

# Crystal structure of *N,N'*-bis(2,4-difluorobenzo-yloxy)benzene-1,2:4,5-tetracarboximide

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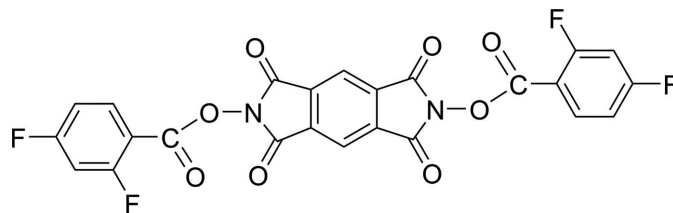
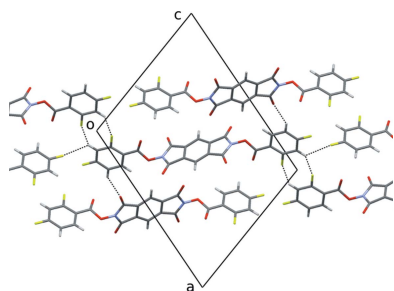
Molecules of the title compound,  $C_{24}H_8F_4N_2O_8$ , have  $C_i$  point-group symmetry in the crystal, as they lie on crystallographic inversion centres ( $Z' = 1/2$ ). The difluorophenyl ring is disordered over two orientations; the final refined occupancy factors of the two components of disorder are 0.947 (4) and 0.053 (4). In the crystal, some  $C_{ar}-H \cdots F$  interactions are present, which involve the most acidic H atom of the molecule.

## 1. Chemical context

Heterocycles are key compounds in synthetic chemistry. In addition to their applications in drugs, bioactive and tautomeric compounds (D'Errico *et al.*, 2012; Piccialli *et al.*, 2007; Centore *et al.*, 2013), aromatic heterocycles play an important role in modern materials chemistry, because they are used as building blocks of active molecules in many emerging fields of advanced materials, for example, conducting polymers (Heeger, 2010), organic field-effect transistors (Miao, 2014), organic solar cells (Nielsen *et al.*, 2015), liquid crystals (Centore *et al.*, 1996) and nonlinear optically active compounds (Carella *et al.*, 2007; Centore *et al.*, 1999).

Aromatic diimides, in particular, are a class of heterocyclic compounds well known for their outstanding properties as *n*-type organic semiconductors. Very high electron mobilities have been measured for perylenediimides (Schmidt *et al.*, 2007) and naphthalenediimides (Yan *et al.*, 2009). The research on *n*-type organic semiconductors has also shown that electron mobilities and device performances can be improved by extensive replacement of H atoms by fluorine (Facchetti *et al.*, 2003).

Following these issues, we report here the structural investigation of the title compound, *N,N'*-bis(2,4-difluorobenzo-yloxy)benzene-1,2:4,5-tetracarboximide, which is a fluorinated derivative of the simplest aromatic bis(imide).



## 2. Structural commentary

Molecules of the title compound in the crystal lie on crystallographic inversion centres and have  $C_i$  point-group symmetry.

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

| $D-H\cdots A$           | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------|-------|-------------|-------------|---------------|
| $C1-H1\cdots O2^i$      | 0.95  | 2.37        | 3.271 (3)   | 158           |
| $C9-H9\cdots F1A^{ii}$  | 0.95  | 2.51        | 3.287 (3)   | 139           |
| $C9-H9\cdots F2^{iii}$  | 0.95  | 2.63        | 3.307 (3)   | 129           |
| $C11-H11\cdots O1^{iv}$ | 0.95  | 2.39        | 3.200 (3)   | 143           |

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

Thus, the asymmetric unit is formed by half a molecule, as shown in Fig. 1. The difluorophenyl ring is disordered over two orientations that differ by a rotation of  $180^\circ$  around the C6–C7 bond. The atomic positions for the two orientations of the difluorophenyl ring are completely superimposed for all atoms, except for the *ortho*-F atom, for which split positions were observed. The final refined occupancy factors of the two components of disorder are 0.947 (4) and 0.053 (4). Molecules adopt a nonplanar conformation, mainly because of a torsion around the O3–N1 bond. In particular, the pentaatomic ring (atoms C2/C3/C4/N1/C5) is planar within 0.0164 (14) Å, while the phenyl ring (C7/C8a/C9/C10/C11/C12a) is planar within 0.002 (2) Å. The dihedral angle between the mean planes of the two rings is  $86.14 (8)^\circ$ .

