

# Crystal structure and Hirshfeld surface analysis of dimethyl (3*aS*,6*R*,6*aS*,7*S*)-2-(2,2,2-trifluoroacetyl)-2,3-dihydro-1*H*,6*H*,7*H*-3*a*,6:7,9*a*-diepoxybenzo-*[de]*isoquinoline-3*a*<sup>1</sup>,6*a*-dicarboxylate

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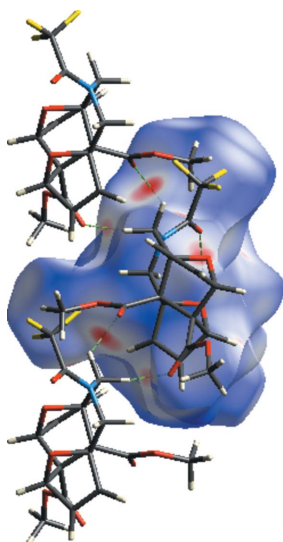
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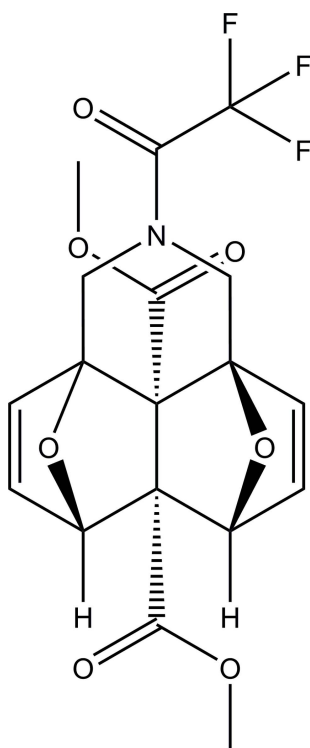
The title molecule, C<sub>18</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>7</sub>, comprises a fused cyclic system containing four five-membered (two dihydrofuran and two tetrahydrofuran) rings and one six-membered (piperidine) ring. The five-membered dihydrofuran and tetrahydrofuran rings adopt envelope conformations, and the six-membered piperidine ring adopts a distorted chair conformation. Intramolecular O···F interactions help to stabilize the conformational arrangement. In the crystal structure, molecules are linked by weak C—H···O and C—H···F hydrogen bonds, forming a three-dimensional network. The Hirshfeld surface analysis confirms the dominant role of H···H contacts in establishing the packing.

## 1. Chemical context

Non-covalent interactions, such as hydrogen, aerogen, halogen, chalcogen, pnictogen, tetrel and icosagen bonds, as well as *n*– $\pi^*$ ,  $\pi$ – $\pi$  stacking,  $\pi$ –cation,  $\pi$ –anion and hydrophobic interactions, have an impact on the synthesis, catalysis and design of materials and on biological processes (Shikhaliyev *et al.*, 2018; Hazra *et al.*, 2018). These weak forces can also control or organize the aggregation, conformation, tertiary and quaternary structure of a molecule, and its stabilization or other particular properties (Legon, 2017; Mahmudov *et al.*, 2017*a,b*). In comparison with well-established hydrogen and halogen bonds (Cavallo *et al.*, 2016; Mahmoudi *et al.*, 2018; Vandyshev *et al.*, 2017), chalcogen, pnictogen, tetrel and icosagen bonds are much less explored (Mahmudov *et al.*, 2017*a*; Scheiner, 2013; Mikherdov *et al.*, 2016).

The title compound, C<sub>18</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>7</sub>, has a 7-oxabicyclo-[2.2.1]heptene scaffold, thus making it a potential tool for the design and synthesis of new organic materials with various useful properties such as electronic materials, molecular tweezers, *etc* (Borisova *et al.*, 2018*a,b*). During the structure determination, we noted rather unusual intramolecular O···F interactions. Here we report the synthesis, molecular and crystal structure of this compound as well as a Hirshfeld surface analysis.





## 2. Structural commentary

The molecule of the title compound (Fig. 1) is made up from a fused cyclic system containing four five-membered rings (two dihydrofuran and two tetrahydrofuran) in the usual envelope conformations and a six-membered piperidine ring in a chair conformation. The latter is distorted because the environment of the N1 atom is intermediate between trigonal-planar and trigonal-pyramidal. The puckering parameters of the five-membered dihydrofuran [*A* (O1/C1/C2/C5/C6), *B* (O2/C1/C6/C7/C10)] and tetrahydrofuran [*C* (O1/C2–C5), *D* (O2/C7–C10)] rings are *A*:  $Q(2) = 0.5780$  (15) Å,  $\varphi(2) = 359.75$  (17)°; *B*:  $Q(2) = 0.5737$  (16) Å,  $\varphi(2) = 4.53$  (17)°; *C*:  $Q(2) = 0.5173$  (15) Å,  $\varphi(2) = 179.60$  (19)°; *D*:  $Q(2) = 0.5154$  (16) Å,  $\varphi(2) = 178.2$  (2)°. The puckering parameters of the six-membered piperidine ring (N1/C1/C2/C10–C12) are  $Q_T = 0.5312$  (17) Å,  $\theta = 9.58$  (18)°,  $\varphi = 329.1$  (11)°.

The molecular conformations are stabilized by weak intramolecular C–H···O and C–H···F interactions (Table 1) between methylene groups (C11; C12) and a methoxy group and the –CF<sub>3</sub> group, respectively. A rather unusual intramolecular O···F interaction between one of the oxygen bridgehead atoms (O1) and one of the F atoms of the –CF<sub>3</sub> group [C5–O1···F2 = 2.9336 (16) Å; C5–O1···F2 = 153.60 (9)°] might help to consolidate the conformational arrangement.

