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2,3,12,13-Tetrabromo-5,10,15,20-tetrakis(4-butoxyphenyl)porphyrin 1,2-dichloroethane solvate

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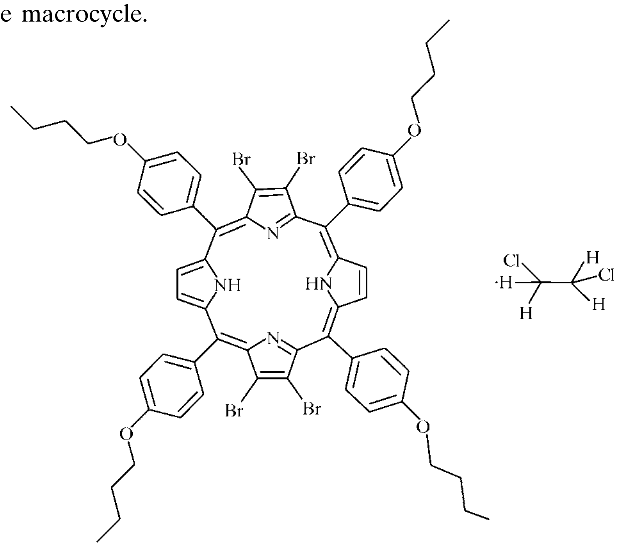
Nonmesogenic 2,3,12,13-tetrabromo-5,10,15,20-tetrakis(4-butoxyphenyl)porphyrin crystallizes as the title 1,2-dichloroethane solvate, $C_{60}H_{58}Br_4N_4O_4\cdot C_2H_4Cl_2$. The porphyrin ring shows a nonplanar conformation, with an average mean plane displacement of the β-pyrrole C atoms from the 24-atom ($C_{20}N_4$) core of ±0.50 (3) Å. The 1,2-dichloroethane solvent is incorporated between the porphyrin units and induces the formation of one-dimensional chains *via* interhalogen Cl···Br and butyl–aryl C—H···π interactions. These chains are oriented along the unit-cell *a* axis, with the macrocyclic ring planes lying almost parallel to the (010) plane. The chains are arranged in an offset fashion by aligning the butoxy chains approximately above or below the faces of the adjacent porphyrin core, resulting in decreased interporphyrin π–π interactions, and they are held together by weak intermolecular (C—Br···π, C—H···π and C—H···Br) interactions. The nonplanar geometry of the macrocyclic ring is probably due to the weak interporphyrin interactions induced by the solvent molecule and the peripheral butoxy groups. The nonplanarity of the mesogens could influence the mesogenic behaviour differently relative to planar porphyrin mesogens.

Comment

Porphyrins and metalloporphyrins have been widely used as molecular scaffolds in the formation of clathrates by incorporating a wide range of guests (Byrn *et al.*, 1993). Sterically crowded porphyrins have been developed as model compounds of nonplanar conformations of tetrapyrrole pigments in nature (Shelnutt *et al.*, 1998). The variation in nonplanarity of the macrocyclic ring has been attributed to the degree of steric crowding around the periphery of the porphyrin (Senge, 2000). The crystal structure of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin (TPPBr$_4$) exhibits a nearly planar geometry of the porphyrin ring (Zou *et al.*, 1995). In this study, the effect of substitution at the phenyl rings on the stereochemistry and intermolecular interactions of the 2,3,12,13-tetrabromo-5,10,15,20-tetrakis[4-(1-butoxyphenyl)]porphyrin molecule has been examined through the structure of the title 1,2-dichloroethane solvate, $H_2T(4\text{-}OC_4P)PBr_4\cdot C_2H_4Cl_2$, (I), which reveals a nonplanar conformation of the macrocycle.