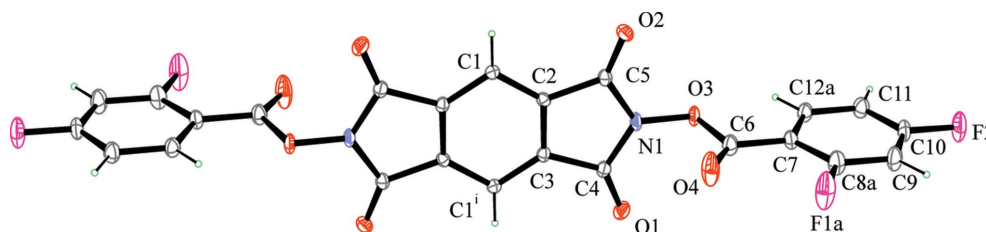
The C6–O3 bond length [1.402 (3) Å] is significantly longer than the mean value for esters of aromatic acids (1.337 Å; Allen *et al.*, 1987). This suggests a reduced contribution of the minor resonance form of the ester group, in which one of the lone pairs of the alkoxy oxygen forms a double bond with the carbonyl C atom that breaks its double

bond with the other O atom, thereby giving it a negative charge. This, in turn, can be due to the presence of the electronegative N atom bonded to O3.

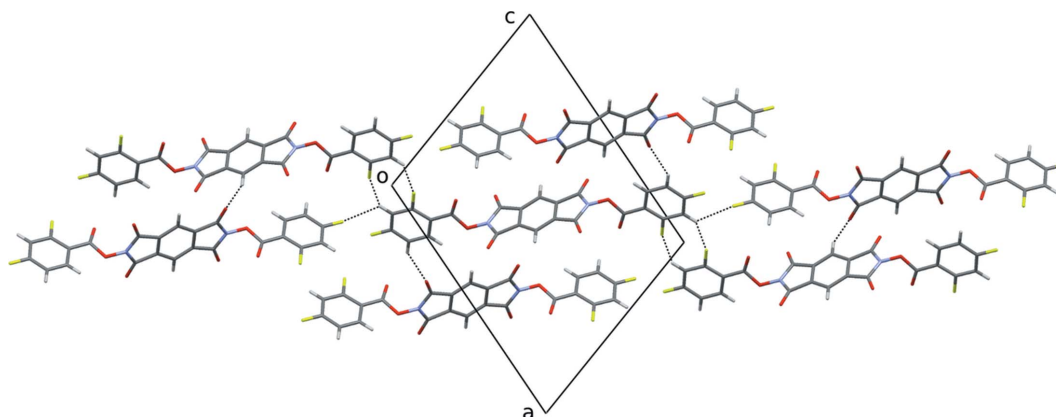
### 3. Supramolecular features

There are weak hydrogen-bond donors ( $C_{ar}-H$ ) and strong hydrogen-bond acceptors (carbonyl O atoms) in the title compound. Moreover, F atoms are present as well, whose low hydrogen-bonding-acceptor capability, if any, has been the subject of a long debate in the literature (Dunitz & Taylor, 1997; Dunitz, 2004). Actually, it is now established that the  $C-H\cdots F$  interaction is generally weak and does not play a significant structural role in crystal packing when stronger and more polarizable acceptors than the C–F group are present. On the other hand, when the carbon acidity is suitably enhanced, and in the absence of competing acceptors, the (weak) hydrogen-bonding nature of the  $C-H\cdots F$  interaction is revealed (Thalladi *et al.*, 1998).

