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N,*N*′-Bis(2,2,3,3,4,4,4-heptafluorobutyl)-naphthalene-1,4:5,8-tetracarboximide

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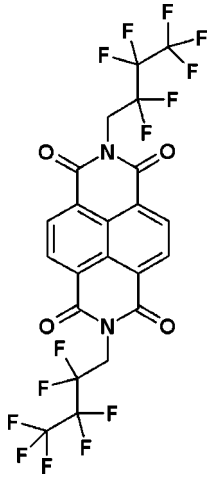
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.008 Å; R factor = 0.067; wR factor = 0.223; data-to-parameter ratio = 11.0.

The title molecule, $C_{22}H_8F_{14}N_2O_4$, lies across a crystallographic inversion center with the naphthalene diimide core essentially planar (mean deviation from plane is 0.0583 Å). The CF_2 groups in the perfluorobutyl chains are in an energetically favorable all *trans* conformation. In the crystal structure, molecules are packed in slightly displaced layers so that the side chains overlap the aromatic naphthalene diimide rings, thus minimizing any possible π–π overlap.

Related literature

For general background on the semic-conducting properties and use of this class of materials in organic thin-film transistor applications, see: Chesterfield *et al.* (2004*a*,*b*); Facceti *et al.* (2008); Jones *et al.* (2004); Katz *et al.* (2000*a*,*b*); Kazmaier & Hoffmann (1994); Klebe *et al.* (1989); Shukla *et al.* (2008); Wurthner (2004).



Experimental

Crystal data

$C_{22}H_8F_{14}N_2O_4$
M_r = 630.30
Triclinic, $P\overline{1}$
a = 5.1910 (5) Å
b = 10.1459 (12) Å
c = 11.5988 (15) Å
α = 66.693 (4)°
β = 79.064 (4)°
γ = 89.115 (7)°
V = 549.64 (11) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.21 mm^{-1}
T = 293 (2) K
0.15 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
3049 measured reflections
2094 independent reflections
909 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.223
S = 0.93
2094 reflections
190 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *Materials Studio* (Accelrys, 2002); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2728).

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N,*N*′-Bis(2,2,3,3,4,4,4-heptafluorobutyl)naphthalene-1,4:5,8-tetracarboximide

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S1. Comment

Amongst n-type semiconductors used in organic thin film transistors, perylene diimides (PDIs) and naphthalene diimides (NDIs) have attracted considerable attention. The π -orbital wavefunctions in these systems form nodes at the two nitrogen positions in the imide rings. Indeed, it has been shown that semiconducting properties and device performance of these materials is very sensitive to the nature of substituents on the diimide nitrogen atoms. The title compound *N*,*N*′-Bis(1*H*,1*H*-perfluorobutyl) naphthalene- 1,4,5,8-tetracarboxylic acid diimide(I) has been shown to exhibit good n-type semiconducting behavior and OTFTs made incorporating I can be operated in air. The latter property has been ascribed to the denser packing of fluorinated alkyl chains in thin film.

Naphthalene diimide (NDI) and perylene diimide (PDI) based systems have been studied extensively (Chesterfield, *et al.*, 2004*a*; Chesterfield *et al.*, 2004*b*; Facceti *et al.*, 2008; Jones, *et al.*, 2004; Katz, *et al.*, 2000*a*; Katz, *et al.*, 2000*b*). We report here the structure of the title diimide molecule (I) (Fig. 1 and Fig 2). In the crystal structure, molecules are packed in slightly displaced layers so that the side chains overlap the aromatic naphthalene diimide rings, thus resulting in minimizing any possible π-π overlap (Fig .3).

S2. Experimental

The method described in Katz *et al.*, 2000*a*, was followed for preparation of the title compound (I). Crystals of title (I) appeared during powder X-ray diffraction data collection of the dry lot sample. The crystals were weakly diffracting, but we were unable to get better quality crystals. Diffraction data were collected on various crystals, and the results of structure determination using best data set results are reported here.

S3. Refinement

All H-atoms were positioned geometrically and refined using a riding model with d(C—H) = 0.93 Å, U_{iso}=1.2U_{eq} (C) for aromatic 0.97 Å, U_{iso} = 1.2U_{eq} (C) for CH_2 atoms.

