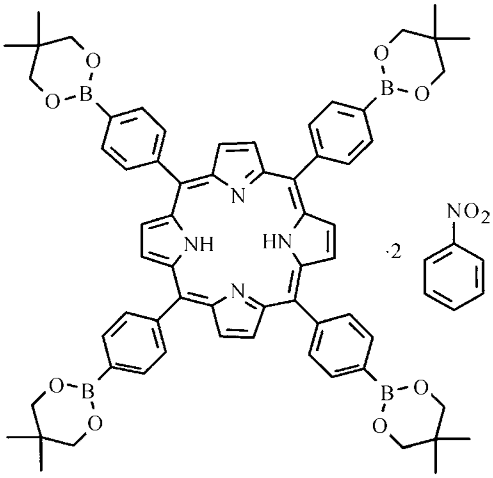
School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, 69978 Tel-Aviv, Israel
Correspondence e-mail: goldberg@post.tau.ac.il

Received 3 February 2008
Accepted 18 February 2008
Online 23 February 2008

The title compound, $C_{64}H_{66}B_4N_4O_8{\cdot}2C_6H_5NO_2$, is a nitrobenzene solvate of a *meso*-tetraphenylporphyrin species with unconventional peripheral boronic ester substituents. The porphyrin units reside in the crystal on centers of inversion and exhibit a channel clathrate-type structure, wherein molecules of nitrobenzene are accommodated in tunnels of width 7–8 Å that propagate through the crystal parallel to the *b* axis between layers of tightly offset-stacked porphyrins. The scientific significance of the reported results is twofold. They describe the synthetic route to newly functionalized building blocks for the formulation of porphyrin-based supramolecular assemblies, namely the corresponding tetraboronic acid derivative; the title compound represents an essential intermediate in this process. They reveal also that channel-type clathrates can be formed not only with the parent tetraphenylporphyrins but also with their laterally extended derivatives.

Comment

This study is part of our ongoing effort to formulate framework solids with suitably functionalized porphyrin building blocks. We and others have shown to this end that *meso*-tetrakis(4-carboxyphenyl)porphyrin (TCPP) is a uniquely versatile building block for the construction of molecular sieve-type architectures (Goldberg, 2005, and references therein; Suslick *et al.*, 2005; Lipstman *et al.*, 2007). The peripheral COOH functional groups provide multiple active sites for co-operative intermolecular hydrogen bonding and for effective inter-coordination through external metal ion bridges. As a next step, we attempted the synthesis of the boronic tetraacid porphyrin analog (TBPP). Boronic acid represents an alternative $BOOH_2$ molecular recognition function for supramolecular assembly. However, due to its high reactivity and sensitivity to experimental conditions, the synthesis of the TBPP porphyrin from the corresponding 4-formylphenylboronic acid and pyrrole starting materials (see *Experimental*) required initial protection of the $BOOH_2$ residue by esterification with an appropriate alcohol reagent. This led to the title porphyrin as an intermediate product. The crystallographic characterization of the nitrobenzene disolvate, (I), is described in this report, revealing an interesting intermolecular organization. Only a few porphyrins appended with one or two boronic ester groups have been previously structurally characterized (Hyslop *et al.*, 1998; Hata *et al.*, 2005).



(I)

The porphyrin macrocycle in (I) is essentially planar (Fig. 1), with minimal distortions of its atoms from the mean plane of the 24-atom ring (within ±0.05 Å). The compound resides on a crystallographic center of inversion at $(0, \frac{1}{2}, \frac{1}{2})$. The dioxaborinane residues diverge in the four equatorial directions, adopting envelope-type conformations. The molecular structure of (I) is characterized by common geometric features, yet its supramolecular organization is of particular interest and deserves further attention. As shown in Fig. 2, the molecules are arranged in open layers, sustained by van der Waals interactions between the diverging boronic-ester-appended aryl arms. These layers are perpendicular to the *b* axis of the crystal. There are no short intermolecular contacts within the layers that may indicate a possible significance of specific interactions other than dispersion. Yet, the open-layer organization prevails (Fig. 2) even in the absence of any of the direct π–π or T-shaped phenyl–phenyl attractions observed previously in common clathrates of unsubstituted tetraphenylporphyrins (Byrn *et al.*, 1993, and references therein). By measuring the shortest interatomic distances between molecules located across the interporphyrin voids, and considering the van der Waals radii of the corresponding fragments that line these voids, their effective width is estimated to be 7–8 Å. Consecutive layers are tightly stacked along the *b* axis in an offset manner, with a *c*/2 shift along the *c* axis. Fig. 3 illustrates the crystal packing in (I), along with the inclusion of the nitrobenzene solvent molecules in the channel voids created in the porphyrin-stacked lattice. The resulting structure resembles the channel clathrates observed in many solvates of the unsubstituted tetraphenylporphyrins (Byrn *et*

