organic compounds

5,10,15,20-Tetrakis(3,5-difluorophenyl)-porphyrin

P. Bhyrappa,[a]* V. Velkannan[a] and B. Varghese[b]

[a]Department of Chemistry, Indian Institute of Technology Madras, Chennai-600 036, India, and [b]Sophisticated Analytical Instrument Facility, Indian Institute of Technology Madras, Chennai-600 036, India
Correspondence e-mail: pbhyrappa@hotmail.com

The crystal structure of the title compound, $C_{44}H_{22}F_8N_4$, shows an unusual non-planar geometry of the porphyrin ring although the molecule is free of steric crowding around the periphery of the macrocycle. The molecular packing exhibits weak intermolecular hydrogen bonding (C—H···F) and C—H···π interactions. The molecular symmetry is $\bar{4}$.

Related literature

For the stereochemistry of porphyrins and metalloporphyrins, see: Senge (2000); Scheidt & Lee (1987). For a related structure, see: Silvers & Tulinsky (1967). For the preparation of the title compound, see: Tamiaki *et al.* (2000). For C—H···π and C—H···F interactions, see: Steiner (2002); Thalladi *et al.* (1998).
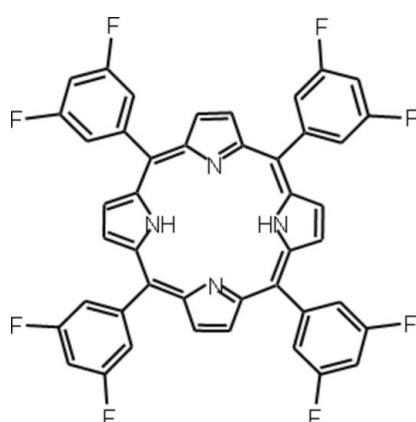
Experimental

Crystal data

$C_{44}H_{22}F_8N_4$	Tetragonal, $I\bar{4}2d$
$M_r = 758.66$	$a = 15.426$ (5) Å
$c = 13.991$ (5) Å	$\mu = 0.12$ mm^{-1}
$V = 3329.3$ (19) Å^3	$T = 233$ (2) K
$Z = 4$	$0.30 \times 0.20 \times 0.20$ mm
Mo $K\alpha$ radiation	

Data collection

Bruker APEXII CCD area-detector diffractometer	20353 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	1145 independent reflections
$T_{min} = 0.965$, $T_{max} = 0.986$	1049 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	127 parameters
$wR(F^2) = 0.098$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
1145 reflections	$\Delta\rho_{min} = -0.15$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···C1[i]	0.93	2.87	3.634 (2)	140
C3—H3···F1[ii]	0.93	2.66	3.484 (2)	148

Symmetry codes: (i) $y + 1, x - \frac{1}{2}, z + \frac{1}{4}$; (ii) $-x + 2, -y, z$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-32* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

References

Bruker (1999). *SADABS*. Brucker AXS Inc., Madison, Wisconsin, USA.
Bruker (2004). *APEX2* (Version 1.22) and *SAINT-Plus* (Version 7.6). Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
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.
Scheidt, W. R. & Lee, Y. J. (1987). *Struct. Bonding (Berlin)*, **64**, 1–73.
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. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Silvers, S. J. & Tulinsky, A. (1967). *J. Am. Chem. Soc.* **89**, 3331–3336.
Steiner, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.
Tamiaki, H., Matsumoto, N., Unno, S., Shinoda, S. & Tsukube, H. (2000). *Inorg. Chim. Acta*, **300–302**, 243–249.
Thalladi, V. R., Weiss, H.-C., Blaser, D., Boese, R., Nangia, A. & Desiraju, G. R. (1998). *J. Am. Chem. Soc.* **120**, 8702–8710.

