

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 $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.215 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.265 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
SHELXL97 (Sheldrick,
 1997a)
 Extinction coefficient:
 0.0260 (14)
 Scattering factors from
International Tables for
Crystallography (Vol. C)

Sheldrick, G. M. (1997b). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
 Stoe & Cie (1987a). *EMPIR. Empirical Absorption Correction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
 Stoe & Cie (1987b). *DIF4. Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
 Stoe & Cie (1987c). *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
 Taylor, R., Kennard, O. & Versichel, W. (1984). *J. Am. Chem. Soc.* **106**, 244–248.

Table 3. Selected geometric parameters ($\text{\AA}$, $^\circ$) 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 ($\text{\AA}$, $^\circ$) 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: *DIF4* (Stoe & Cie, 1987b); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1987c); program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997b); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); 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: 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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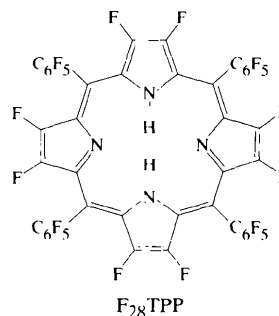
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Abstract

The core of the title compound, C₄₄H₂F₂₈N₄, is essentially planar while the pentafluorophenyl groups are nearly perpendicular to the mean porphyrin plane. The molecule is centrosymmetric.

Comment

The title compound, F₂₈TPP, 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 F₂₈TPP (Fig. 1) was determined, amongst others, in an attempt to correlate this porphyrin structure with the unusual spectroscopic data observed.



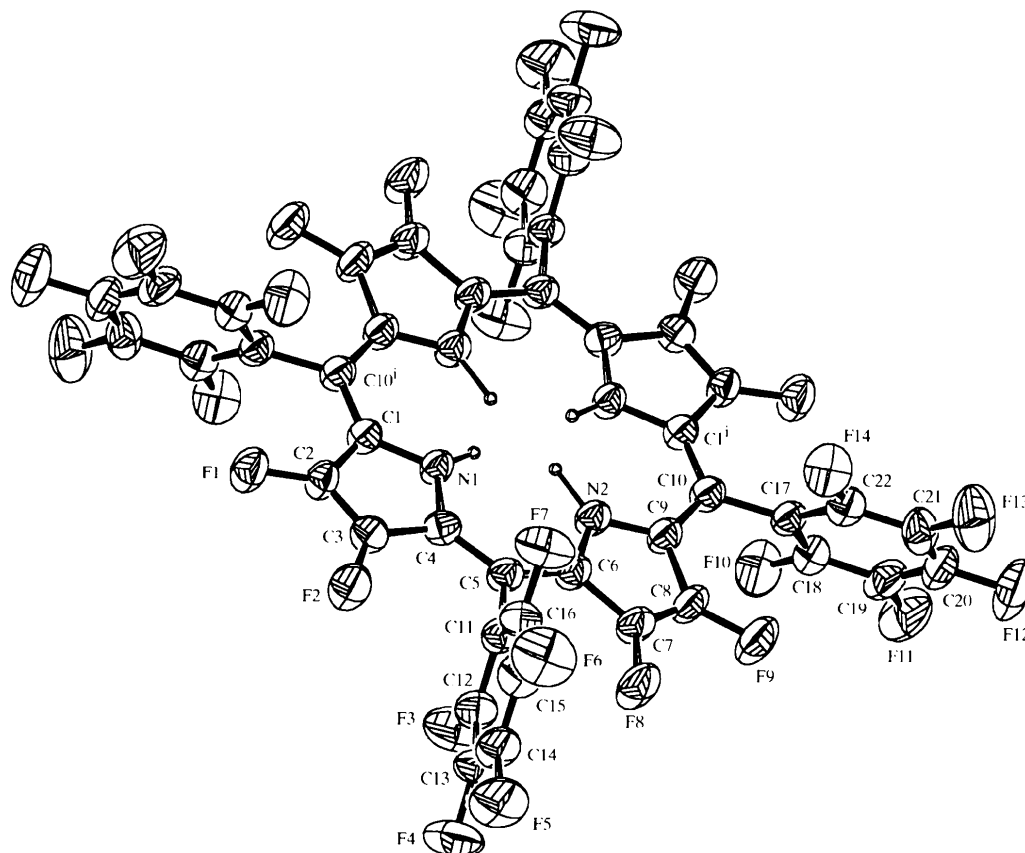
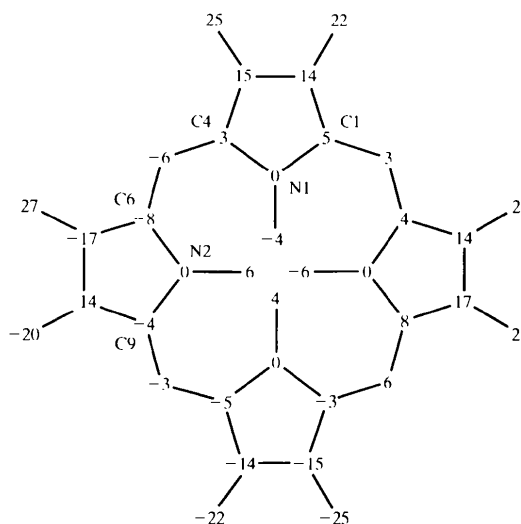