## 3. Supramolecular features

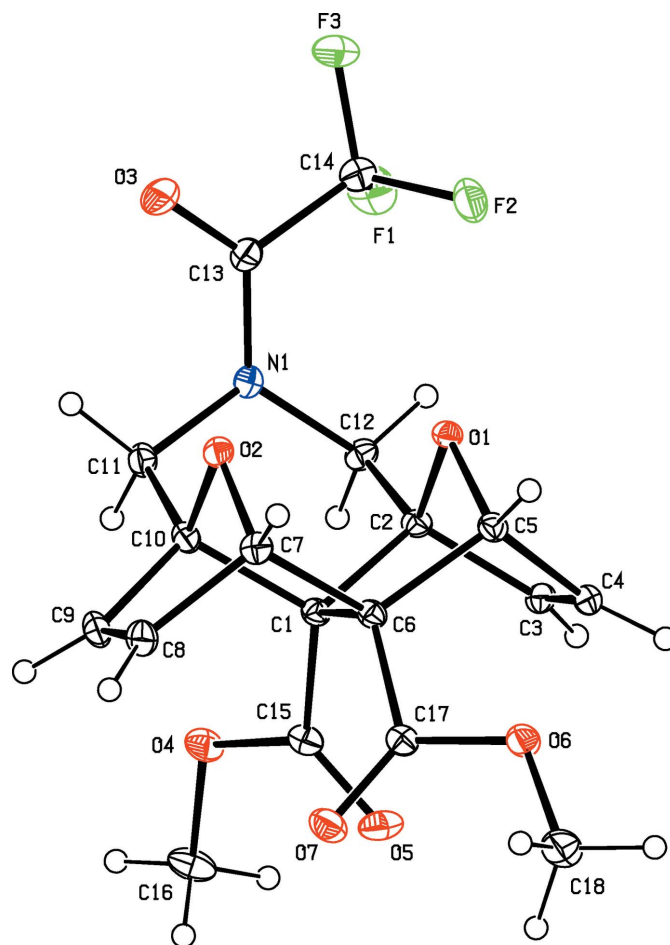
Intermolecular C–H···O interactions involving the O atoms of carbonyl groups, the oxygen bridgehead atoms and meth-

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C4–H4···O3 <sup>i</sup>	0.95	2.44	3.116 (2)	128
C5–H5···O2 <sup>ii</sup>	1.00	2.60	3.1960 (19)	118
C7–H7···O1 <sup>ii</sup>	1.00	2.54	3.2091 (19)	124
C11–H11 <i>B</i> ···O4	0.99	2.57	3.093 (2)	113
C12–H12 <i>A</i> ···O7 <sup>iii</sup>	0.99	2.52	3.328 (2)	138
C12–H12 <i>B</i> ···O5 <sup>iii</sup>	0.99	2.34	3.030 (2)	127
C12–H12 <i>B</i> ···F1	0.99	2.40	3.043 (2)	122
C12–H12 <i>B</i> ···F2	0.99	2.33	2.962 (2)	121
C16–H16 <i>A</i> ···F3 <sup>iv</sup>	0.98	2.62	3.475 (2)	146

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (iv)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ .

oxy O atoms, as well as C–H···F hydrogen bonds define the crystal packing, which is shown in Fig. 2. These packing features lead to the formation of a three-dimensional network structure. C–H··· $\pi$  and  $\pi$ – $\pi$  interactions are not observed, but H···H interactions dominate in the packing as detailed in the next section.



**Figure 1**  
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are shown as spheres of arbitrary radius.

#### 4. Hirshfeld surface analysis

Hirshfeld surface and fingerprint plots were generated using *CrystalExplorer* (McKinnon *et al.*, 2007). Hirshfeld surfaces enable the visualization of intermolecular interactions by different colors and color intensity, representing short or long contacts and indicating the relative strength of the interactions. Fig. 3 shows the Hirshfeld surface of the title compound mapped over  $d_{\text{norm}}$  where it is evident from the bright-red spots appearing near the oxygen atoms that these atoms play a significant role in the molecular packing. The red spots represent closer contacts and negative  $d_{\text{norm}}$  values on the surface, corresponding to the C—H...O interactions. The percentage contributions of various contacts to the total Hirshfeld surface are given in Table 2 and are also shown as two-dimensional fingerprint plots in Fig. 4. The H...H interactions appear in the middle of the scattered points in the two-dimensional fingerprint plots with an overall contribution to the Hirshfeld surface of 35.6% (Fig. 4b). The contribution from the O...H/H...O contacts, corresponding to C—H...O interactions, is represented by a pair of sharp spikes characteristic of a strong hydrogen-bonding interaction (28.5%; Fig. 4c). The contribution of the F...H/H...F intermolecular contacts to the Hirshfeld surfaces is 23.8% (Fig. 4d). The small percentage contributions from the remaining interatomic

Table 2

Percentage contributions of interatomic contacts to the Hirshfeld surface for the title compound.

Contact	Percentage contribution
H...H	35.6
O...H/H...O	28.5
F...H/H...F	23.8
C...H/H...C	5.5
F...F	2.7
F...O/O...F	1.6
N...H/H...N	1.1
O...O	1.1
C...O/O...C	0.2

contacts are summarized in Table 2 and indicated by their fingerprint plots for C...H/H...C (Fig. 4e), F...F (Fig. 4f),