doi:10.1107/S010827010800468X

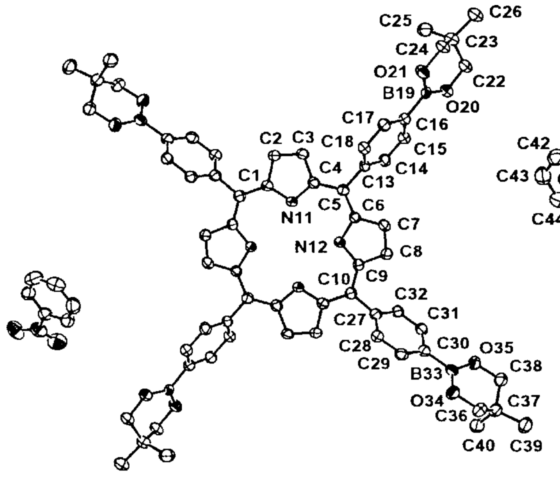


Figure 1
The molecular structure of the title compound, showing the atom-labeling scheme. Ellipsoids are drawn at the 50% probability level at *ca* 110 K. Compound (I) is located on a center of inversion at $(0, \frac{1}{2}, \frac{1}{2})$ and only atoms of the asymmetric unit are labeled. H atoms have been omitted.

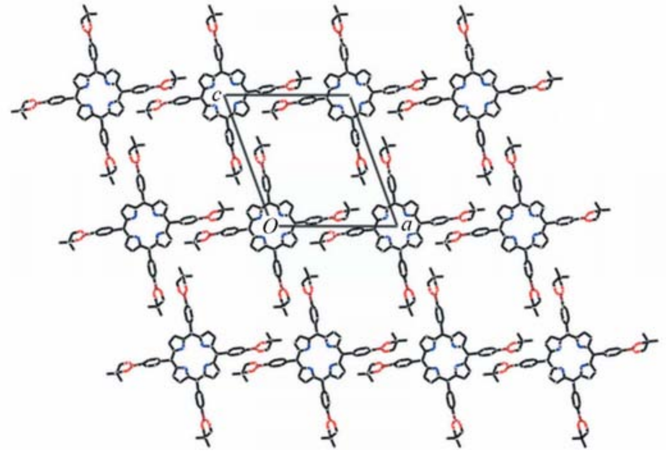


Figure 2
The intermolecular organization in a single layered porphyrin array projected down the *b* axis of the crystal. Note the large interporphyrin voids within such an assembly. The nitrobenzene solvent molecules and the H atoms have been omitted.

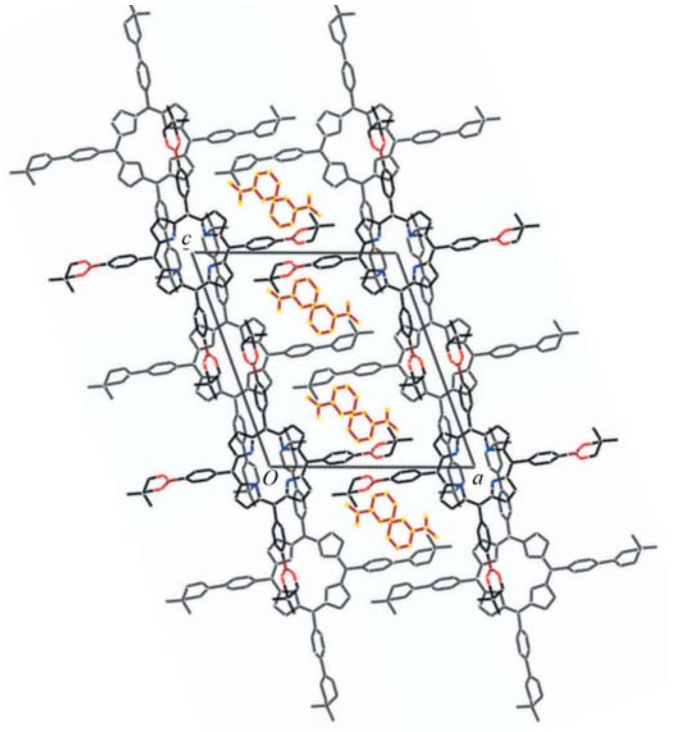


Figure 3
The crystal packing of (I), projected down the *b* axis, showing occlusion of the solvent molecules in the channel voids. H atoms have been omitted. The four porphyrin units in the upper layer are indicated by darker wireframe, while the six units of the lower layer are indicated by all-gray wireframe. Adjacent layers along *b* are related to each other by the screw/glide symmetry. The nitrobenzene solvent molecules are depicted as dotted atoms.