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids [symmetry code: (i) $1 - x, -y, 2 - z$]. The H atoms are disordered over the N atoms.

The crystal structure of the Zn^{II} derivative of F_{28}TPP was determined by Woller & DiMaggio (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) (Birnbbaum *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 $72.2(1)^\circ$ and $89.1(1)^\circ$ 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 $\text{N}\cdots\text{Ct}$ 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 ($\text{N}\cdots\text{Ct}$



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 ₂ F ₂₈ N ₄	Mo K α radiation
$M_r = 1118.5$	$\lambda = 0.71073 \text{ \AA}$
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	$\theta = 9.0\text{--}12.5^\circ$
$a = 6.182 (1) \text{ \AA}$	$\mu = 0.197 \text{ mm}^{-1}$
$b = 13.008 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 13.605 (9) \text{ \AA}$	Prism
$\alpha = 105.00 (3)^\circ$	$0.48 \times 0.42 \times 0.33 \text{ mm}$
$\beta = 92.46 (3)^\circ$	Purple
$\gamma = 101.74 (2)^\circ$	
$V = 1029.3 (7) \text{ \AA}^3$	
$Z = 1$	
$D_x = 1.804 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.015$
ω scans	$\theta_{\text{max}} = 26.97^\circ$
Absorption correction: none	$h = 0 \rightarrow 7$
4909 measured reflections	$k = -16 \rightarrow 16$
4481 independent reflections	$l = -17 \rightarrow 17$
2901 reflections with $I > 2\sigma(I)$	3 standard reflections
	frequency: 60 min
	intensity decay: 0.5%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$\Delta\rho_{\text{max}} = 0.608 \text{ e \AA}^{-3}$
$wR(F^2) = 0.127$	$\Delta\rho_{\text{min}} = -0.219 \text{ e \AA}^{-3}$
$S = 1.024$	Extinction correction:
4481 reflections	<i>SHELXL97</i> (Sheldrick, 1997a)
344 parameters	Extinction coefficient:
H-atom parameters not refined	$0.010 (2)$
$w = 1/[\sigma^2(F_o^2) + (0.0644P)^2 + 0.2708P]$	Scattering factors from
where $P = (F_o^2 + 2F_c^2)/3$	<i>International Tables for Crystallography</i> (Vol. C)

Table 1. Selected geometric parameters ($\text{\AA}$, $^\circ$)

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 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 ⁱ	127.11 (18)	N2—C6—C7	106.99 (17)
N1—C1—C2	108.15 (18)	C5—C6—C7	127.13 (18)
C10 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 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: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *ORTEPII* (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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