supporting information

5,10,15,20-Tetrakis(3,5-difluorophenyl)porphyrin

P. Bhyrappa, V. Velkannan and B. Varghese

S1. Comment

Free base porphyrin, $H_2T(3',5'-DFP)P$ was synthesised using literature method (Tamiaki et al. 2000). The compound (I) crystallizes in a tetragonal space group, I-4 2d with four molecules in the unit cell. ORTEP of the compound (I) is shown in Fig. 1. The observed bond lengths of the $C_{20}N_4$ core is similar to the related H_2TPP structure (Silvers & Tulinsky, 1967). The molecule shows considerable nonplanar geometry (Fig. 1b) with the extent of distortion of the porphyrin ring atoms is as high as + - 0.343 (4) Å and the average displacement of the β-pyrrole carbon is + - $\Delta C\beta$ = 0.129 (3) Å. Macrocyclic ring (24-atom core) shows ruffled geometry (Senge, 2000) while the related H_2TPP shows nearly planar structure. The opposite nitrogens are situated at 4.082Å and it is shorter than that reported for H_2TPP (4.20 Å)(Silvers & Tulinsky, 1967). The 3,5-difluorophenyl groups are nearly planar and oriented perpendicular to the porphyrin ring mean plane with an average dihedral angle of 72.7 (5) °. In adition, the meso-*i*-carbon to aryl carbon, C5-C6 distance is found to be 1.499 (2) Å indicating that the aryl group is not significantly conjugated with the porphyrin π-system. The core hydrogens are disordered and are fixed with 50% occupancy on each N atom of the N_4H_2 core.

   Molecular packing diagram of the compound (I) is shown in Fig 2. Unit cell ab plane forms the 2-dimensional (C-H⋯F) hydrogen-bonded framework parallel to (001) plane. Each porphyrin in the layer is surrounded by four other nearest neighbours through weak hydrogen bonding (C3-H3⋯F1) interactions. A pair of such C-H⋯F hydrogen bonding is observed with each adjacent porphyrin with a shortest H3⋯F1 distance of 2.656 Å. Such a long hydrogen bonding distance is expected for weak C-H⋯F interactions (Thalladi et al., 1998). Furthermore, layers are interconnected via C-H⋯π interactions (Fig.3). On each face of the porphyrin, there is a pair of symmetry related C-H⋯π interactions for aryl-(C7-H7)⋯C1(α-pyrrole) with H7⋯C1 distance of 2.869 Å between the two other adjacent porphyrins from the neighbouring layer. This H7⋯C1 distance indicates weak C-H⋯π interactions (Steiner, 2002). The title compound shows unusual nonplanar geometry of the macrocyclic ring.

S2. Experimental

5,10,15,20-tetrakis(3',5'-difluorophenyl)porphyrin, $H_2T(3',5'-DFP)P$ was prepared using literature method (Tamiaki *et al.*, 2000). Crystals of $H_2T(3',5'-DFP)P$ were grown by vapor diffusion of hexane to the $CHCl_3$ solution of the porphyrin over a period of five days.