(I)

The nonplanarity of the macrocycle in (I) (Fig. 1*a*) is evidenced from the side-on view in Fig. 1(*b*), as well as from the diagram of the mean-plane deviations of the 24-atom core (Fig. 1*c*). The average deviation of the β-pyrrole C atoms is ±0.50 (3) Å, while the mean deviation of the *meso* C atoms is ±0.038 (3) Å. Interestingly, the β-pyrrole C atoms of the brominated pyrroles show a greater mean-plane displacement than their counterparts in the unbrominated pyrroles. The pyrrole groups themselves are alternately displaced up and down from the mean plane formed by the 24-atom core, indicating that the distortion of the ring is more of a saddle-shaped conformation combined with a gently ruffled conformation (Senge, 2000). This shows an enhanced distortion of the 24-atom core in (I) compared with the nearly planar free H$_2$TPPBr$_4$ molecule (Zou *et al.*, 1995) and it is also greater than the distortion reported for the five-coordinated ZnTPPBr$_4$(CH$_3$OH)·DMF structure (DMF is dimethylformamide; Terazono *et al.*, 2002). The Cβ···Cβ distance along the transannular brominated pyrrole groups in (I) [8.48 (2) Å] is longer than the corresponding distance along the unbrominated pyrroles [8.25 (5) Å]. Similarly, the N···N distance along the brominated pyrroles [4.19 (1) Å] is longer than that in the opposite direction [4.07 (3) Å]. The corresponding $C_\beta\cdots C_\beta$ and N···N distances in H$_2$TPPBr$_4$ are slightly longer, as expected from the flattening of the macrocycle. An increase in the mean value of the torsion angles $N-C\alpha-C_{meso}-C\alpha' = 9.0\ (8)^\circ$ (*e.g.* N1—C4—C5—C6) and $C\alpha-N-C\alpha-C_\beta = 3.0\ (8)^\circ$ is observed in (I), in contrast with the corresponding values of 4.9 and 0.7°, respectively, for H$_2$TPPBr$_4$.

Similar trends in behaviour were reported for the solvate-free structures H$_2$TPPR_4 (R = C$_6$H$_5$ or CH$_3$; Chan *et al.*, 1994; Bhyrappa *et al.*, 2007). The relaxation of the steric strain in the macrocyclic ring is reflected in the elongation of the core along the substituted pyrrole direction (Scheidt, 2000). In the case of

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(I), the *meso*-aryl and pyrrole groups make average dihedral angles of 68.1 (5) and 12.3 (7)°, respectively, with the mean plane of the 24-atom core. It is anticipated that the extent of steric crowding around the periphery of the macrocycle in (I) is comparable with that in the nonsolvated structures H_2TTPPR_4 ($R = CH_3$, Br or C_6H_5), since the butoxy groups are farther away from the core. However, the presence of the solvent molecule and the weak interporphyrin interactions (see below) seem to have a greater influence on the nonplanar geometry of (I) (Krupitsky *et al.*, 1994).

