Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.106$
$S = 1.060$
1707 reflections
132 parameters
H atoms were restrained (included as riding atoms) and atom H2 which was refined
$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.5899P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.215$ e Å^{-3}
$\Delta\rho_{min} = -0.265$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0260 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (2)*

S1—N2	1.627 (2)	C3—N4	1.463 (3)
N2—C3	1.435 (3)	N4—C5	1.353 (3)
N2—H2	0.75 (3)	N4—C11	1.465 (3)
N2—S1—C10	100.97 (11)	C5—N4—C3	121.4 (2)
C3—N2—S1	111.66 (17)	C5—N4—C11	122.9 (2)
C3—N2—H2	115 (2)	C3—N4—C11	115.7 (2)
S1—N2—H2	110 (2)	N4—C11—C12	112.0 (2)
N2—C3—N4	113.7 (2)		
C10—S1—N2—C3	54.77 (19)	N2—C3—N4—C11	−150.9 (2)
S1—N2—C3—N4	−63.6 (3)	C3—N4—C5—C10	1.7 (4)
N2—C3—N4—C5	32.5 (3)		

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N8^{i}	0.75 (3)	2.20 (3)	2.937 (3)	168 (3)

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

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1987*b*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1987*c*); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1021). Services for accessing these data are described at the back of the journal.

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2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin

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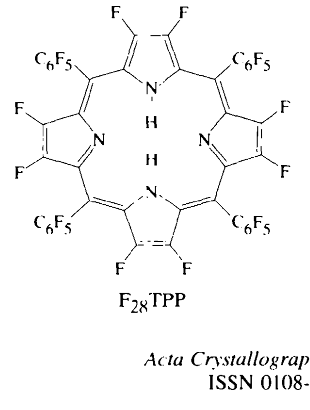
Abstract

The core of the title compound, $C_{44}H_2F_{28}N_4$, is essentially planar while the pentafluorophenyl groups are nearly perpendicular to the mean porphyrin plane. The molecule is centrosymmetric.

Comment

The title compound, F_{28}TPP, was prepared as part of a study of β-octafluoroporphyrins (Leroy *et al.*, 1997), a new class of highly electron-deficient ligands. The crystal structure of F_{28}TPP (Fig. 1) was determined, amongst others, in an attempt to correlate this porphyrin structure with the unusual spectroscopic data observed.



F_{28}TPP

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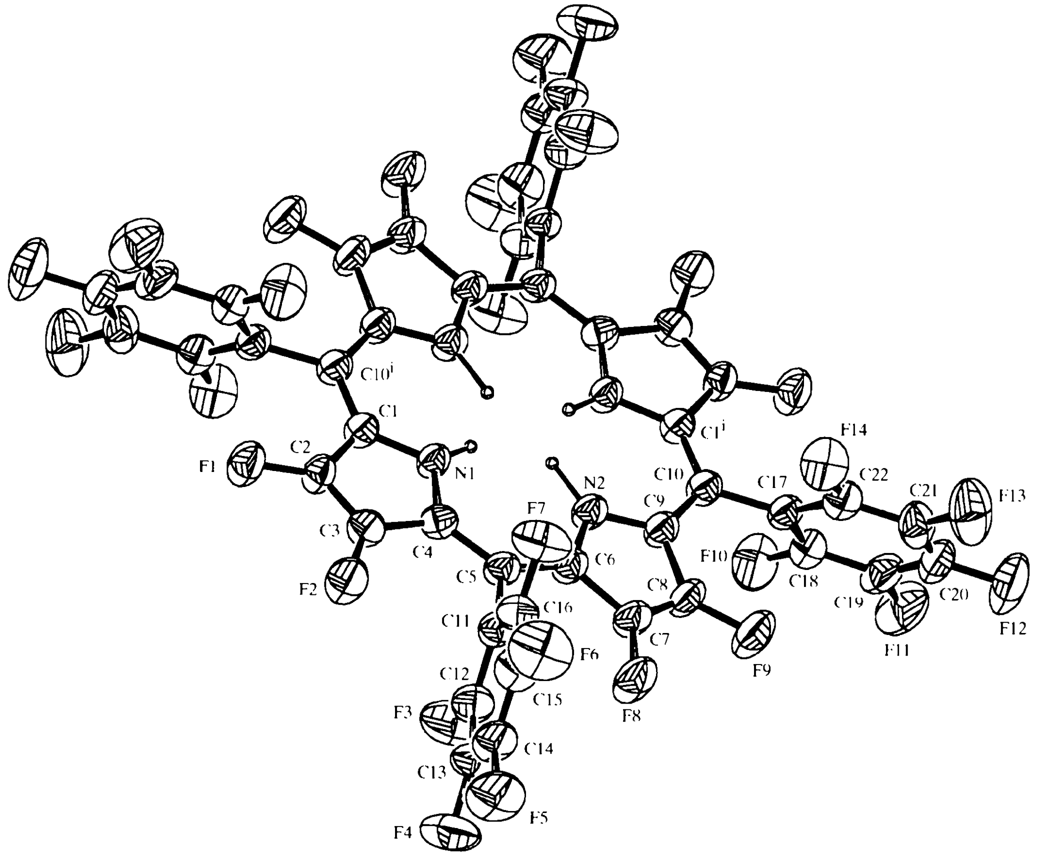

Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids [symmetry code: (i) $1-x, -y, 2-z$]. The H atoms are disordered over the N atoms.

The crystal structure of the Zn^{II} derivative of F$_{28}$TPP was determined by Woller & DiMagno (1997). It was found to be five coordinate with split occupancy of the axial site (between acetonitrile and tetrahydrofuran), and nearly planar. Nevertheless, a slight ruffle distortion (for a definition of ruffling and saddling, see Scheidt & Lee, 1987) was observed at the *meso*-positions. The Zn^{II} complex of the tetraphenyl analogue of F$_{28}$TPP was also found to be five coordinate with a water molecule as an axial ligand. The structure appeared to be more severely distorted, displaying a pronounced saddle shape (Leroy *et al.*, 1997). As a fifth, axial ligand is present in Zn^{II} complexes, the structure of F$_{28}$TPP can be compared more closely with those of tetraphenylporphyrin (TPP) (Silvers & Tulinsky, 1967) and 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TFPP) (Birnbaum *et al.*, 1995).

The porphyrin ring of F$_{28}$TPP is distorted with a slight ruffling, with the largest deviations of the C atoms of the porphyrin ring (from the plane defined by the four N atoms) occurring at the β positions (C2, C3, C7 and C8) as shown in Fig. 2. The phenyl groups are rotated out of the mean porphyrin plane by 72.2 (1) and 89.1 (1)° compared with 61.0 and 63.1° for TPP and an average value of 79° for TFPP. The geometry of the porphyrin core in F$_{28}$TPP is as expected with N$\cdots$*Ct* distances of 2.048 (3) and 2.097 (3) Å compared with 2.03 and 2.10 Å for TPP, and 2.02 and 2.09 Å for TFPP (N$\cdots$*Ct*

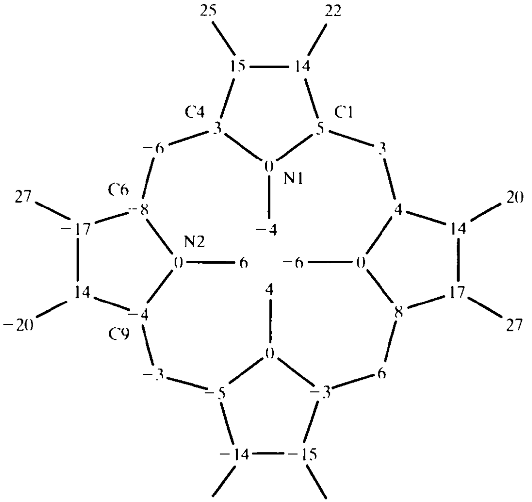

Fig. 2. Formal diagram of the porphyrinato core showing deviation of each unique atom from the mean plane of the core (units 0.01 Å, s.u.'s 0.003 Å).

is defined as the distance between the centre of the molecule and a projection of the N atoms onto the porphyrin plane).