The most acidic  $C_{ar}-H$  group in the title compound is C9–H, because it has two *ortho* C–F-group neighbours. It is involved in weak hydrogen-bonding interactions with fluorine, as shown in Fig. 2 and Table 1. In particular, C9–H acts as bifurcated donor to the F1A and F2 atoms. In the first case,  $R_2^2(8)$  ring motifs are formed across inversion centres. In the second case, chain patterns running parallel to  $a - b + c/2$  are formed. These patterns are quite similar to the supramolecular synthons **II** and **IV** reported in the Scheme 2 of Thalladi *et al.* (1998). It is quite remarkable that significant  $C-H\cdots F$



**Figure 1**  
The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. Only the most populated orientation of the disordered difluorophenyl ring is shown. [Symmetry code: (i)  $-x + 1, -y, -z + 1$ .]



**Figure 2**  
Partial crystal packing of the title compound, showing the  $C-H\cdots F$  and  $C-H\cdots O$  interactions as dashed lines. Only the most populated orientation of the disordered difluorophenyl ring is shown.

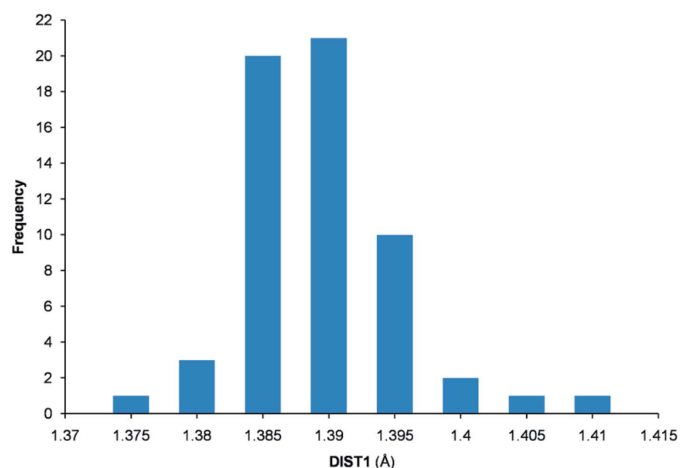
interactions are only given by C9—H, which is the most acidic H atom of the molecule.

Other acidic H atoms are C11—H, because it has one *ortho* C—F group, and C1—H. They are involved in weak hydrogen-bonding interactions with the O1 and O2 carbonyl acceptors, respectively, see Table 1 and Fig. 2.

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.38, last update May 2017; Groom *et al.*, 2016) gave no match for the title compound. We have searched for *N*-oxycarbonylimides using two filters (three-dimensional coordinates determined and not disordered). 47 hits were found. Within this set, 40 hits are *N*-oxycarbonyl derivatives of succinimide and 6 hits are derivatives of phthalimide. Here follows the full list of refcodes for the CSD search: ADEFUL, AFUXEE, ALOPAU, AWUXOF, BANTOA, CILBUV, COZFOM, DOFTEZ, EABXIO, EABXIO01, FUPPEM, GULRAI, GUV CAB, ICEWIY, LOZFAH, MAMDOU, MILFOE, MIPHUP, MIZJEM, MOZYOQ, NANWUU, OQUPOG, PIGKIZ, SEZWIE, SOSDEK, SUDJIM, SUDWUL, SUDXAS, SUDXAS01, TEQDEY, TUJRIB, UJAFER, UJUBOS, UJUBUY, VALSUZ, WALPEH, WIDKEB, YAFMEY, YAFPOL, YAGBEP, YUJZIN, YUJZOT, ZEPSES, ZEPSIW, ZOQQOL, ZOQQUR, ZALKUV.

The hits found are crystal structures determined at temperatures in the range 90–298 K. In the 47 hits, the N1—O3 distance (DIST1) ranges between 1.375 and 1.408 Å, with an average value of 1.388 (6) Å. On the other hand, the distance O3—C6 (DIST2) is between 1.350 and 1.423 Å, with an average value of 1.393 (15) Å. The histogram of the distribution of DIST1 over the 47 hits found is shown in Fig. 3. The values of DIST1 and DIST2 found in the title compound [N1—O3 = 1.381 (2) Å and O3—C6 = 1.402 (3) Å] are fully consistent with the average values determined from the 47 hits.