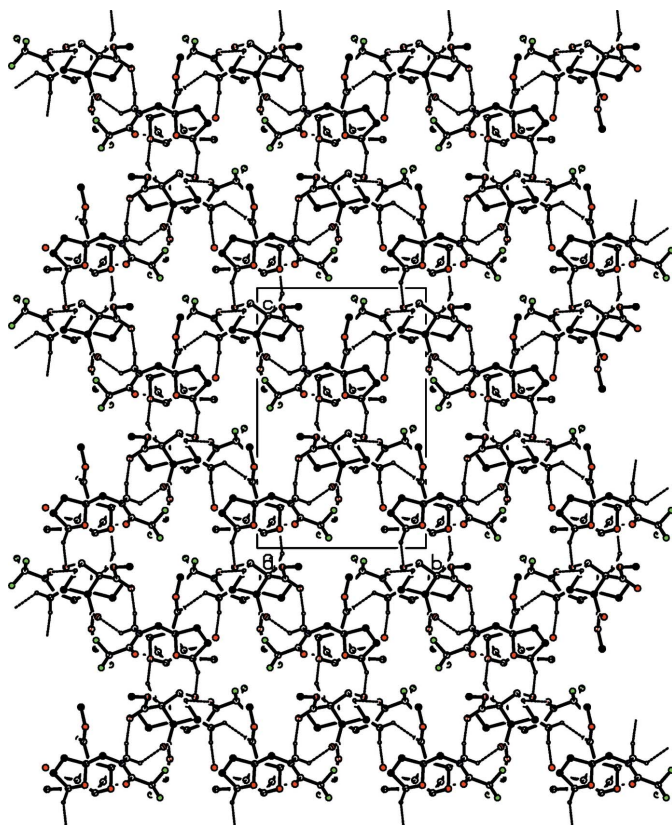


Figure 2

The crystal structure of the title compound in a view along [100], emphasizing the intermolecular C—H...O and C—H...F hydrogen bonds (dashed lines).

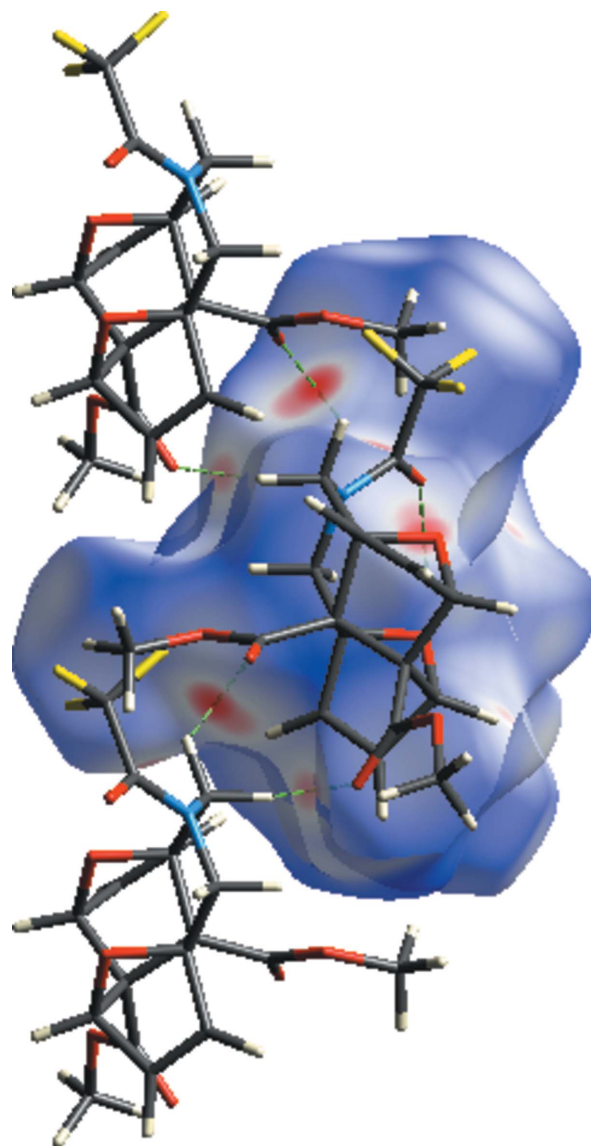


Figure 3

Hirshfeld surface of the title compound mapped over  $d_{\text{norm}}$ .