Experimental

The title compound was prepared from 3,4-difluoropyrrole (Leroy & Wakselman, 1994) and pentafluorobenzaldehyde under Lindsey conditions (Lindsey *et al.*, 1987) as described for β-octafluorotetraphenyl porphyrin (Leroy *et al.*, 1997; Woller & DiMagno, 1997). A suitable crystal for X-ray diffraction was obtained by slow evaporation of a chloroform solution.

Crystal data

$C_{44}H_2F_{28}N_4$
$M_r = 1118.5$
Triclinic
$P\bar{1}$
$a = 6.182\,(1)$ Å
$b = 13.008\,(3)$ Å
$c = 13.605\,(9)$ Å
$\alpha = 105.00\,(3)°$
$\beta = 92.46\,(3)°$
$\gamma = 101.74\,(2)°$
$V = 1029.3\,(7)$ Å^3
$Z = 1$
$D_x = 1.804$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.0–12.5°$
$\mu = 0.197$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.48 × 0.42 × 0.33 mm
Purple

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
4909 measured reflections
4481 independent reflections
2901 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.015$
$\theta_{\rm max} = 26.97°$
$h = 0 \rightarrow 7$
$k = -16 \rightarrow 16$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.127$
$S = 1.024$
4481 reflections
344 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0644P)^2 + 0.2708P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.608$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.219$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.010 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C4	1.367 (3)	C4—C5	1.402 (3)
N1—C1	1.369 (3)	C5—C6	1.400 (3)
N2—C6	1.370 (2)	C5—C11	1.491 (3)
N2—C9	1.374 (3)	C6—C7	1.436 (3)
C1—C10$^{\rm i}$	1.402 (3)	C7—C8	1.338 (3)
C1—C2	1.438 (3)	C8—C9	1.431 (3)
C2—C3	1.326 (3)	C9—C10	1.391 (3)
C3—C4	1.447 (3)		
C4—N1—C1	108.03 (16)	C6—C5—C4	125.25 (18)
C6—N2—C9	109.41 (16)	N2—C6—C5	125.87 (18)
N1—C1—C10$^{\rm i}$	127.11 (18)	N2—C6—C7	106.99 (17)
N1—C1—C2	108.15 (18)	C5—C6—C7	127.13 (18)
C10$^{\rm i}$—C1—C2	124.75 (18)	C8—C7—C6	108.16 (18)
C3—C2—C1	108.06 (19)	C7—C8—C9	108.49 (18)
C2—C3—C4	107.81 (19)	N2—C9—C10	126.63 (18)
N1—C4—C5	126.86 (18)	N2—C9—C8	106.94 (17)
N1—C4—C3	107.93 (18)	C10—C9—C8	126.39 (18)
C5—C4—C3	125.21 (19)	C9—C10—C1$^{\rm i}$	125.45 (18)

Symmetry code: (i) $1 - x, -y, 2 - z$.

During the refinement calculations, the H atoms were found in a difference electron-density map. They appear as two half-atoms disordered between the two N atoms in the asymmetric unit (half a molecule). As a result of this situation, the possibility of the space group $P1$ was also investigated. In this hypothesis, a difference electron-density map reveals four peaks which are assigned to four half-H atoms. The delocalization of these two H atoms across four N atoms may therefore be assigned to statistical disorder and not to a symmetry problem.

Backgrounds were obtained from analysis of the scan profile (Blessing *et al.*, 1974).

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1059). Services for accessing these data are described at the back of the journal.

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