**Figure 3**  
Histogram of the N—O bond lengths (DIST1) in the 47 *N*-oxycarbonylimide hits found in the CSD search.

**Table 2**  
Experimental details.

|  |   |
|--|---|
| Crystal data   |   |
| Chemical formula   | C <sub>24</sub> H <sub>8</sub> F <sub>4</sub> N <sub>2</sub> O <sub>8</sub> |
| <i>M<sub>r</sub></i>   | 528.32  |
| Crystal system, space group  | Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>                   |
| Temperature (K)  | 173   |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)   | 17.100 (6), 4.744 (2), 13.662 (4)   |
| β (°)  | 106.83 (2)  |
| <i>V</i> (Å <sup>3</sup> )   | 1060.8 (7)  |
| <i>Z</i>   | 2   |
| Radiation type   | Mo <i>K</i> α   |
| μ (mm <sup>-1</sup> )  | 0.15  |
| Crystal size (mm)  | 0.40 × 0.15 × 0.01  |
| Data collection  |   |
| Diffractometer   | Bruker–Nonius KappaCCD  |
| Absorption correction  | Multi-scan ( <i>SADABS</i> ; Bruker, 2001)                                  |
| <i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>  | 0.931, 0.986  |
| No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections                             | 7948, 2396, 1440  |
| <i>R<sub>int</sub></i>   | 0.061   |
| (sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )  | 0.650   |
| Refinement   |   |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.048, 0.120, 1.05  |
| No. of reflections   | 2396  |
| No. of parameters  | 176   |
| No. of restraints  | 1   |
| H-atom treatment   | H-atom parameters constrained   |
| Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )   | 0.26, −0.32   |

Computer programs: *COLLECT* (Nonius, 1999), *DIRAX/LSQ* (Duisenberg *et al.*, 2000), *EVALCCD* (Duisenberg *et al.*, 2003), *SIR97* (Altomare *et al.*, 1999), *SHELXL2016* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

#### 5. Synthesis and crystallization

*N,N'*-Dihydroxybenzene-1,2,4,5-tetracarboximide (Centore & Carella, 2013) (1.000 g, 4.030 mmol) was suspended in 20 ml of dry pyridine and the system was kept under stirring at room temperature. 2,4-Difluorobenzoylchloride (1.991 g, 11.28 mmol) was added dropwise and the previous suspension turned into a dark solution. The solution was warmed and boiled gently for 45 min. Absolute ethanol (2 ml) and, after 2 min, distilled water (0.2 ml) were then added and the system cooled slowly to room temperature and filtered. The white crystals were washed on the filter with absolute ethanol. From the recovered material it was possible to isolate several single crystals suitable for X-ray analysis. The yield was 55% (m.p. 604 K).

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were generated stereochemically and were refined by the riding model. For all H atoms, *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(carrier). The difluorophenyl ring is disordered over two orientations, which differ by a rotation of 180° around the phenyl to carbonyl bond. Split positions were only observed for the *ortho*-F atom. The two split positions were refined by applying SADI restraints on bond lengths. The final refined occupancy factors of the two components of disorder are 0.947 (4) and 0.053 (4).

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## supporting information

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## Crystal structure of *N,N'*-bis(2,4-difluorobenzoyloxy)benzene-1,2:4,5-tetracarboximide

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### Computing details

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

### *N,N'*-Bis(2,4-difluorobenzoyloxy)benzene-1,2:4,5-tetracarboximide

#### Crystal data

$C_{24}H_8F_4N_2O_8$

$M_r = 528.32$

Monoclinic,  $P2_1/c$

$a = 17.100$  (6) Å

$b = 4.744$  (2) Å

$c = 13.662$  (4) Å

$\beta = 106.83$  (2)°

$V = 1060.8$  (7) Å<sup>3</sup>

$Z = 2$

$F(000) = 532$

$D_x = 1.654$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 85 reflections

$\theta = 5.1$ – $21.4$ °

$\mu = 0.15$  mm<sup>-1</sup>

$T = 173$  K

Plate, colourless

$0.40 \times 0.15 \times 0.01$  mm

#### Data collection

Bruker–Nonius KappaCCD  
diffractometer

Radiation source: normal-focus sealed tube

Graphite monochromator

Detector resolution: 9 pixels mm<sup>-1</sup>

CCD rotation images, thick slices scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2001)

$T_{\min} = 0.931$ ,  $T_{\max} = 0.986$

7948 measured reflections

2396 independent reflections

1440 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.061$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 3.4$ °

$h = -22 \rightarrow 21$

$k = -6 \rightarrow 6$

$l = -15 \rightarrow 17$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.120$

$S = 1.05$

2396 reflections

176 parameters

1 restraint

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

$$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.4397P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$$

*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.