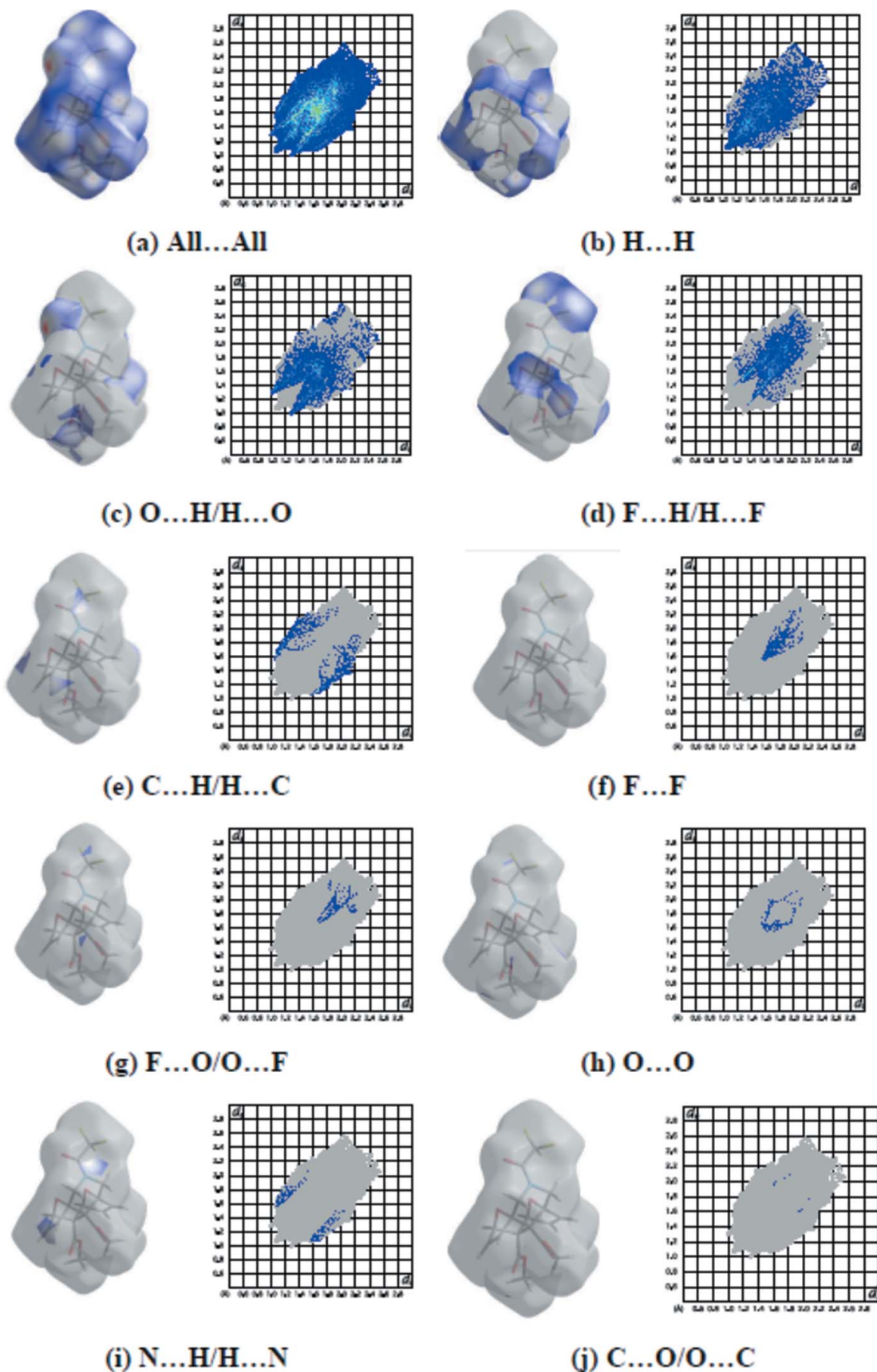


Figure 4

The two-dimensional fingerprint plots of the title compound, showing (a) all interactions, and delineated into (b) H...H, (c) O...H/H...O, (d) F...H/H...F, (e) C...H/H...C, (f) F...F, (g) F...O/O...F, (h) O...O, (i) N...H/H...N and (j) C...O/O...C interactions [ $d_e$  and  $d_i$  represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

F···O/O···F (Fig. 4g), O···O (Fig. 4h), N···H/H···N (Fig. 4i) and C···O/O···C (Fig. 4j). The large number of H···H, O···H/H···O and F···H/H···F interactions suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing (Hathwar *et al.*, 2015).

## 5. Database survey

A search of the Cambridge Structural Database (Version 5.39; Groom *et al.*, 2016) for similar structures showed the two closest are those of 2-benzyl-6a,9b-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1*H*,6*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]-isoquinoline (CSD refcode HENLAQ; Borisova *et al.*, 2018c) and 2-benzyl-4,5-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1*H*,6*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isoquinoline (HENLEU; Borisova *et al.*, 2018d). In the crystal of HENLAQ, inversion-related pairs of molecules are linked into dimers by C—H···O hydrogen bonds. These dimers form sheets lying parallel to (100). C—H··· $\pi$  interactions are also observed in the crystal structure of HENLAQ, together with intramolecular F···F contacts. The asymmetric unit of HENLEU contains two molecules. In the crystal, molecules are linked by C—H···O and C—H···F hydrogen bonds, forming columns along [010]. Likewise, C—H··· $\pi$  interactions and F···F intramolecular contacts are also present.

## 6. Synthesis and crystallization

The synthesis of the title compound and its characterization by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and HRMS spectroscopy have previously been reported (Borisova *et al.*, 2018a). Dimethyl acetylenedicarboxylate (DMAD, 1.84 ml, 0.015 mol) was added to a solution of 2,2,2-trifluoro-*N,N*-bis(furan-2-ylmethyl)acetamide (0.01 mol) in benzene (30 ml). The mixture was heated at reflux for 15.5–40 h at 353 K (GC–MS monitoring until disappearance of the starting material). The reaction mixture was cooled and left overnight at room temperature. The solvent was removed under reduced pressure. The residue (brown oil) was triturated with diethyl ether. The obtained crystals were filtered off and recrystallized from hexane/EtOAc (*v:v* = 2:1) to give the pure compound as a white powder (2.57 g, 6.2 mmol, yield 62%).  $R_f$  = 0.56 (EtOAc/hexane, 2:1, Sorbfil). M.p. 467.2–467.9 K (from hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.74–6.71 (2H, *m*, H-4 and H-9), 6.46 (2H, *dd*,  $J$  = 2.3 and  $J$  = 5.5 Hz, H-5 and H-8), 5.14 (2H, *br s*, H-6 and H-7), 5.10 (1H, *d*,  $J$  = 14.9 Hz, H-1A), 4.43 (1H, *br d*,  $J$  = 14.9 Hz, H-3A), 4.08 (1H, *d*,  $J$  = 14.9 Hz, H-3B), 3.64 (6H, *s*, 2  $\times$  CO<sub>2</sub>Me), 3.59 (1H, *d*,  $J$  = 14.9, H-1B). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.1 (2  $\times$  CO<sub>2</sub>Me), 157.2 ( $q$ ,  $J$  = 35.5 Hz, F3C—C), 141.2 (C-5 and C-8), 137.5 (C-4 and C-9), 116.4 ( $q$ ,  $J$  = 288.1 Hz, CF<sub>3</sub>), 87.1 (C-3a and C-9a), 83.8 (C-6 and C-7), 71.4 and 68.8 (C-9 and C-6a), 52.4 (2  $\times$  CO<sub>2</sub>Me), 44.8 ( $q$ ,  $J$  = 3.8 Hz, C-1), 42.4 (C-3). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>):  $\delta$  -67.7 (*s*, CF<sub>3</sub>). IR  $\nu_{\max}$ /cm<sup>-1</sup> (KBr): 3109, 3055, 2956, 1713, 1688, 1197. HRMS (ESI–TOF): calculated for C<sub>18</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>7</sub> [ $M + H$ ]<sup>+</sup>, 415.0879; found, 415.0889.