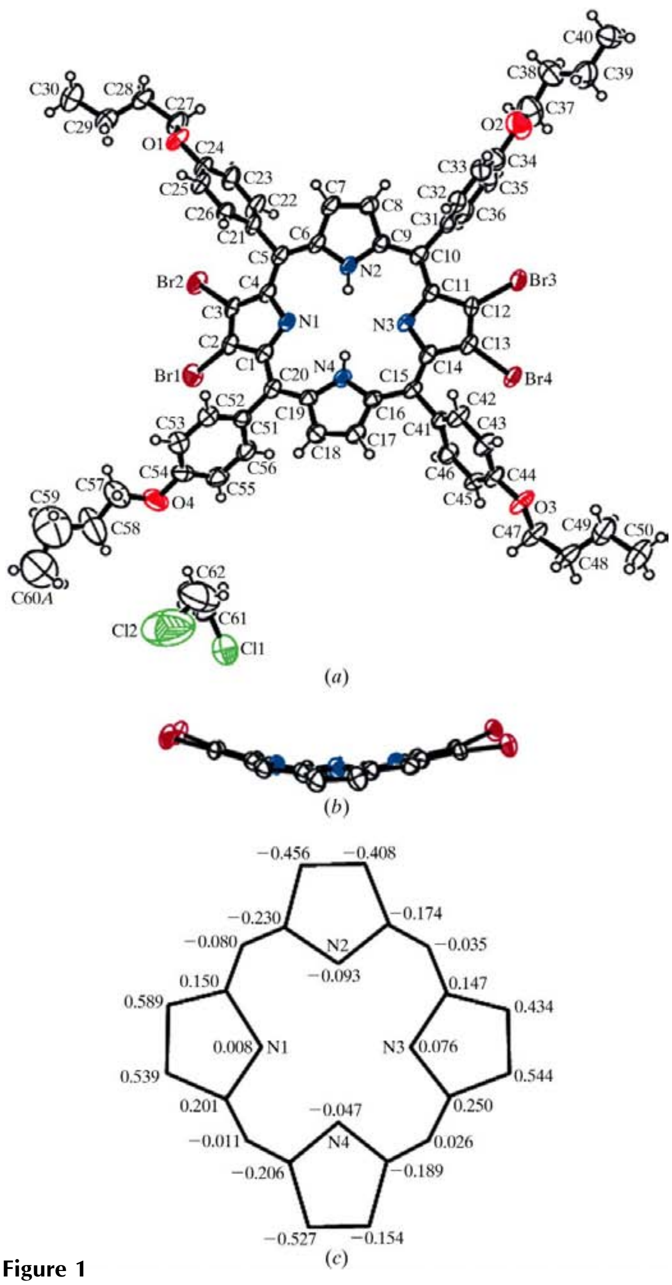

Figure 1
(*a*) A diagram of the title complex, (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. (*b*) A side-on view of the complex. Displacement ellipsoids are drawn at the 50% probability level. The *meso*-aryl groups and H atoms have been omitted for clarity. (*c*) The deviation of the core atoms from the mean plane formed by the 24-atom core. The deviations are in Angstroms (Å) with s.u. values of 0.004 Å.

Notably, the complex molecules in (I) form a one-dimensional array oriented approximately along the unit-cell *a* axis, with the macrocyclic ring planes lying almost parallel to the (010) plane. Atom Cl1 of the 1,2-dichloroethane solvent molecule bridges two porphyrin molecules *via* Cl···Br and C—H···π interactions to form a one-dimensional array (Fig. 2). The short interhalogen contacts are Br1···Cl1^{iv} [3.496 (2) Å], Br3···Cl1^{v} [3.458 (2) Å] and C—H···π (H60*C*···C45^{iii} = 2.70 Å) [symmetry codes: (iii) $x - 1, y, z$; (iv) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (v) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$]. Such interhalogen and C—H···π interactions are known to generate interesting structural motifs (Freytag & Jones, 2000; Desiraju & Steiner, 1999). These one-dimensional chains are further stabilized by weak intermolecular interactions. Selected intermolecular hydrogen-bonding distances are listed in Table 1. These chains are bridged by closest arrays from above and below the plane

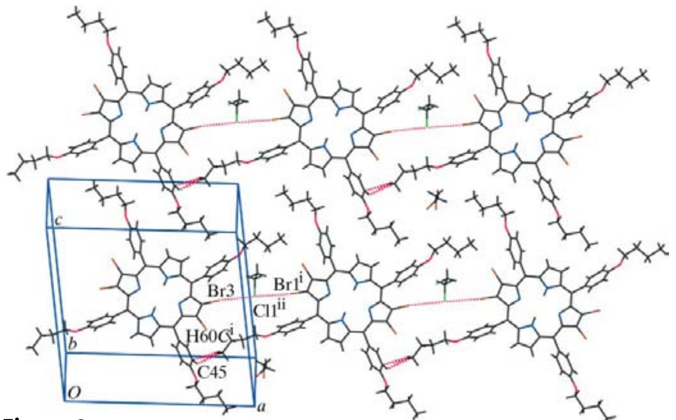

Figure 2
A molecular packing diagram for (I), viewed approximately down the unit-cell *b* axis. Intermolecular Br···Cl···Br and C—H···π short contacts are shown as dotted lines. [Symmetry codes: (i) $1 + x, y, z$; (ii) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$.]