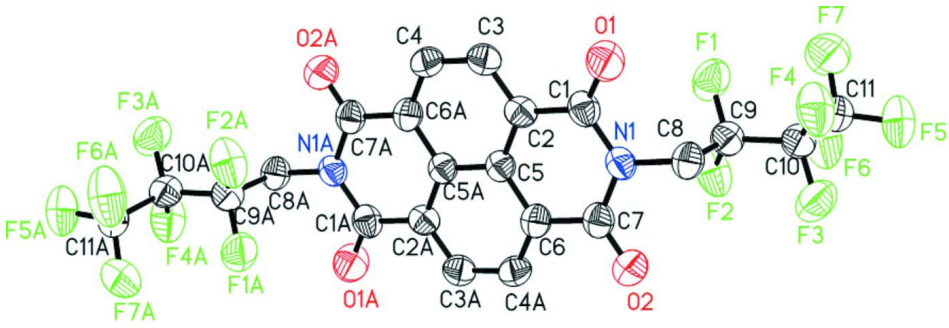

Figure 1

Molecular structure of the title compound, with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

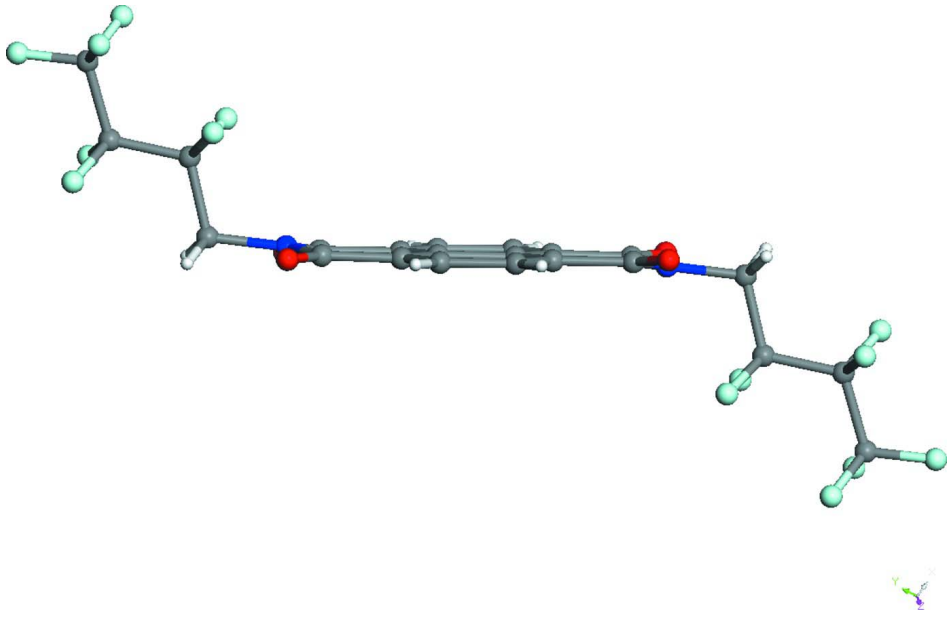

Figure 2

A diagram illustrating planar naphthalene diimide core and *trans* configuration of perfluorobutyl chains on diiimide N atoms.

