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(1*RS*,4*SR*,8*SR*,11*RS*,15*SR*,18*RS*,22*RS*,25*SR*)-1,4:8,11:15,18:22,25-Tetraethano-29*H*,31*H*-tetrabenzo[*b*,*g*,*l*,*q*]porphine chloroform disolvate

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Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.008 Å
R factor = 0.125
wR factor = 0.311
Data-to-parameter ratio = 14.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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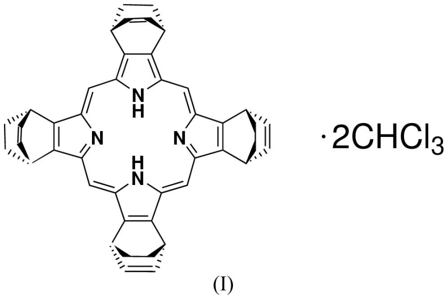
In the title compound, $C_{44}H_{38}N_4 \cdot 2CHCl_3$, the porphine (CP) is a soluble precursor of metal-free porphyrin which exhibits an excellent field-effect transistor characteristic. The CP skeleton is entirely flat and characterized by crystallographic C_i symmetry. In the present geometrical isomer, the C—C single-bond linkages of the four peripheries are arranged in an above–above–below–below manner with respect to the CP skeleton.

Comment

Organic field-effect transistors (FET) are advantageous in lowering fabrication costs and being large-area devices compared with inorganic FETs. We have recently reported that the metal-free porphyrin, the so-called benzoporphyrin (BP), exhibits excellent FET characteristics (Aramaki *et al.*, 2004). Our FET system is characterized by the use of a soluble BP-precursor (*i.e.* porphine in the title compound, called CP) and its thermal transformation into BP directly on the substrate at about 473 K. In order to improve the FET performance further, it is crucial to study the correlation between the structure and the solid-state properties. The structures of BP and toluene-solvated CP have previously been reported (Aramaki & Mizuguchi, 2003; Aramaki *et al.*, 2005). The present paper deals with the structure of the title compound, (I), which is chloroform-solvated CP.



(I)

The skeleton of the centrosymmetric CP molecule is entirely planar (Fig. 1). As shown in the scheme, there is one C—C single bond and one double bond in the four groups at the periphery of the molecule, and the C—C single-bond linkages are arranged in an above–above–below–below manner with respect to the CP skeleton. This is clearly seen from the difference in bond lengths (Table 1): 1.519 (9)–1.525 (9) Å for C7—C8 and C17—C18, and 1.339 (9)–1.356 (9) Å for C10═C11 and C20═C21. By contrast, in toluene-solvated CP (Aramaki *et al.*, 2005), the single and double bonds are averaged, giving an intermediate bond length. This provides a striking difference between the

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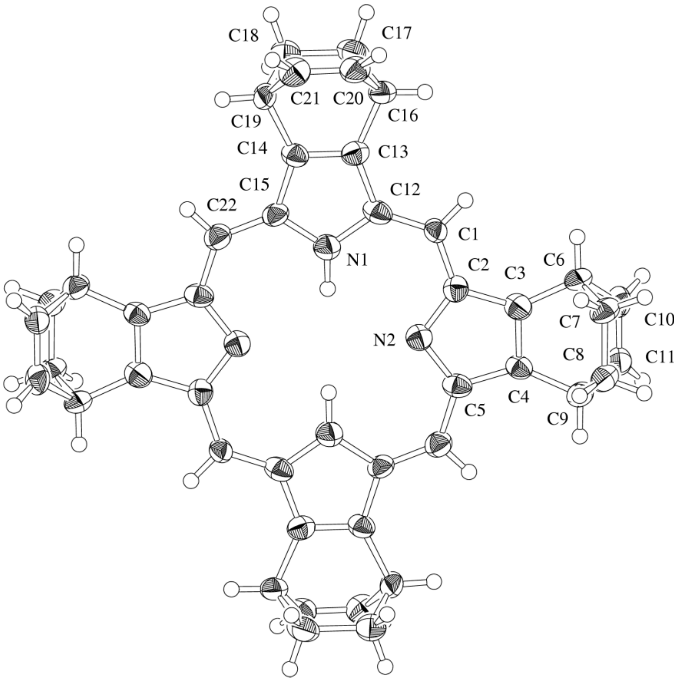

Figure 1
A view of the structure of the CP molecule in (I), showing 50% probability displacement ellipsoids. Unlabelled atoms are related to labelled atoms by ($-x, -y, -z$).

chloroform and toluene-solvated crystals of CP. It is also to be noted that we have isolated two isomers by column chromatography (see *Experimental*) and their ^{1}H NMR spectra are different at the *meso* site. However, these isomers in toluene-solvated crystals showed similar disordered structures with similar cell constants. By contrast, in chloroform-solvated CPs, we still have a chance to study the structure of both isomers. Fig. 2 shows the packing arrangement of CP with the chloroform molecules.

Experimental

CP was synthesized according to the method previously reported by Ito *et al.* (1998). The product was purified by column chromatography, using toluene as eluent. Two geometrical isomers of CP were clearly isolated, as indicated by ^{1}H NMR data (fast-eluted component: 10.388 and 10.394 p.p.m.; slow-eluted component: 10.382 and 10.388 p.p.m.). Single crystals of (I) were grown from a chloroform solution of the fast-eluted component. After a week, a number of dark-red block-shaped crystals were isolated. The crystal used for analysis was found to include solvent molecules. Therefore, X-ray intensity data were collected at 93 K.