**Refinement.** The difluorophenyl ring is disordered over two orientations. The two split positions were refined by applying SADI restraints on bond lengths.

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

|      | x            | y           | z             | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|--------------|-------------|---------------|----------------------------------|-----------|
| C1   | 0.53428 (13) | -0.2108 (5) | 0.44840 (16)  | 0.0196 (5)                       |           |
| H1   | 0.557147     | -0.349497   | 0.414668      | 0.024*                           |           |
| C2   | 0.47095 (12) | -0.0358 (5) | 0.39704 (15)  | 0.0177 (5)                       |           |
| C3   | 0.43844 (12) | 0.1672 (5)  | 0.44705 (16)  | 0.0191 (5)                       |           |
| C4   | 0.37402 (13) | 0.3243 (5)  | 0.36996 (17)  | 0.0226 (5)                       |           |
| C5   | 0.42706 (13) | -0.0236 (5) | 0.28530 (16)  | 0.0208 (5)                       |           |
| C6   | 0.24590 (14) | 0.1960 (6)  | 0.15987 (18)  | 0.0306 (6)                       |           |
| C7   | 0.19802 (14) | 0.3233 (6)  | 0.06271 (17)  | 0.0260 (5)                       |           |
| C9   | 0.07036 (16) | 0.3516 (7)  | -0.0723 (2)   | 0.0406 (7)                       |           |
| H9   | 0.015390     | 0.292807    | -0.101232     | 0.049*                           |           |
| C10  | 0.10527 (16) | 0.5453 (7)  | -0.11934 (18) | 0.0354 (7)                       |           |
| C11  | 0.18428 (15) | 0.6341 (6)  | -0.08085 (19) | 0.0333 (6)                       |           |
| H11  | 0.206836     | 0.769181    | -0.116313     | 0.040*                           |           |
| C8A  | 0.11781 (16) | 0.2431 (6)  | 0.0194 (2)    | 0.0369 (7)                       | 0.947 (4) |
| F1A  | 0.08458 (11) | 0.0511 (5)  | 0.06620 (15)  | 0.0714 (8)                       | 0.947 (4) |
| C12A | 0.23029 (14) | 0.5223 (6)  | 0.01072 (18)  | 0.0289 (6)                       | 0.947 (4) |
| H12A | 0.285205     | 0.582553    | 0.038893      | 0.035*                           | 0.947 (4) |
| C8B  | 0.11781 (16) | 0.2431 (6)  | 0.0194 (2)    | 0.0369 (7)                       | 0.053 (4) |
| H8B  | 0.094436     | 0.108079    | 0.053933      | 0.044*                           | 0.053 (4) |
| C12B | 0.23029 (14) | 0.5223 (6)  | 0.01072 (18)  | 0.0289 (6)                       | 0.053 (4) |
| F1B  | 0.3060 (9)   | 0.615 (6)   | 0.037 (2)     | 0.043*                           | 0.053 (4) |
| F2   | 0.05967 (10) | 0.6562 (4)  | -0.20823 (12) | 0.0554 (6)                       |           |
| N1   | 0.37352 (12) | 0.1997 (5)  | 0.27779 (14)  | 0.0256 (5)                       |           |
| O1   | 0.33327 (10) | 0.5199 (4)  | 0.38057 (13)  | 0.0315 (4)                       |           |
| O2   | 0.43410 (10) | -0.1664 (4) | 0.21582 (12)  | 0.0258 (4)                       |           |
| O3   | 0.32607 (9)  | 0.2995 (4)  | 0.18452 (11)  | 0.0268 (4)                       |           |
| O4   | 0.22619 (12) | 0.0326 (6)  | 0.21309 (16)  | 0.0623 (8)                       |           |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|    | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$   | $U^{23}$    |
|----|-------------|-------------|-------------|-------------|------------|-------------|
| C1 | 0.0185 (10) | 0.0213 (12) | 0.0195 (10) | 0.0013 (10) | 0.0062 (8) | 0.0007 (10) |
| C2 | 0.0187 (10) | 0.0186 (12) | 0.0162 (9)  | -0.0022 (9) | 0.0056 (8) | 0.0006 (9)  |
| C3 | 0.0162 (10) | 0.0209 (12) | 0.0195 (10) | -0.0013 (9) | 0.0040 (8) | 0.0037 (10) |