**Table 3**

Experimental details.

Crystal data	
Chemical formula	C <sub>18</sub> H <sub>16</sub> F <sub>3</sub> NO <sub>7</sub>
$M_r$	415.32
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
$a, b, c$ (Å)	8.7661 (2), 11.2908 (3), 17.5089 (4)
$\beta$ (°)	96.021 (1)
$V$ (Å <sup>3</sup> )	1723.41 (7)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.14
Crystal size (mm)	0.35 $\times$ 0.32 $\times$ 0.30
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\min}$ , $T_{\max}$	0.942, 0.946
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	11170, 3496, 2739
$R_{\text{int}}$	0.028
( $\sin \theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.036, 0.091, 1.01
No. of reflections	3496
No. of parameters	264
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.30, -0.25

Computer programs: APEX2 and SAINT (Bruker, 2007), SHELXS97 (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2009).

## 7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were fixed and allowed to ride on the parent atoms, with C—H = 0.95–1.00 Å, and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and  $1.2U_{\text{eq}}(\text{C})$  for all other H atoms. Eight outliers [(101), (011), ( $\bar{1}$ 01), (002), (110), (363), ( $\bar{3}$ 03), (111)] were omitted in the final cycles of refinement.

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## supporting information

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## Crystal structure and Hirshfeld surface analysis of dimethyl (3a*S*,6*R*,6a*S*,7*S*)-2-(2,2,2-trifluoroacetyl)-2,3-dihydro-1*H*,6*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isoquinoline-3a<sup>1</sup>,6a-dicarboxylate

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### Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2009).

Crystal structure and Hirshfeld surface analysis of dimethyl (3a*S*,6*R*,6a*S*,7*S*)-2-(2,2,2-trifluoroacetyl)-2,3-dihydro-1*H*,6*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isoquinoline-3a<sup>1</sup>,6a-dicarboxylate, dimethyl (3a*S*,6*R*,6a*S*,7*S*)-2-(2,2,2-trifluoroacetyl)-2,3-dihydro-1*H*,6*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isoquinoline-3a<sup>1</sup>,6a-dicarboxylate

### Crystal data

C<sub>18</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>7</sub>

*M<sub>r</sub>* = 415.32

Monoclinic, *P*2<sub>1</sub>/*n*

*a* = 8.7661 (2) Å

*b* = 11.2908 (3) Å

*c* = 17.5089 (4) Å

β = 96.021 (1)°

*V* = 1723.41 (7) Å<sup>3</sup>

*Z* = 4

*F*(000) = 856

*D<sub>x</sub>* = 1.601 Mg m<sup>-3</sup>

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 3572 reflections

θ = 3.0–25.9°

μ = 0.14 mm<sup>-1</sup>

*T* = 150 K

Block, colourless

0.35 × 0.32 × 0.30 mm

### Data collection

Bruker APEXII CCD  
diffractometer

φ and ω scans

Absorption correction: multi-scan  
(*SADABS*; Krause *et al.*, 2015)

*T<sub>min</sub>* = 0.942, *T<sub>max</sub>* = 0.946

11170 measured reflections

3496 independent reflections

2739 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.028

θ<sub>max</sub> = 26.4°, θ<sub>min</sub> = 3.1°

*h* = -10→10

*k* = -14→11

*l* = -21→20

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.091$   
 $S = 1.01$   
 3496 reflections  
 264 parameters  
 0 restraints

Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 0.8462P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.39473 (17)	0.49611 (14)	0.67777 (9)	0.0151 (3)
C2	0.34636 (17)	0.36454 (14)	0.65512 (9)	0.0159 (3)
C3	0.17517 (18)	0.35392 (15)	0.66061 (10)	0.0188 (4)
H3	0.125910	0.313775	0.698918	0.023*
C4	0.10926 (18)	0.41275 (15)	0.60044 (9)	0.0190 (4)
H4	0.002414	0.423058	0.586488	0.023*
C5	0.23948 (17)	0.46040 (14)	0.55824 (9)	0.0166 (3)
H5	0.211134	0.478143	0.502604	0.020*
C6	0.31682 (17)	0.56580 (14)	0.60653 (9)	0.0156 (3)
C7	0.46580 (18)	0.61837 (14)	0.57545 (9)	0.0181 (3)
H7	0.450625	0.648514	0.521478	0.022*
C8	0.53785 (19)	0.70697 (16)	0.63430 (10)	0.0223 (4)
H8	0.534938	0.790901	0.630565	0.027*
C9	0.60537 (19)	0.64310 (16)	0.69172 (10)	0.0215 (4)
H9	0.663054	0.671359	0.737022	0.026*
C10	0.57077 (18)	0.51491 (15)	0.66959 (9)	0.0173 (3)
C11	0.67413 (18)	0.41488 (15)	0.70014 (9)	0.0196 (4)
H11A	0.777907	0.426465	0.683886	0.023*
H11B	0.683028	0.415179	0.756980	0.023*
C12	0.45739 (18)	0.27365 (15)	0.69121 (9)	0.0187 (3)
H12A	0.456518	0.274715	0.747704	0.022*
H12B	0.426248	0.193647	0.672394	0.022*
C13	0.68211 (18)	0.24366 (16)	0.61696 (10)	0.0213 (4)
C14	0.61562 (19)	0.12361 (17)	0.58786 (11)	0.0268 (4)
C15	0.34324 (19)	0.52840 (15)	0.75488 (9)	0.0187 (4)
C16	0.4132 (2)	0.54441 (18)	0.88782 (9)	0.0294 (4)
H16A	0.502378	0.535376	0.926090	0.044*
H16B	0.332265	0.489567	0.899623	0.044*
H16C	0.375106	0.625921	0.888922	0.044*
C17	0.20610 (18)	0.66654 (15)	0.61749 (9)	0.0171 (3)