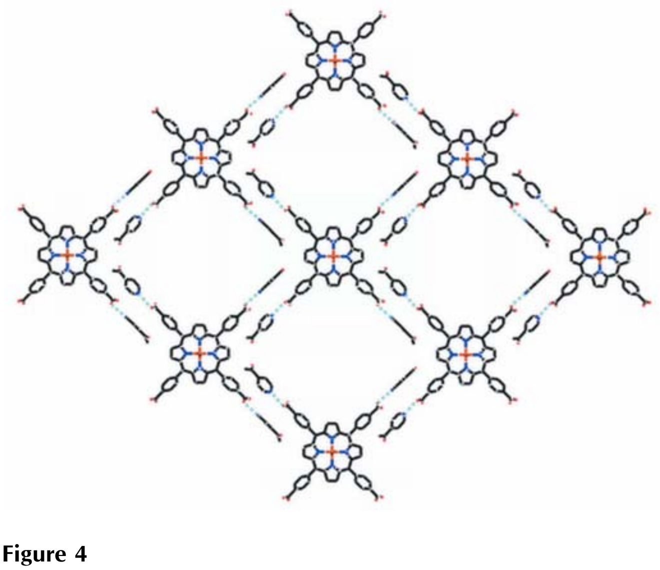


Figure 4
The open layered porphyrin assembly of the hydrogen-bonded 1:4 adduct of Cu–TCPP with 4-acetylpyridine (Lipstman *et al.*, 2006). Hydrogen bonds are indicated by dotted lines and H atoms have been omitted.

al., 1993, and references therein), as well as their tetrakis(4-cyanophenyl) analogs (Krishna Kumar *et al.*, 1998).

The formation of channel-type clathrates by laterally extended tetraphenylporphyrins is not very common, as such open-structure formation is associated with large inter-porphyrin voids. Usually, this represents a thermodynamically unfavorable molecular organization *versus* a more tightly packed alternative arrangement. In the absence of specific directional intermolecular synthons, it is affected mostly by dispersion forces, shape features of the porphyrin scaffold, and the presence of suitable templates in the crystallization mixture. It the latter context, nitrobenzene was found to be an excellent template for an open-porphyrin assembly to organize porphyrin molecules around it (Goldberg, 2005, and references therein). Indeed, only a small number of similar channel-type clathrates has been observed with alkyl/aryl-extended porphyrin scaffolds. An interesting example is illustrated in Fig. 4. It relates to the open assembly of copper(II)-metalated TCPP, in which the four carboxylic acid functions associate by hydrogen bonds to 4-acetylpyridine groups at the four corners of TCPP. The laterally extended 1:4 porphyrin–4-acetylpyridine aggregates assemble into open-channel voids with very wide channels (Fig. 4) filled with uncoordinated solvent (Lipstman *et al.*, 2006). In spite of the large interporphyrin pores, characterized by a van der Waals width of about 17 Å, these layers do not interweave in this structure. Rather, they are stacked one on top of the other in a partly offset manner, giving rise to tunnels of approximate width 14 Å (accessible to the solvent) that propagate through the crystal perpendicular to the layers.

In summary, we have described the synthetic route to the title compound, (I), and to the tetraboronic acid porphyrin analog that represents a new scaffold for the construction of porphyrin-based supramolecular assemblies. Another focus is on the interesting clathrate-type organization observed in tetraphenylporphyrin compounds extended in the four lateral directions by additional substituents without coordination or hydrogen-bonding functions. Such interporphyrin layered arrangements sustain large voids primarily by dispersion forces and are rarely observed with such expanded tetraphenylporphyrin scaffolds.