S3. Refinement

H atoms were placed in constrained positions (C—H = 0.93 Å and N—H = 0.86 Å) and refined using riding model with $U_{iso}(H)$ = 1.2 or 1.5 times $U_{eq}(C)$. The Friedel pairs have been merged, because the Flack parameter could not be reliably determined. The structure mostly contains C, H, N atoms only and the data was collected with Mo $K\alpha$ radiation, so no anomalous dispersion effects could be observed.
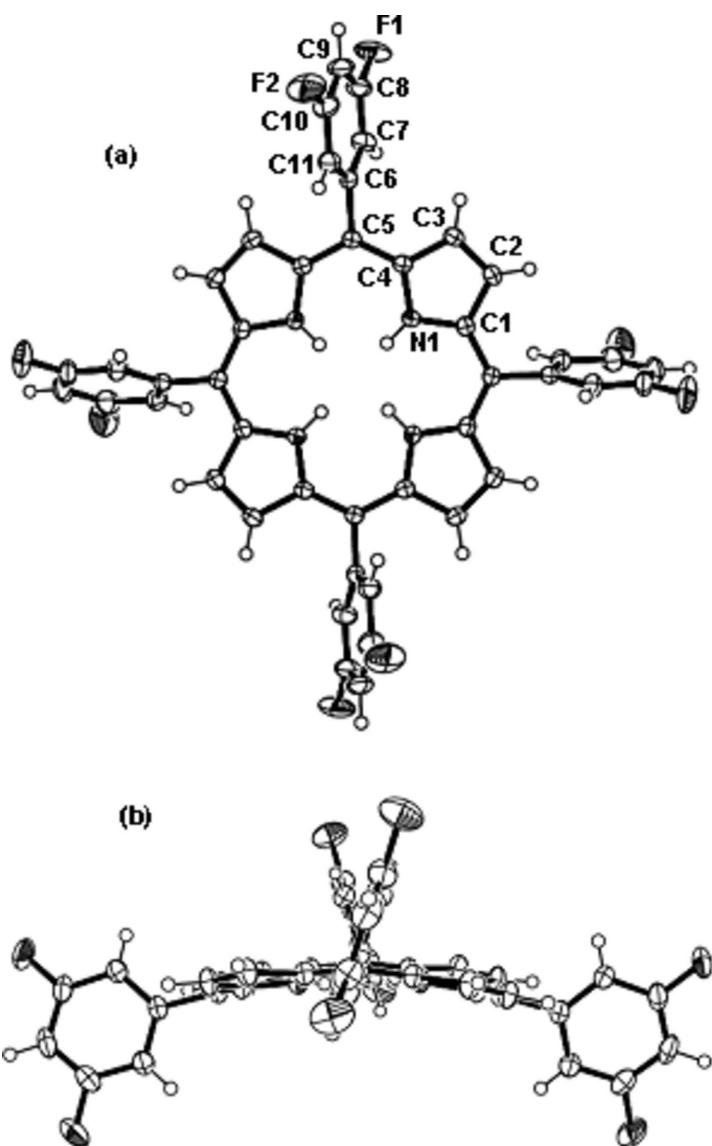
Figure 1

(*a*) The structure of (I) with the atom numbering scheme. Side view of the compound is shown in (*b*). Thermal ellipsoids shown at 50% probability level.
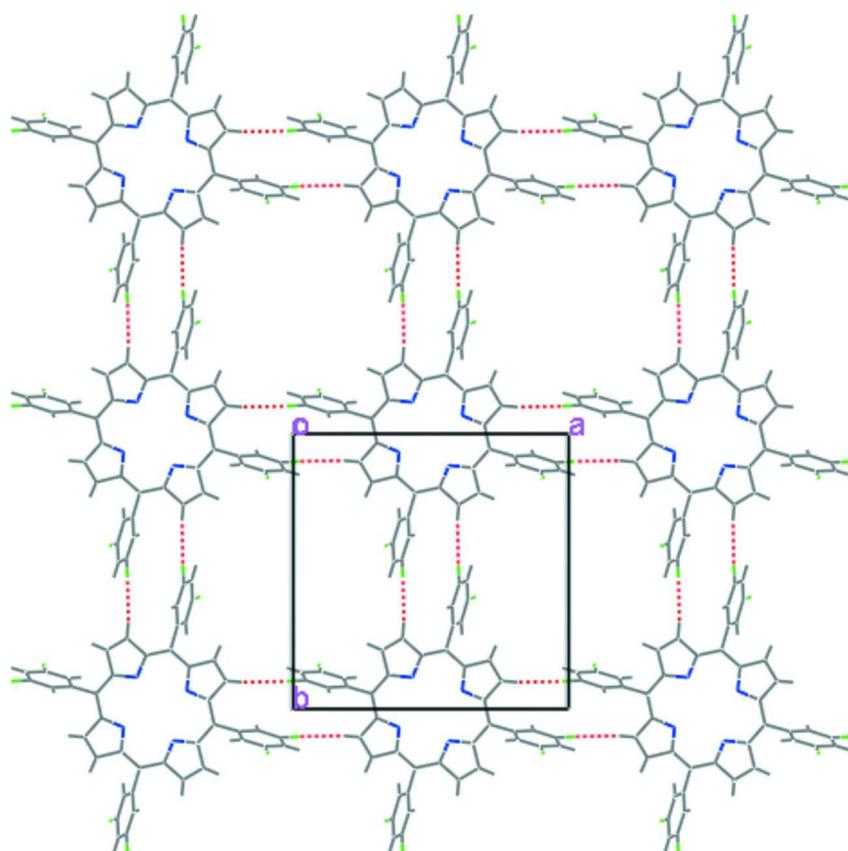
Figure 2