C18	-0.0373 (2)	0.74427 (17)	0.57152 (12)	0.0332 (5)
H18A	-0.136339	0.716249	0.547019	0.050*
H18B	-0.001422	0.810491	0.541928	0.050*
H18C	-0.048909	0.770680	0.623910	0.050*
N1	0.61226 (15)	0.30034 (12)	0.67137 (8)	0.0174 (3)
O1	0.35051 (12)	0.36756 (10)	0.57348 (6)	0.0157 (2)
O2	0.57083 (12)	0.52159 (10)	0.58756 (6)	0.0171 (3)
O3	0.79898 (15)	0.27623 (13)	0.59189 (8)	0.0386 (4)
O4	0.45760 (13)	0.51821 (11)	0.81186 (6)	0.0234 (3)
O5	0.21495 (14)	0.55547 (12)	0.76498 (7)	0.0274 (3)
O6	0.07292 (13)	0.64922 (10)	0.57403 (7)	0.0226 (3)
O7	0.23490 (14)	0.75410 (11)	0.65517 (7)	0.0263 (3)
F1	0.60895 (14)	0.04589 (10)	0.64497 (7)	0.0422 (3)
F2	0.47566 (12)	0.13074 (10)	0.55061 (6)	0.0350 (3)
F3	0.70476 (14)	0.07621 (12)	0.53923 (8)	0.0509 (4)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0169 (8)	0.0155 (8)	0.0130 (8)	-0.0009 (6)	0.0023 (6)	-0.0006 (6)
C2	0.0181 (8)	0.0163 (8)	0.0139 (8)	-0.0018 (6)	0.0051 (6)	-0.0002 (6)
C3	0.0172 (8)	0.0149 (8)	0.0254 (9)	-0.0042 (6)	0.0082 (7)	-0.0020 (7)
C4	0.0163 (8)	0.0167 (9)	0.0244 (9)	-0.0025 (6)	0.0033 (6)	-0.0048 (7)
C5	0.0173 (8)	0.0169 (8)	0.0153 (8)	0.0008 (6)	0.0002 (6)	-0.0011 (7)
C6	0.0185 (8)	0.0150 (8)	0.0134 (8)	-0.0012 (6)	0.0022 (6)	-0.0005 (6)
C7	0.0199 (8)	0.0168 (9)	0.0179 (8)	-0.0009 (6)	0.0039 (6)	0.0027 (7)
C8	0.0226 (9)	0.0184 (9)	0.0268 (9)	-0.0068 (7)	0.0060 (7)	-0.0007 (7)
C9	0.0213 (8)	0.0222 (9)	0.0205 (9)	-0.0071 (7)	-0.0002 (7)	-0.0038 (7)
C10	0.0191 (8)	0.0184 (9)	0.0144 (8)	-0.0048 (6)	0.0024 (6)	-0.0019 (7)
C11	0.0173 (8)	0.0230 (9)	0.0180 (8)	-0.0029 (7)	-0.0003 (6)	-0.0014 (7)
C12	0.0181 (8)	0.0198 (9)	0.0193 (8)	-0.0011 (7)	0.0064 (6)	0.0027 (7)
C13	0.0171 (8)	0.0241 (10)	0.0225 (9)	0.0007 (7)	0.0020 (7)	-0.0008 (7)
C14	0.0226 (9)	0.0268 (10)	0.0315 (10)	0.0019 (7)	0.0048 (7)	-0.0048 (8)
C15	0.0254 (9)	0.0149 (8)	0.0161 (8)	-0.0005 (7)	0.0042 (7)	0.0006 (7)
C16	0.0470 (11)	0.0304 (11)	0.0114 (8)	0.0037 (9)	0.0057 (8)	-0.0025 (8)
C17	0.0211 (8)	0.0172 (9)	0.0131 (8)	-0.0012 (6)	0.0030 (6)	0.0016 (7)
C18	0.0299 (10)	0.0263 (11)	0.0409 (11)	0.0115 (8)	-0.0074 (8)	-0.0080 (9)
N1	0.0158 (7)	0.0180 (7)	0.0184 (7)	-0.0010 (5)	0.0016 (5)	0.0014 (6)
O1	0.0176 (5)	0.0157 (6)	0.0141 (6)	-0.0001 (4)	0.0034 (4)	-0.0016 (4)
O2	0.0170 (6)	0.0201 (6)	0.0148 (6)	-0.0021 (5)	0.0039 (4)	0.0005 (5)
O3	0.0259 (7)	0.0424 (9)	0.0509 (9)	-0.0105 (6)	0.0205 (6)	-0.0156 (7)
O4	0.0297 (7)	0.0287 (7)	0.0116 (6)	0.0004 (5)	0.0019 (5)	-0.0020 (5)
O5	0.0296 (7)	0.0322 (8)	0.0215 (6)	0.0095 (6)	0.0086 (5)	-0.0015 (5)
O6	0.0212 (6)	0.0194 (6)	0.0261 (6)	0.0044 (5)	-0.0023 (5)	-0.0039 (5)
O7	0.0296 (7)	0.0210 (7)	0.0272 (7)	0.0035 (5)	-0.0020 (5)	-0.0069 (5)
F1	0.0515 (7)	0.0218 (6)	0.0523 (8)	0.0029 (5)	0.0002 (6)	0.0056 (5)
F2	0.0279 (6)	0.0320 (6)	0.0427 (7)	-0.0024 (5)	-0.0073 (5)	-0.0102 (5)
F3	0.0405 (7)	0.0496 (8)	0.0662 (9)	-0.0048 (6)	0.0225 (6)	-0.0341 (7)