Crystal data

$C_{44}H_{38}N_4\cdot 2CHCl_3$
$M_r = 861.52$
Monoclinic, $P2_1/c$
$a = 10.282$ (2) Å
$b = 17.433$ (3) Å
$c = 11.664$ (2) Å
$\beta = 106.51$ (1)°
$V = 2004.5$ (6) Å^3
$Z = 2$
$D_x = 1.427$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 9212 reflections
$\theta = 4.5$–$68.0°$
$\mu = 4.22$ mm^{-1}
$T = 93.1$ K
Block, dark red
$0.20 \times 0.20 \times 0.20$ mm

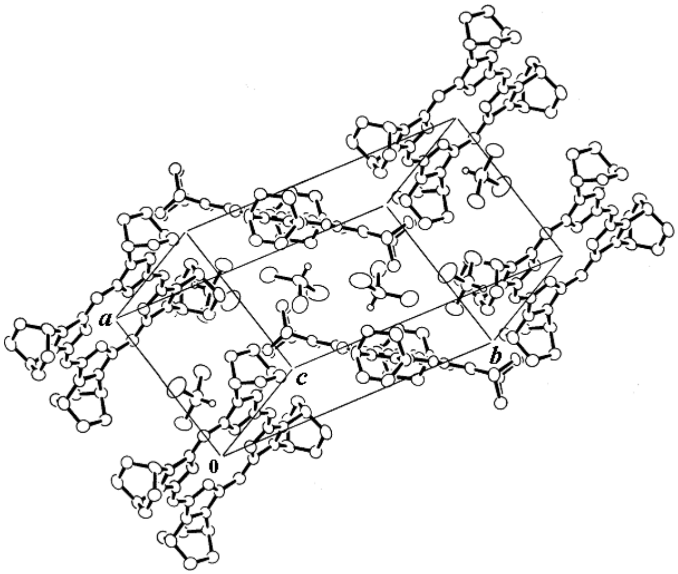

Figure 2
The crystal structure of (I). H atoms of CP have been omitted.

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.400$, $T_{max} = 0.430$
18 024 measured reflections
3592 independent reflections
1286 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.183$
$\theta_{max} = 68.2°$
$h = -11 \rightarrow 11$
$k = -20 \rightarrow 20$
$l = -13 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.125$
$wR(F^2) = 0.311$
$S = 1.32$
3592 reflections
254 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C12	1.381 (7)	C7—C8	1.525 (9)
N1—C15	1.377 (8)	C10—C11	1.339 (9)
N2—C2	1.375 (7)	C12—C13	1.443 (9)
N2—C5	1.385 (9)	C13—C14	1.350 (8)
C1—C2	1.401 (9)	C14—C15	1.434 (8)
C1—C12	1.367 (9)	C15—C22	1.385 (8)
C2—C3	1.446 (9)	C17—C18	1.519 (9)
C3—C4	1.370 (9)	C20—C21	1.356 (9)
C4—C5	1.446 (8)	C22—C5^{i}	1.404 (8)
C5—C22^{i}	1.404 (8)		
N1—C12—C1	126.5 (6)	C12—C1—C2	127.4 (5)
N1—C12—C13	104.7 (5)	C1—C2—C3	125.2 (5)
C15—N1—C12	111.8 (5)	C1—C12—C13	128.8 (5)
N1—C15—C14	105.6 (5)	C2—C3—C4	107.3 (5)
N1—C15—C22	125.2 (6)	C3—C4—C5	105.8 (6)
N2—C2—C1	124.4 (5)	C4—C5—C22^{i}	124.4 (6)
N2—C2—C3	110.4 (5)	C12—C13—C14	109.3 (5)
C5—N2—C2	105.3 (5)	C13—C14—C15	108.6 (6)
N2—C5—C4	111.1 (5)	C14—C15—C22	129.2 (6)
N2—C5—C22^{i}	124.5 (5)	C15—C22—C5^{i}	128.9 (6)

Symmetry code: (i) $-x, -y, -z$.

All the H atoms were positioned geometrically and included in the riding-model approximation, with N—H and C—H distances of 0.95 Å, and with $U_{iso}(H) = 1.2U_{eq}$(parent atom). The position of the

H atom bonded to N1 was calculated by assuming sp^2 hybridization, since a positive peak was found only near atom N1 (but not N2) in the difference-density map.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC and Rigaku, 2004); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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References

Aramaki, S. & Mizuguchi, J. (2003). *Acta Cryst.* E**59**, o1556–o1558.
Aramaki, S., Sakai, Y. & Ono, N. (2004). *Appl. Phys. Lett.* **84**, 2085–2087.
Aramaki, S., Sakai, Y., Yanagisawa, H. & Mizuguchi, J. (2005). *Acta Cryst.* E**61**, o659–o661.
Burla, M. C., Camalli, M., Carrozzini, B., Casarano, G. L., Giacovazzo, C., Polidori, G. & Spagna, R. (2003). *J. Appl. Cryst.* **36**, 1103.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory. Tennessee, USA.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Ito, S., Ochi, N., Murashima, T., Uno, H. & Ono, N. (1998). *Chem. Commun.* pp. 1661–1662.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2004). *CrystalStructure*. Version 3.6.0. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.