Molecular packing diagram of the compound, (I). The two-dimensional framework shows the C—H···F interactions parallel to *ab* plane.
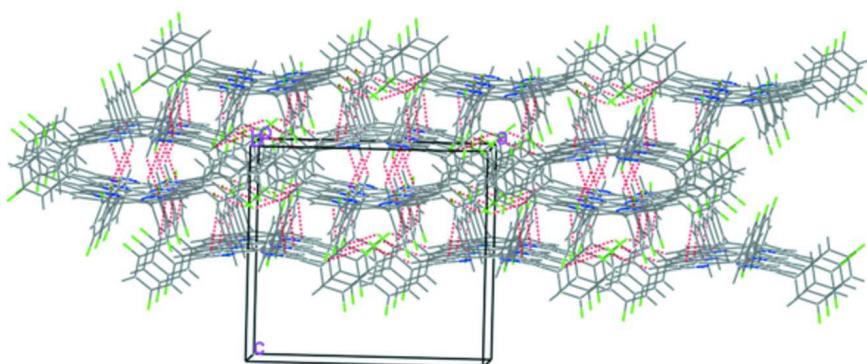
Figure 3

Shows the bridging of two layers by interporphyrin (C—H···π) interactions (viewed along unit cell 'b′ axis). The short contacts are shown in dotted red lines. The flourine atoms are shown in green.

5,10,15,20-Tetrakis(3,5-difluorophenyl)porphyrin

Crystal data

|	
$C_{44}H_{22}F_8N_4$	$D_x = 1.514$ Mg m^{-3}
$M_r = 758.66$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Tetragonal, $I\bar{4}2d$	Cell parameters from 5676 reflections
Hall symbol: I -4 2bw	$\theta = 2.7$–$27.4°$
$a = 15.426$ (5) Å	$\mu = 0.12$ mm^{-1}
$c = 13.991$ (5) Å	$T = 233$ K
$V = 3329.3$ (19) Å^3	Plate, purple
$Z = 4$	$0.30 \times 0.20 \times 0.20$ mm
$F(000) = 1544$	

Data collection

Bruker APEXII CCD area-detector diffractometer	20353 measured reflections
Radiation source: fine-focus sealed tube	1145 independent reflections
Graphite monochromator	1049 reflections with $I > 2\sigma(I)$
ω and φ scan	$R_{int} = 0.041$
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	$\theta_{max} = 28.4°$, $\theta_{min} = 2.0°$
$T_{min} = 0.965$, $T_{max} = 0.986$	$h = -20 \rightarrow 20$
	$k = -19 \rightarrow 18$
	$l = -18 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.036$	H-atom parameters constrained
$wR(F^2) = 0.098$	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 1.6388P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
1145 reflections	$\Delta\rho_{max} = 0.20$ e Å^{-3}
127 parameters	$\Delta\rho_{min} = -0.15$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.62343 (12)	−0.15392 (12)	0.26244 (14)	0.0234 (4)	
C2	0.71372 (13)	−0.17616 (13)	0.25131 (18)	0.0289 (4)	
H2	0.7375	−0.2314	0.2561	0.035*	
C3	0.75734 (13)	−0.10209 (12)	0.23267 (16)	0.0285 (4)	
H3	0.8164	−0.0970	0.2205	0.034*	