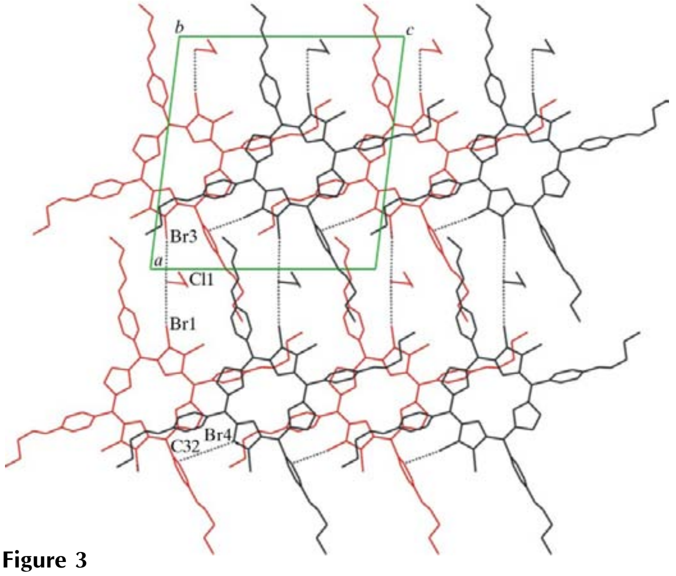

Figure 3
A projection diagram of the packing in (I) along the *b* axis. Molecules drawn with heavy lines are in front and are oriented in a slipped stack fashion relative to the molecules at the back (lighter). Intermolecular Cl···Br and C—Br···π interactions are shown as dotted lines.

in a slipped stack fashion and are held together by C—H⋯Br (H52⋯Br2^{i} and H49*B*⋯Br3^{i}) and C—H⋯π (H56⋯C14^{ii} and H47*A*⋯C11^{i}) interactions (Table 1) [symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + 1, -y, -z + 1$]. These hydrogen-bonding distances are indicative of weak intermolecular interactions (Desiraju & Steiner, 1999). In addition, a weak intermolecular C—Br⋯π [Br4⋯C32^{i} = 3.414 (5) Å] short contact is observed. Fig. 3 shows the relative orientation of the one-dimensional chains, with the butoxy groups lying approximately on the faces of the other adjacent porphyrins, leading to decreased intermolecular π–π interactions that perhaps partly influence the distortion of the macrocyclic ring.

The structure of (I) shows decreased intermolecular π–π interactions and enhanced nonplanar geometry of the 24-atom core, in contrast with that found in unbrominated 5,10,15,20-tetrakis(4-hexyloxyphenyl)porphyrin (Walawalkar *et al.*, 1993) and [5,10,15,20-tetrakis(4-octyloxyphenyl)porphinato]zinc(II) (Chiaroni *et al.*, 1988), suggesting that the Br atoms, butoxy chains and solvent influence the conformational behaviour in this system.

Experimental

Compound (I) was prepared by bromination of 5,10,15,20-tetrakis(4-butoxyphenyl)porphyrin according to the procedure of Kumar *et al.* (2003) (yield 70%). UV–vis data [CH$_2$Cl$_2$, λ_{max}, nm (log ε)]: 447 (5.65), 545 (4.40), 595 (3.90), 625 (*sh*), 704 (4.10); ^{1}H NMR (CDCl$_3$): δ 8.70 (*s*, 4H, β-pyrrole-H), 8.09 (*d*, 8H, *J* = 8.56 Hz, *o*-phenyl-H), 7.32 (*d*, 8H, *J* = 8.56 Hz, *m*-phenyl-H), 4.26 (*t*, 8H, *J* = 6.52 Hz, α-CH$_2$), 1.97 (*qnt*, 8H, *J* = 7.50 Hz, β-CH$_2$), 1.65 (*qnt*, 8H, *J* = 7.49 Hz, γ-CH$_2$), 1.10 (*t*, 12H, *J* = 7.38 Hz, –CH$_3$), −2.71 (*s*, 2H, imino-H); MALDI-TOF mass spectrum in α-cyano-4-hydroxycinnamic acid as the matrix, *m*/*z* calculated for $C_{60}H_{58}Br_4N_4O_4$: 1218.76; found 1220.36; analysis calculated for $C_{60}H_{58}Br_4N_4O_4$: C 59.14, H 4.82, N 4.61%; found: C 59.31, H 4.81, N 4.33%. Single crystals of (I) suitable for X-ray analysis were obtained by slow vapour diffusion of hexane into a 1,2-dichloroethane solution of the porphyrin over a period of 4 d.