|      |             |             |             |              |              |             |
|------|-------------|-------------|-------------|--------------|--------------|-------------|
| C4   | 0.0197 (10) | 0.0247 (13) | 0.0220 (11) | 0.0006 (10)  | 0.0038 (8)   | 0.0030 (11) |
| C5   | 0.0214 (10) | 0.0206 (12) | 0.0189 (10) | -0.0006 (10) | 0.0037 (8)   | 0.0034 (10) |
| C6   | 0.0236 (12) | 0.0388 (16) | 0.0262 (12) | -0.0060 (12) | 0.0023 (10)  | 0.0058 (12) |
| C7   | 0.0241 (11) | 0.0309 (14) | 0.0197 (11) | -0.0020 (11) | 0.0012 (9)   | 0.0036 (11) |
| C9   | 0.0254 (12) | 0.055 (2)   | 0.0326 (14) | -0.0102 (13) | -0.0051 (10) | 0.0056 (14) |
| C10  | 0.0307 (13) | 0.0479 (18) | 0.0209 (11) | 0.0052 (13)  | -0.0034 (10) | 0.0070 (13) |
| C11  | 0.0286 (12) | 0.0401 (17) | 0.0294 (13) | -0.0004 (12) | 0.0055 (10)  | 0.0120 (12) |
| C8A  | 0.0308 (13) | 0.0423 (17) | 0.0331 (14) | -0.0113 (13) | 0.0021 (11)  | 0.0098 (13) |
| F1A  | 0.0388 (10) | 0.0959 (19) | 0.0636 (13) | -0.0361 (11) | -0.0101 (9)  | 0.0451 (13) |
| C12A | 0.0209 (11) | 0.0368 (16) | 0.0262 (11) | -0.0034 (11) | 0.0021 (9)   | 0.0042 (12) |
| C8B  | 0.0308 (13) | 0.0423 (17) | 0.0331 (14) | -0.0113 (13) | 0.0021 (11)  | 0.0098 (13) |
| C12B | 0.0209 (11) | 0.0368 (16) | 0.0262 (11) | -0.0034 (11) | 0.0021 (9)   | 0.0042 (12) |
| F2   | 0.0409 (9)  | 0.0744 (14) | 0.0363 (9)  | -0.0026 (9)  | -0.0119 (7)  | 0.0227 (9)  |
| N1   | 0.0271 (10) | 0.0289 (12) | 0.0162 (9)  | 0.0073 (9)   | -0.0010 (7)  | 0.0046 (9)  |
| O1   | 0.0284 (9)  | 0.0306 (10) | 0.0324 (9)  | 0.0103 (8)   | 0.0037 (7)   | 0.0007 (8)  |
| O2   | 0.0313 (9)  | 0.0267 (10) | 0.0194 (8)  | 0.0009 (7)   | 0.0074 (7)   | -0.0017 (8) |
| O3   | 0.0214 (8)  | 0.0352 (10) | 0.0180 (7)  | 0.0013 (8)   | -0.0035 (6)  | 0.0083 (8)  |
| O4   | 0.0424 (12) | 0.0860 (19) | 0.0466 (12) | -0.0228 (12) | -0.0057 (9)  | 0.0414 (13) |