C4	0.69521 (12)	−0.03261 (13)	0.23514 (15)	0.0233 (4)	
C5	0.71381 (12)	0.05575 (12)	0.22542 (14)	0.0225 (4)	
C6	0.80391 (13)	0.08176 (12)	0.19734 (15)	0.0240 (4)	
C7	0.87363 (13)	0.07798 (15)	0.25940 (16)	0.0310 (5)	
H7	0.8665	0.0583	0.3217	0.037*	
C8	0.95385 (14)	0.10405 (16)	0.22687 (18)	0.0353 (5)	
C9	0.96818 (14)	0.13294 (16)	0.1348 (2)	0.0385 (6)	
H9	1.0230	0.1496	0.1141	0.046*	
C10	0.89782 (17)	0.13583 (16)	0.07556 (17)	0.0380 (5)	
C11	0.81595 (13)	0.11143 (15)	0.10383 (16)	0.0299 (5)	
H11	0.7695	0.1146	0.0616	0.036*	
N1	0.61430 (10)	−0.06642 (10)	0.25215 (12)	0.0230 (4)	
H1	0.5666	−0.0377	0.2557	0.028*	0.50
F1	1.02219 (8)	0.10061 (13)	0.28671 (12)	0.0550 (5)	
F2	0.90872 (12)	0.16429 (14)	−0.01500 (13)	0.0632 (5)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0216 (9)	0.0199 (8)	0.0288 (10)	0.0015 (7)	−0.0003 (8)	0.0020 (7)
C2	0.0221 (9)	0.0225 (9)	0.0420 (11)	0.0048 (7)	0.0006 (9)	0.0041 (9)
C3	0.0190 (9)	0.0260 (9)	0.0404 (11)	0.0033 (7)	0.0033 (8)	0.0040 (9)
C4	0.0180 (8)	0.0239 (9)	0.0280 (9)	0.0000 (7)	0.0029 (8)	0.0009 (7)
C5	0.0193 (8)	0.0209 (9)	0.0273 (9)	0.0001 (7)	0.0017 (7)	0.0001 (7)
C6	0.0211 (9)	0.0183 (8)	0.0325 (9)	0.0001 (7)	0.0040 (8)	−0.0020 (8)
C7	0.0237 (10)	0.0389 (11)	0.0302 (10)	−0.0006 (8)	0.0031 (8)	−0.0023 (9)
C8	0.0207 (9)	0.0393 (12)	0.0458 (12)	−0.0035 (9)	−0.0008 (9)	−0.0085 (11)
C9	0.0239 (10)	0.0382 (12)	0.0533 (14)	−0.0089 (9)	0.0134 (10)	−0.0070 (11)
C10	0.0377 (12)	0.0366 (12)	0.0396 (12)	−0.0041 (10)	0.0124 (10)	0.0048 (10)
C11	0.0252 (9)	0.0305 (10)	0.0340 (10)	−0.0003 (9)	0.0014 (8)	0.0046 (9)
N1	0.0169 (7)	0.0201 (8)	0.0319 (9)	−0.0001 (6)	0.0009 (7)	0.0015 (6)
F1	0.0214 (7)	0.0862 (13)	0.0575 (9)	−0.0066 (7)	−0.0062 (6)	−0.0118 (10)
F2	0.0548 (10)	0.0853 (13)	0.0495 (9)	−0.0146 (9)	0.0159 (8)	0.0246 (9)

Geometric parameters (Å, º)

C1—N1	1.365 (2)	C6—C11	1.398 (3)
C1—C5ⁱ	1.404 (3)	C7—C8	1.378 (3)
C1—C2	1.443 (3)	C7—H7	0.9300
C2—C3	1.351 (3)	C8—F1	1.347 (3)
C2—H2	0.9300	C8—C9	1.381 (4)
C3—C4	1.438 (3)	C9—C10	1.366 (4)
C3—H3	0.9300	C9—H9	0.9300
C4—N1	1.373 (3)	C10—F2	1.351 (3)
C4—C5	1.400 (3)	C10—C11	1.376 (3)
C5—C1ⁱⁱ	1.404 (3)	C11—H11	0.9300
C5—C6	1.499 (3)	N1—H1	0.8600
C6—C7	1.383 (3)		