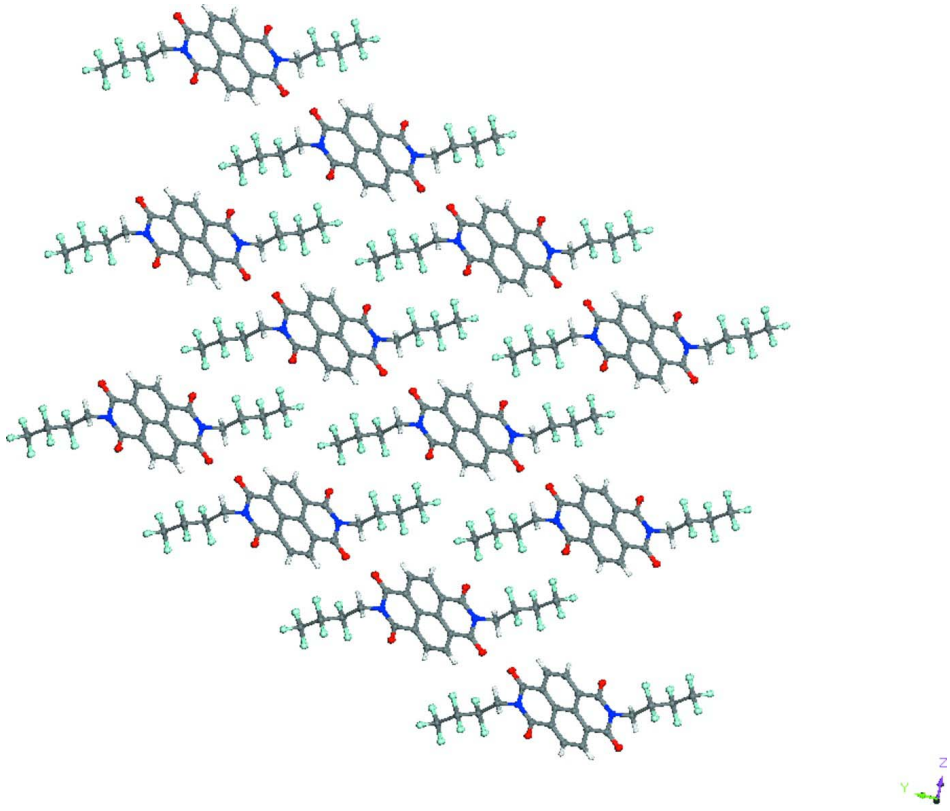

Figure 3

Unit cell packing showing layered structure.

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Crystal data

$C_{22}H_8F_{14}N_2O_4$
$M_r = 630.30$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 5.1910\ (5)$ Å
$b = 10.1459\ (12)$ Å
$c = 11.5988\ (15)$ Å
$\alpha = 66.693\ (4)°$
$\beta = 79.064\ (4)°$
$\gamma = 89.115\ (7)°$
$V = 549.64\ (11)$ Å^3
$Z = 1$
$F(000) = 312$
$D_x = 1.904$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4558 reflections
$\theta = 1.0–26.7°$
$\mu = 0.21$ mm^{-1}
$T = 293$ K
Needle, pink
0.15 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 9 pixels mm^{-1}
φ and ω scans
3049 measured reflections
2094 independent reflections
909 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 26.6°$, $\theta_{min} = 4.1°$
$h = -6\rightarrow6$
$k = -12\rightarrow11$
$l = -14\rightarrow12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.223$
$S = 0.93$
2094 reflections
190 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.3623P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.1050 (6)	0.4145 (3)	0.7561 (3)	0.0814 (11)
F2	0.1713 (6)	0.5174 (3)	0.8788 (3)	0.0828 (12)
F3	0.5849 (6)	0.3623 (4)	0.9393 (3)	0.0873 (12)
F4	0.5572 (7)	0.2684 (3)	0.8049 (3)	0.0883 (12)
F5	0.3622 (7)	0.0974 (4)	1.0537 (3)	0.0931 (12)
F6	0.0806 (7)	0.2472 (4)	1.0654 (4)	0.1050 (15)
F7	0.0800 (9)	0.1477 (4)	0.9346 (4)	0.1234 (17)
O1	0.2493 (8)	0.6081 (4)	0.4924 (4)	0.0742 (12)
O2	0.5194 (8)	0.8024 (4)	0.7439 (4)	0.0725 (12)
N1	0.3566 (7)	0.6967 (4)	0.6298 (4)	0.0484 (11)
C1	0.2325 (10)	0.7037 (5)	0.5308 (5)	0.0528 (14)
C2	0.0799 (9)	0.8305 (5)	0.4790 (5)	0.0467 (12)
C3	−0.0607 (10)	0.8401 (5)	0.3865 (5)	0.0562 (14)
H3	−0.0557	0.7679	0.3559	0.067*
C4	−0.2109 (10)	0.9584 (5)	0.3386 (5)	0.0541 (14)
H4	−0.3058	0.9637	0.2767	0.065*
C5	0.0752 (9)	0.9387 (5)	0.5243 (4)	0.0440 (12)
C6	0.2199 (9)	0.9345 (5)	0.6184 (5)	0.0482 (13)
C7	0.3779 (10)	0.8079 (5)	0.6691 (5)	0.0523 (14)
C8	0.4892 (9)	0.5658 (5)	0.6912 (5)	0.0537 (14)
H8A	0.6355	0.5891	0.7224	0.064*
H8B	0.5580	0.5257	0.6292	0.064*
C9	0.2958 (10)	0.4562 (6)	0.8023 (5)	0.0544 (14)
C10	0.4188 (10)	0.3238 (5)	0.8827 (5)	0.0550 (14)
C11	0.2281 (13)	0.2022 (6)	0.9871 (6)	0.0676 (16)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.061 (2)	0.082 (2)	0.086 (2)	−0.0057 (16)	−0.0279 (18)	−0.0114 (19)
F2	0.091 (2)	0.063 (2)	0.074 (2)	0.0213 (17)	0.0167 (18)	−0.0222 (18)
F3	0.074 (2)	0.098 (3)	0.083 (3)	−0.0005 (18)	−0.0340 (18)	−0.021 (2)
F4	0.108 (3)	0.077 (2)	0.070 (2)	0.0396 (19)	−0.0012 (19)	−0.0278 (19)
F5	0.107 (3)	0.071 (2)	0.078 (2)	0.025 (2)	−0.018 (2)	−0.0064 (19)
F6	0.101 (3)	0.087 (3)	0.082 (3)	0.023 (2)	0.026 (2)	−0.007 (2)
F7	0.147 (4)	0.081 (3)	0.125 (4)	−0.039 (3)	−0.057 (3)	−0.008 (3)
O1	0.095 (3)	0.070 (3)	0.073 (3)	0.031 (2)	−0.024 (2)	−0.042 (2)
O2	0.079 (3)	0.067 (3)	0.080 (3)	0.0131 (19)	−0.038 (2)	−0.029 (2)
N1	0.054 (2)	0.040 (2)	0.051 (3)	0.0061 (18)	−0.010 (2)	−0.018 (2)
C1	0.059 (3)	0.046 (3)	0.052 (3)	0.009 (3)	−0.006 (3)	−0.021 (3)
C2	0.049 (3)	0.048 (3)	0.044 (3)	0.003 (2)	−0.002 (2)	−0.023 (3)
C3	0.068 (3)	0.051 (3)	0.057 (3)	0.006 (3)	−0.015 (3)	−0.028 (3)
C4	0.064 (3)	0.058 (3)	0.047 (3)	0.005 (3)	−0.016 (2)	−0.026 (3)
C5	0.045 (3)	0.044 (3)	0.038 (3)	0.001 (2)	−0.002 (2)	−0.014 (2)
C6	0.046 (3)	0.051 (3)	0.041 (3)	0.003 (2)	−0.003 (2)	−0.014 (3)
C7	0.051 (3)	0.052 (3)	0.044 (3)	0.000 (2)	−0.004 (3)	−0.012 (3)
C8	0.050 (3)	0.055 (3)	0.051 (3)	0.009 (2)	−0.010 (2)	−0.017 (3)
C9	0.053 (3)	0.056 (3)	0.057 (4)	0.010 (3)	−0.010 (3)	−0.026 (3)
C10	0.060 (3)	0.058 (3)	0.054 (3)	0.014 (3)	−0.011 (3)	−0.031 (3)
C11	0.085 (4)	0.056 (4)	0.058 (4)	0.003 (3)	−0.024 (4)	−0.015 (3)