Experimental

The synthesis of the title compound proceeded in two steps, using commercially available reagents, following the procedures reported by Lindsey & Wagner (1989) and Hyslop *et al.* (1998). First, a mixture of 4-formylphenylboronic acid (2.35 g) and 2,2-dimethylpropane-1,3-diol (1.80 g) in dry tetrahydrofuran (THF; 25 ml) was stirred for 3 h. After evaporation of the solvent under reduced pressure, the resulting residue was dissolved in CH_2Cl_2 (20 ml), washed several times with water, dried with anhydrous sodium sulfate and concentrated in a vaccum. The residue was added to hexane with shaking (50 ml) and the resulting suspension was concentrated under vacuum to give the desired white solid product 2-(4-formylphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (yield 3.54 g, 90%). In the next step, the title compound was synthesized by condensing the product (2.51 g) from the first step dissolved in CH_2Cl_2 (1000 ml) with pyrrole (0.8 ml) (purged with nitrogen gas). To this, 0.9 *M* BF_3–etherate (10 ml) was added under nitrogen, followed by addition of *p*-chloranil (2.12 g). After the normal work-up procedure (Lindsey & Wagner, 1989), the raw product was passed through a silica-gel column with a 4% acetone-in-chloroform eluent. Recrystallization from a 1:3 chloroform–methanol mixture, containing a few drops of nitrobenzene, afforded pure (I) (yield 0.59 g, 16%).^{1}H NMR ($CDCl_3$): δ 8.82 (*s*, 8H), 8.18 (*s*, 16H), 3.93 (*s*, 16H), 1.16 (*s*, 24H), −2.85 (*s*, 2H). FAB mass spectrum (*m*/*z*) for $C_{64}H_{66}B_4N_4O_8$: found 1058, calculated 1058.3. Conversion of (I) to the corresponding tetraboronic acid (deprotection of the tetra-ester) was made by treatment with a solution of KOH in a mixture of THF and methanol at 363 K for 2 d. The crude product was washed with 10% HCl, filtered and neutralized with a 10% solution of Et_3N in methanol and pyridine. The final product was washed with water and dried. ^{1}H NMR (DMSO-d_6): δ 8.77 (*s*, 8H), 8.32 (*s*, 8H), 8.15 (*q*, 16H, *J* = 8.2 Hz, *J* = 2.1 Hz), −2.98 (*s*, 2H). MALDI–TOF mass spectrum (*m*/*z*) for $C_{44}H_{34}B_4N_4O_8$: found 791.3, calculated 790.02. Compound (I) crystallized as long thin red needles which exhibited relatively weak diffraction. Repeated attempts to crystallize TBPP has thus far resulted in solids of very poor crystallinity.

Crystal data

$C_{64}H_{66}B_4N_4O_8\cdot 2C_6H_5NO_2$
$M_r = 1308.67$
Monoclinic, $P2_1/c$
$a = 18.6511 (7)$ Å
$b = 9.2969 (3)$ Å
$c = 20.7606 (9)$ Å
$\beta = 110.1016 (13)^\circ$
$V = 3380.5 (2)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 110 (2)$ K
0.55 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
23064 measured reflections
6333 independent reflections
3223 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.089$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.179$
$S = 0.97$
6333 reflections
446 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

H atoms bound to C atoms were located in calculated positions and constrained to ride on their parent atoms, with C—H = 0.95 (aryl), 0.98 (methyl) or 0.99 Å (methylene) and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(aryl and methylene) and 1.5$U_{\rm eq}$(methyl). The two N-bound pyrrole H atoms are disordered between the four N-atom sites. Some of the B atoms exhibit minor conformational disorder. Large-amplitude anisotropic displacement parameters characterize the nitrobenzene solvent species.

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, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3072). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Byrn, M. P., Curtis, C. J., Hsiou, Y., Khan, S. I., Sawin, P. A., Tendick, S. K., Terzis, A. & Strouse, C. E. (1993). *J. Am. Chem. Soc.* **115**, 9480–9497.

Goldberg, I. (2005). *Chem. Commun.* pp. 1243–1254.

Hata, H., Shinokubo, H. & Osuka, A. (2005). *J. Am. Chem. Soc.* **127**, 8264–8265.

Hyslop, A. G., Kellet, M. A., Iovine, P. M. & Therien, M. J. (1998). *J. Am. Chem. Soc.* **120**, 12676–12677.

Krishna Kumar, R., Balasubramanian, S. & Goldberg, I. (1998). *Inorg. Chem.* **37**, 541–552.

Lindsey, J. S. & Wagner, R. W. (1989). *J. Org. Chem.* **54**, 828–836.

Lipstman, S., Muniappan, S., George, S. & Goldberg, I. (2006). *CrystEngComm*, **8**, 601–607.

Lipstman, S., Muniappan, S., George, S. & Goldberg, I. (2007). *Dalton Trans.* pp. 3273–3281.

Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.

Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Suslick, K. N., Bhyrappa, P., Chou, J.-H., Kosal, M. E., Nagakaki, S., Smithenry, D. W. & Wilson, S. R. (2005). *Acc. Chem. Res.* **38**, 283–291.