*Geometric parameters (Å, °)*

|                        |             |              |            |
|------------------------|-------------|--------------|------------|
| C1—C2                  | 1.384 (3)   | C7—C12A      | 1.388 (4)  |
| C1—C3 <sup>i</sup>     | 1.384 (3)   | C9—C10       | 1.355 (4)  |
| C1—H1                  | 0.9500      | C9—C8B       | 1.379 (4)  |
| C2—C3                  | 1.387 (3)   | C9—C8A       | 1.379 (4)  |
| C2—C5                  | 1.494 (3)   | C9—H9        | 0.9500     |
| C3—C4                  | 1.485 (3)   | C10—F2       | 1.346 (3)  |
| C4—O1                  | 1.194 (3)   | C10—C11      | 1.367 (4)  |
| C4—N1                  | 1.389 (3)   | C11—C12B     | 1.377 (3)  |
| C5—O2                  | 1.200 (3)   | C11—C12A     | 1.377 (3)  |
| C5—N1                  | 1.384 (3)   | C11—H11      | 0.9500     |
| C6—O4                  | 1.177 (3)   | C8A—F1A      | 1.331 (3)  |
| C6—O3                  | 1.402 (3)   | C12A—H12A    | 0.9500     |
| C6—C7                  | 1.472 (3)   | C8B—H8B      | 0.9500     |
| C7—C8B                 | 1.381 (3)   | C12B—F1B     | 1.315 (10) |
| C7—C8A                 | 1.381 (3)   | N1—O3        | 1.381 (2)  |
| C7—C12B                | 1.388 (4)   |              |            |
| C2—C1—C3 <sup>i</sup>  | 114.5 (2)   | C10—C9—H9    | 121.3      |
| C2—C1—H1               | 122.8       | C8A—C9—H9    | 121.3      |
| C3 <sup>i</sup> —C1—H1 | 122.8       | F2—C10—C9    | 118.3 (2)  |
| C1—C2—C3               | 122.23 (19) | F2—C10—C11   | 118.5 (3)  |
| C1—C2—C5               | 129.0 (2)   | C9—C10—C11   | 123.3 (2)  |
| C3—C2—C5               | 108.78 (19) | C10—C11—C12B | 118.2 (2)  |
| C1 <sup>i</sup> —C3—C2 | 123.3 (2)   | C10—C11—C12A | 118.2 (2)  |
| C1 <sup>i</sup> —C3—C4 | 128.0 (2)   | C10—C11—H11  | 120.9      |
| C2—C3—C4               | 108.65 (19) | C12A—C11—H11 | 120.9      |
| O1—C4—N1               | 126.2 (2)   | F1A—C8A—C9   | 118.1 (2)  |