Geometric parameters (Å, º)

F1—C9	1.357 (6)	C2—C5	1.389 (6)
F2—C9	1.341 (6)	C3—C4	1.402 (7)
F3—C10	1.325 (6)	C3—H3	0.9300
F4—C10	1.338 (6)	C4—C6^{i}	1.360 (7)
F5—C11	1.321 (6)	C4—H4	0.9300
F6—C11	1.294 (7)	C5—C6	1.425 (6)
F7—C11	1.314 (6)	C5—C5^{i}	1.435 (9)
O1—C1	1.213 (6)	C6—C4^{i}	1.360 (7)
O2—C7	1.223 (6)	C6—C7	1.491 (7)
N1—C7	1.387 (6)	C8—C9	1.522 (7)
N1—C1	1.398 (6)	C8—H8A	0.9700
N1—C8	1.467 (6)	C8—H8B	0.9700
C1—C2	1.477 (7)	C9—C10	1.513 (7)
C2—C3	1.380 (7)	C10—C11	1.539 (8)
C7—N1—C1	124.8 (4)	N1—C8—C9	109.7 (4)
C7—N1—C8	117.3 (5)	N1—C8—H8A	109.7
C1—N1—C8	117.8 (4)	C9—C8—H8A	109.7
O1—C1—N1	120.4 (5)	N1—C8—H8B	109.7
O1—C1—C2	123.0 (5)	C9—C8—H8B	109.7
N1—C1—C2	116.6 (5)	H8A—C8—H8B	108.2