*Geometric parameters (Å, °)*

C1—C15	1.512 (2)	C11—N1	1.471 (2)
C1—C6	1.569 (2)	C11—H11A	0.9900
C1—C10	1.579 (2)	C11—H11B	0.9900
C1—C2	1.584 (2)	C12—N1	1.467 (2)
C2—O1	1.4341 (19)	C12—H12A	0.9900
C2—C12	1.507 (2)	C12—H12B	0.9900
C2—C3	1.519 (2)	C13—O3	1.213 (2)
C3—C4	1.326 (2)	C13—N1	1.347 (2)
C3—H3	0.9500	C13—C14	1.541 (3)
C4—C5	1.522 (2)	C14—F3	1.327 (2)
C4—H4	0.9500	C14—F2	1.330 (2)
C5—O1	1.4363 (19)	C14—F1	1.336 (2)
C5—C6	1.572 (2)	C15—O5	1.196 (2)
C5—H5	1.0000	C15—O4	1.343 (2)
C6—C17	1.520 (2)	C16—O4	1.455 (2)
C6—C7	1.582 (2)	C16—H16A	0.9800
C7—O2	1.4303 (19)	C16—H16B	0.9800
C7—C8	1.525 (2)	C16—H16C	0.9800
C7—H7	1.0000	C17—O7	1.2006 (19)
C8—C9	1.325 (2)	C17—O6	1.3393 (19)
C8—H8	0.9500	C18—O6	1.441 (2)
C9—C10	1.521 (2)	C18—H18A	0.9800
C9—H9	0.9500	C18—H18B	0.9800
C10—O2	1.4382 (19)	C18—H18C	0.9800
C10—C11	1.510 (2)		
C15—C1—C6	116.28 (13)	C9—C10—C1	106.00 (13)
C15—C1—C10	115.76 (13)	N1—C11—C10	110.50 (12)
C6—C1—C10	102.03 (12)	N1—C11—H11A	109.5
C15—C1—C2	110.64 (13)	C10—C11—H11A	109.5
C6—C1—C2	100.86 (12)	N1—C11—H11B	109.5
C10—C1—C2	109.99 (12)	C10—C11—H11B	109.5
O1—C2—C12	110.57 (12)	H11A—C11—H11B	108.1
O1—C2—C3	101.16 (12)	N1—C12—C2	109.50 (13)
C12—C2—C3	121.25 (13)	N1—C12—H12A	109.8
O1—C2—C1	101.14 (11)	C2—C12—H12A	109.8
C12—C2—C1	112.92 (13)	N1—C12—H12B	109.8
C3—C2—C1	107.37 (13)	C2—C12—H12B	109.8
C4—C3—C2	105.15 (14)	H12A—C12—H12B	108.2
C4—C3—H3	127.4	O3—C13—N1	125.15 (16)
C2—C3—H3	127.4	O3—C13—C14	116.83 (15)
C3—C4—C5	106.05 (14)	N1—C13—C14	117.88 (14)
C3—C4—H4	127.0	F3—C14—F2	106.54 (15)
C5—C4—H4	127.0	F3—C14—F1	106.87 (16)
O1—C5—C4	100.37 (12)	F2—C14—F1	107.23 (14)
O1—C5—C6	101.94 (12)	F3—C14—C13	109.82 (14)

C4—C5—C6	108.05 (13)	F2—C14—C13	113.97 (15)
O1—C5—H5	114.9	F1—C14—C13	112.02 (15)
C4—C5—H5	114.9	O5—C15—O4	123.51 (15)
C6—C5—H5	114.9	O5—C15—C1	124.53 (15)
C17—C6—C1	120.34 (13)	O4—C15—C1	111.90 (14)
C17—C6—C5	112.90 (13)	O4—C16—H16A	109.5
C1—C6—C5	100.09 (12)	O4—C16—H16B	109.5
C17—C6—C7	108.88 (13)	H16A—C16—H16B	109.5
C1—C6—C7	98.94 (12)	O4—C16—H16C	109.5
C5—C6—C7	115.09 (13)	H16A—C16—H16C	109.5
O2—C7—C8	100.74 (12)	H16B—C16—H16C	109.5
O2—C7—C6	101.77 (12)	O7—C17—O6	123.57 (15)
C8—C7—C6	108.18 (13)	O7—C17—C6	125.81 (15)
O2—C7—H7	114.8	O6—C17—C6	110.43 (13)
C8—C7—H7	114.8	O6—C18—H18A	109.5
C6—C7—H7	114.8	O6—C18—H18B	109.5
C9—C8—C7	106.02 (15)	H18A—C18—H18B	109.5
C9—C8—H8	127.0	O6—C18—H18C	109.5
C7—C8—H8	127.0	H18A—C18—H18C	109.5
C8—C9—C10	105.27 (14)	H18B—C18—H18C	109.5
C8—C9—H9	127.4	C13—N1—C12	124.77 (14)
C10—C9—H9	127.4	C13—N1—C11	118.78 (13)
O2—C10—C11	109.26 (13)	C12—N1—C11	114.62 (13)
O2—C10—C9	100.58 (13)	C2—O1—C5	96.60 (11)
C11—C10—C9	121.69 (14)	C7—O2—C10	96.93 (11)
O2—C10—C1	101.56 (11)	C15—O4—C16	114.29 (13)
C11—C10—C1	115.03 (13)	C17—O6—C18	116.74 (13)
C15—C1—C2—O1	158.98 (12)	C6—C1—C10—C9	73.08 (14)
C6—C1—C2—O1	35.33 (13)	C2—C1—C10—C9	179.49 (12)
C10—C1—C2—O1	-71.87 (14)	O2—C10—C11—N1	-65.07 (16)
C15—C1—C2—C12	-82.85 (16)	C9—C10—C11—N1	178.56 (14)
C6—C1—C2—C12	153.50 (12)	C1—C10—C11—N1	48.35 (17)
C10—C1—C2—C12	46.30 (16)	O1—C2—C12—N1	57.13 (17)
C15—C1—C2—C3	53.42 (16)	C3—C2—C12—N1	175.15 (14)
C6—C1—C2—C3	-70.24 (14)	C1—C2—C12—N1	-55.37 (17)
C10—C1—C2—C3	-177.43 (13)	O3—C13—C14—F3	0.8 (2)
O1—C2—C3—C4	-32.33 (16)	N1—C13—C14—F3	-175.17 (15)
C12—C2—C3—C4	-154.93 (15)	O3—C13—C14—F2	-118.68 (18)
C1—C2—C3—C4	73.22 (16)	N1—C13—C14—F2	65.4 (2)
C2—C3—C4—C5	-0.44 (17)	O3—C13—C14—F1	119.35 (18)
C3—C4—C5—O1	32.93 (16)	N1—C13—C14—F1	-56.6 (2)
C3—C4—C5—C6	-73.38 (16)	C6—C1—C15—O5	35.8 (2)
C15—C1—C6—C17	4.8 (2)	C10—C1—C15—O5	155.57 (16)
C10—C1—C6—C17	-122.10 (14)	C2—C1—C15—O5	-78.4 (2)
C2—C1—C6—C17	124.52 (14)	C6—C1—C15—O4	-146.90 (14)
C15—C1—C6—C5	-119.37 (14)	C10—C1—C15—O4	-27.14 (19)
C10—C1—C6—C5	113.70 (12)	C2—C1—C15—O4	98.85 (15)