|                           |             |                  |              |
|---------------------------|-------------|------------------|--------------|
| O1—C4—C3                  | 130.0 (2)   | F1A—C8A—C7       | 119.4 (2)    |
| N1—C4—C3                  | 103.76 (19) | C9—C8A—C7        | 122.5 (2)    |
| O2—C5—N1                  | 126.1 (2)   | C11—C12A—C7      | 121.3 (2)    |
| O2—C5—C2                  | 130.6 (2)   | C11—C12A—H12A    | 119.3        |
| N1—C5—C2                  | 103.36 (19) | C7—C12A—H12A     | 119.3        |
| O4—C6—O3                  | 121.1 (2)   | C9—C8B—C7        | 122.5 (2)    |
| O4—C6—C7                  | 130.0 (2)   | C9—C8B—H8B       | 118.8        |
| O3—C6—C7                  | 108.8 (2)   | C7—C8B—H8B       | 118.8        |
| C8B—C7—C12B               | 117.4 (2)   | F1B—C12B—C11     | 112.2 (13)   |
| C8A—C7—C12A               | 117.4 (2)   | F1B—C12B—C7      | 126.4 (13)   |
| C8B—C7—C6                 | 119.9 (2)   | C11—C12B—C7      | 121.3 (2)    |
| C8A—C7—C6                 | 119.9 (2)   | O3—N1—C5         | 122.00 (19)  |
| C12B—C7—C6                | 122.7 (2)   | O3—N1—C4         | 122.6 (2)    |
| C12A—C7—C6                | 122.7 (2)   | C5—N1—C4         | 115.35 (19)  |
| C10—C9—C8B                | 117.4 (2)   | N1—O3—C6         | 111.96 (18)  |
| C10—C9—C8A                | 117.4 (2)   |                  |              |
|                           |             |                  |              |
| C3 <sup>i</sup> —C1—C2—C3 | 0.5 (4)     | C10—C9—C8A—F1A   | -179.5 (3)   |
| C3 <sup>i</sup> —C1—C2—C5 | 179.9 (2)   | C10—C9—C8A—C7    | -0.5 (5)     |
| C1—C2—C3—C1 <sup>i</sup>  | -0.5 (4)    | C12A—C7—C8A—F1A  | 179.5 (3)    |
| C5—C2—C3—C1 <sup>i</sup>  | 180.0 (2)   | C6—C7—C8A—F1A    | 0.1 (4)      |
| C1—C2—C3—C4               | 178.0 (2)   | C12A—C7—C8A—C9   | 0.4 (4)      |
| C5—C2—C3—C4               | -1.6 (3)    | C6—C7—C8A—C9     | -179.0 (3)   |
| C1 <sup>i</sup> —C3—C4—O1 | 1.0 (4)     | C10—C11—C12A—C7  | 0.5 (4)      |
| C2—C3—C4—O1               | -177.4 (3)  | C8A—C7—C12A—C11  | -0.4 (4)     |
| C1 <sup>i</sup> —C3—C4—N1 | 178.1 (2)   | C6—C7—C12A—C11   | 179.0 (3)    |
| C2—C3—C4—N1               | -0.2 (2)    | C10—C9—C8B—C7    | -0.5 (5)     |
| C1—C2—C5—O2               | 3.1 (4)     | C12B—C7—C8B—C9   | 0.4 (4)      |
| C3—C2—C5—O2               | -177.4 (2)  | C6—C7—C8B—C9     | -179.0 (3)   |
| C1—C2—C5—N1               | -176.8 (2)  | C10—C11—C12B—F1B | 177.2 (15)   |
| C3—C2—C5—N1               | 2.7 (2)     | C10—C11—C12B—C7  | 0.5 (4)      |
| O4—C6—C7—C8B              | -2.9 (5)    | C8B—C7—C12B—F1B  | -176.7 (17)  |
| O3—C6—C7—C8B              | 176.6 (3)   | C6—C7—C12B—F1B   | 2.7 (18)     |
| O4—C6—C7—C8A              | -2.9 (5)    | C8B—C7—C12B—C11  | -0.4 (4)     |
| O3—C6—C7—C8A              | 176.6 (3)   | C6—C7—C12B—C11   | 179.0 (3)    |
| O4—C6—C7—C12B             | 177.8 (3)   | O2—C5—N1—O3      | -6.0 (4)     |
| O3—C6—C7—C12B             | -2.7 (4)    | C2—C5—N1—O3      | 173.86 (19)  |
| O4—C6—C7—C12A             | 177.8 (3)   | O2—C5—N1—C4      | 177.1 (2)    |
| O3—C6—C7—C12A             | -2.7 (4)    | C2—C5—N1—C4      | -3.0 (3)     |
| C8B—C9—C10—F2             | -179.2 (3)  | O1—C4—N1—O3      | 2.6 (4)      |
| C8A—C9—C10—F2             | -179.2 (3)  | C3—C4—N1—O3      | -174.73 (19) |
| C8B—C9—C10—C11            | 0.6 (5)     | O1—C4—N1—C5      | 179.4 (2)    |
| C8A—C9—C10—C11            | 0.6 (5)     | C3—C4—N1—C5      | 2.1 (3)      |
| F2—C10—C11—C12B           | 179.2 (3)   | C5—N1—O3—C6      | 99.6 (3)     |
| C9—C10—C11—C12B           | -0.5 (5)    | C4—N1—O3—C6      | -83.7 (3)    |



|                 |           |             |           |
|-----------------|-----------|-------------|-----------|
| F2—C10—C11—C12A | 179.2 (3) | O4—C6—O3—N1 | -3.5 (4)  |
| C9—C10—C11—C12A | -0.5 (5)  | C7—C6—O3—N1 | 176.9 (2) |

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

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

| <i>D—H...A</i>             | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|----------------------------|------------|--------------|--------------|----------------|
| C1—H1...O2 <sup>ii</sup>   | 0.95       | 2.37         | 3.271 (3)    | 158            |
| C9—H9...F1A <sup>iii</sup> | 0.95       | 2.51         | 3.287 (3)    | 139            |
| C9—H9...F2 <sup>iv</sup>   | 0.95       | 2.63         | 3.307 (3)    | 129            |
| C11—H11...O1 <sup>v</sup>  | 0.95       | 2.39         | 3.200 (3)    | 143            |

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