C3—C2—C5	120.2 (5)	F2—C9—F1	105.5 (4)
C3—C2—C1	119.6 (5)	F2—C9—C10	108.6 (4)
C5—C2—C1	120.2 (5)	F1—C9—C10	108.7 (4)
C2—C3—C4	120.1 (5)	F2—C9—C8	110.1 (4)
C2—C3—H3	119.9	F1—C9—C8	109.2 (4)
C4—C3—H3	119.9	C10—C9—C8	114.3 (4)
C6^{i}—C4—C3	120.9 (5)	F3—C10—F4	107.7 (4)
C6^{i}—C4—H4	119.6	F3—C10—C9	109.0 (4)
C3—C4—H4	119.6	F4—C10—C9	108.5 (4)
C2—C5—C6	122.3 (5)	F3—C10—C11	107.7 (5)
C2—C5—C5^{i}	120.6 (6)	F4—C10—C11	107.2 (5)
C6—C5—C5^{i}	117.2 (6)	C9—C10—C11	116.4 (5)
C4^{i}—C6—C5	121.0 (5)	F6—C11—F7	109.6 (6)
C4^{i}—C6—C7	121.4 (5)	F6—C11—F5	108.2 (5)
C5—C6—C7	117.7 (5)	F7—C11—F5	107.3 (5)
O2—C7—N1	121.5 (5)	F6—C11—C10	111.6 (5)
O2—C7—C6	120.7 (5)	F7—C11—C10	110.2 (5)
N1—C7—C6	117.8 (5)	F5—C11—C10	109.8 (5)

C7—N1—C1—O1	171.2 (4)	C4^{i}—C6—C7—N1	173.8 (4)
C8—N1—C1—O1	−4.5 (7)	C5—C6—C7—N1	−5.4 (6)
C7—N1—C1—C2	−9.8 (7)	C7—N1—C8—C9	95.1 (5)
C8—N1—C1—C2	174.5 (4)	C1—N1—C8—C9	−88.9 (5)
O1—C1—C2—C3	2.8 (8)	N1—C8—C9—F2	−50.4 (6)
N1—C1—C2—C3	−176.1 (4)	N1—C8—C9—F1	65.0 (6)
O1—C1—C2—C5	−178.0 (5)	N1—C8—C9—C10	−173.0 (5)
N1—C1—C2—C5	3.1 (7)	F2—C9—C10—F3	−59.0 (5)
C5—C2—C3—C4	−0.6 (7)	F1—C9—C10—F3	−173.3 (4)
C1—C2—C3—C4	178.6 (4)	C8—C9—C10—F3	64.4 (6)
C2—C3—C4—C6^{i}	0.4 (8)	F2—C9—C10—F4	−176.0 (4)
C3—C2—C5—C6	−179.1 (4)	F1—C9—C10—F4	69.7 (5)
C1—C2—C5—C6	1.7 (7)	C8—C9—C10—F4	−52.6 (6)
C3—C2—C5—C5^{i}	0.0 (8)	F2—C9—C10—C11	63.0 (6)
C1—C2—C5—C5^{i}	−179.2 (5)	F1—C9—C10—C11	−51.3 (7)
C2—C5—C6—C4^{i}	−179.8 (4)	C8—C9—C10—C11	−173.5 (5)
C5^{i}—C5—C6—C4^{i}	1.1 (8)	F3—C10—C11—F6	65.9 (6)
C2—C5—C6—C7	−0.6 (7)	F4—C10—C11—F6	−178.4 (5)
C5^{i}—C5—C6—C7	−179.7 (5)	C9—C10—C11—F6	−56.8 (7)
C1—N1—C7—O2	−169.7 (5)	F3—C10—C11—F7	−172.1 (5)
C8—N1—C7—O2	6.0 (7)	F4—C10—C11—F7	−56.4 (6)
C1—N1—C7—C6	11.0 (7)	C9—C10—C11—F7	65.2 (7)
C8—N1—C7—C6	−173.3 (4)	F3—C10—C11—F5	−54.1 (7)
C4^{i}—C6—C7—O2	−5.5 (7)	F4—C10—C11—F5	61.6 (6)
C5—C6—C7—O2	175.3 (4)	C9—C10—C11—F5	−176.8 (5)

Symmetry code: (i) −*x*, −*y*+2, −*z*+1.