C2—C1—C6—C5	0.31 (13)	C1—C6—C17—O7	58.2 (2)
C15—C1—C6—C7	122.99 (14)	C5—C6—C17—O7	176.13 (15)
C10—C1—C6—C7	-3.95 (14)	C7—C6—C17—O7	-54.7 (2)
C2—C1—C6—C7	-117.33 (12)	C1—C6—C17—O6	-126.65 (15)
O1—C5—C6—C17	-165.16 (12)	C5—C6—C17—O6	-8.77 (18)
C4—C5—C6—C17	-59.95 (17)	C7—C6—C17—O6	120.36 (14)
O1—C5—C6—C1	-35.94 (13)	O3—C13—N1—C12	167.96 (17)
C4—C5—C6—C1	69.27 (14)	C14—C13—N1—C12	-16.5 (2)
O1—C5—C6—C7	68.99 (15)	O3—C13—N1—C11	4.3 (3)
C4—C5—C6—C7	174.20 (13)	C14—C13—N1—C11	179.81 (14)
C17—C6—C7—O2	165.38 (12)	C2—C12—N1—C13	-101.78 (18)
C1—C6—C7—O2	38.92 (14)	C2—C12—N1—C11	62.52 (17)
C5—C6—C7—O2	-66.71 (16)	C10—C11—N1—C13	106.74 (16)
C17—C6—C7—C8	59.79 (16)	C10—C11—N1—C12	-58.57 (17)
C1—C6—C7—C8	-66.68 (15)	C12—C2—O1—C5	-178.88 (12)
C5—C6—C7—C8	-172.31 (13)	C3—C2—O1—C5	51.41 (13)
O2—C7—C8—C9	-31.04 (16)	C1—C2—O1—C5	-59.02 (12)
C6—C7—C8—C9	75.27 (16)	C4—C5—O1—C2	-51.23 (13)
C7—C8—C9—C10	-1.76 (17)	C6—C5—O1—C2	59.90 (13)
C8—C9—C10—O2	33.85 (16)	C8—C7—O2—C10	50.57 (13)
C8—C9—C10—C11	154.49 (15)	C6—C7—O2—C10	-60.77 (13)
C8—C9—C10—C1	-71.55 (16)	C11—C10—O2—C7	179.05 (12)
C15—C1—C10—O2	-158.88 (13)	C9—C10—O2—C7	-51.80 (13)
C6—C1—C10—O2	-31.61 (14)	C1—C10—O2—C7	57.12 (13)
C2—C1—C10—O2	74.81 (14)	O5—C15—O4—C16	-0.7 (2)
C15—C1—C10—C11	83.27 (17)	C1—C15—O4—C16	-178.05 (14)
C6—C1—C10—C11	-149.45 (13)	O7—C17—O6—C18	2.2 (2)
C2—C1—C10—C11	-43.04 (17)	C6—C17—O6—C18	-173.02 (14)
C15—C1—C10—C9	-54.19 (17)		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H4 $\cdots$ O3 <sup>i</sup>	0.95	2.44	3.116 (2)	128
C5—H5 $\cdots$ O2 <sup>ii</sup>	1.00	2.60	3.1960 (19)	118
C7—H7 $\cdots$ O1 <sup>ii</sup>	1.00	2.54	3.2091 (19)	124
C11—H11B $\cdots$ O4	0.99	2.57	3.093 (2)	113
C12—H12A $\cdots$ O7 <sup>iii</sup>	0.99	2.52	3.328 (2)	138
C12—H12B $\cdots$ O5 <sup>iii</sup>	0.99	2.34	3.030 (2)	127
C12—H12B $\cdots$ F1	0.99	2.40	3.043 (2)	122
C12—H12B $\cdots$ F2	0.99	2.33	2.962 (2)	121
C16—H16A $\cdots$ F3 <sup>iv</sup>	0.98	2.62	3.475 (2)	146

Symmetry codes: (i)  $x-1, y, z$ ; (ii)  $-x+1, -y+1, -z+1$ ; (iii)  $-x+1/2, y-1/2, -z+3/2$ ; (iv)  $-x+3/2, y+1/2, -z+3/2$ .