N1—C1—C5ⁱ	125.93 (17)	C8—C7—C6	118.6 (2)
N1—C1—C2	108.87 (16)	C8—C7—H7	120.7
C5ⁱ—C1—C2	125.04 (17)	C6—C7—H7	120.7
C3—C2—C1	107.48 (17)	F1—C8—C7	119.1 (2)
C3—C2—H2	126.3	F1—C8—C9	117.9 (2)
C1—C2—H2	126.3	C7—C8—C9	123.1 (2)
C2—C3—C4	107.07 (17)	C10—C9—C8	116.69 (19)
C2—C3—H3	126.5	C10—C9—H9	121.7
C4—C3—H3	126.5	C8—C9—H9	121.7
N1—C4—C5	124.97 (17)	F2—C10—C9	118.7 (2)
N1—C4—C3	109.07 (16)	F2—C10—C11	118.2 (2)
C5—C4—C3	125.93 (18)	C9—C10—C11	123.1 (2)
C4—C5—C1ⁱⁱ	125.26 (18)	C10—C11—C6	118.7 (2)
C4—C5—C6	118.44 (16)	C10—C11—H11	120.6
C1ⁱⁱ—C5—C6	116.28 (17)	C6—C11—H11	120.6
C7—C6—C11	119.85 (18)	C1—N1—C4	107.47 (16)
C7—C6—C5	123.03 (19)	C1—N1—H1	126.3
C11—C6—C5	117.12 (18)	C4—N1—H1	126.3
N1—C1—C2—C3	−1.2 (3)	C6—C7—C8—F1	−179.98 (19)
C5ⁱ—C1—C2—C3	174.4 (2)	C6—C7—C8—C9	−0.7 (4)
C1—C2—C3—C4	1.9 (3)	F1—C8—C9—C10	−180.0 (2)
C2—C3—C4—N1	−2.0 (3)	C7—C8—C9—C10	0.7 (4)
C2—C3—C4—C5	175.8 (2)	C8—C9—C10—F2	179.5 (2)
N1—C4—C5—C1ⁱⁱ	4.3 (3)	C8—C9—C10—C11	−0.2 (4)
C3—C4—C5—C1ⁱⁱ	−173.2 (2)	F2—C10—C11—C6	179.9 (2)
N1—C4—C5—C6	−174.02 (18)	C9—C10—C11—C6	−0.4 (4)
C3—C4—C5—C6	8.5 (3)	C7—C6—C11—C10	0.4 (3)
C4—C5—C6—C7	−74.1 (3)	C5—C6—C11—C10	−180.0 (2)
C1ⁱⁱ—C5—C6—C7	107.5 (2)	C5ⁱ—C1—N1—C4	−175.62 (19)
C4—C5—C6—C11	106.3 (2)	C2—C1—N1—C4	−0.1 (2)
C1ⁱⁱ—C5—C6—C11	−72.1 (2)	C5—C4—N1—C1	−176.6 (2)
C11—C6—C7—C8	0.1 (3)	C3—C4—N1—C1	1.3 (2)
C5—C6—C7—C8	−179.5 (2)		

Symmetry codes: (i) $y+1/2$, $−x+1/2$, $−z+1/2$; (ii) $−y+1/2$, $x−1/2$, $−z+1/2$.

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C7—H7⋯C1ⁱⁱⁱ	0.93	2.87	3.634 (2)	140
C3—H3⋯F1ⁱᵛ	0.93	2.66	3.484 (2)	148

Symmetry codes: (iii) $y+1$, $x−1/2$, $z+1/4$; (iv) $−x+2$, $−y$, z.