Crystal data

$C_{60}H_{58}Br_4N_4O_4 \cdot C_2H_4Cl_2$
M_r = 1317.70
Monoclinic, $P2_1/c$
a = 18.8426 (4) Å
b = 17.1996 (4) Å
c = 18.0722 (4) Å
β = 97.0800 (10)°
V = 5812.3 (2) Å^3
Z = 4
Mo *K*α radiation
μ = 2.91 mm^{-1}
T = 176 (2) K
0.31 × 0.24 × 0.20 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.445, T_{max} = 0.554
65317 measured reflections
10251 independent reflections
7087 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.144
S = 1.07
10251 reflections
693 parameters
4 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.10 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C52—H52⋯Br2^{i}	0.93	3.00	3.772 (5)	142
C49—H49*B*⋯Br3^{i}	0.97	3.03	3.945 (5)	157
C56—H56⋯C14^{ii}	0.93	2.75	3.588 (7)	151
C47—H47*A*⋯C11^{i}	0.97	2.83	3.714 (7)	151
C60*A*—H60*C*⋯C45^{iii}	0.97	2.70	3.202 (5)	113

Symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + 1, -y, -z + 1$; (iii) $x - 1, y, z$.

All H atoms were placed in constrained positions, with C—H = 0.93–0.98 Å, and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C). Terminal atom C60 of one of the alkyl chains exhibits positional disorder and was refined with split positions of occupancy 0.59 (15) and 0.41 (15).

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *XPREP* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-32* (Farrugia, 1997) and *Mercury* (Bruno *et al.*, 2002); 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: SQ3133). Services for accessing these data are described at the back of the journal.

References

Bhyrappa, P., Karunanithi, K. & Varghese, B. (2007). *Acta Cryst.* E**63**, o4755.
Bruker (2003). *XPREP* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2004). *APEX2* (Version 1.22) and *SAINT-Plus* (Version 7.6). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
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.
Chan, K. S., Zhou, X., Lou, B.-S. & Mak, T. C. W. (1994). *J. Chem. Soc. Chem. Commun.* pp. 271–272.
Chiaroni, A., Riche, C., Bied-Charreton, C. & Dubois, J. C. (1988). *Acta Cryst.* C**44**, 429–432.
Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. Oxford University Press.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Freytag, M. & Jones, P. G. (2000). *Chem. Commun.* pp. 277–278.
Krupitsky, H., Stein, Z., Goldberg, I. & Strouse, C. E. (1994). *J. Inclusion Phenom.* **18**, 177–182.
Kumar, P. K., Bhyrappa, P. & Varghese, B. (2003). *Tetrahedron Lett.* **44**, 4849–4851.
Scheidt, W. R. (2000). *The Porphyrin Handbook*, edited by K. M. Kadish, K. M. Smith & R. Guilard, Vol. 1, ch. 2. New York: Academic Press.
Senge, M. O. (2000). *The Porphyrin Handbook*, edited by K. M. Kadish, K. M. Smith, R. Guilard, Vol. 1, ch. 6. New York: Academic Press.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shelnutt, J. A., Song, X.-Z., Ma, J.-G., Jia, S.-L., Jentzen, W. & Medforth, C. J. (1998). *Chem. Soc. Rev.* **27**, 31–41.
Terazono, Y., Patrick, B. O. & Dolphin, D. H. (2002). *Inorg. Chem.* **41**, 6703–6710.
Walawalkar, M. G., Nethaji, M. & Krishnan, V. (1993). *Acta Cryst.* C**49**, 479–481.
Zou, J.-Z., Xu, Z., Li, M., You, X.-Z. & Wang, H.-Q. (1995). *Acta Cryst.* C**51**, 760–761.