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# 3-Ethyl 5-methyl 2-hydroxy-6-methyl-4-(4-nitrophenyl)-2-trifluoromethyl-1,2,3,4-tetrahydropyridine-3,5-dicarboxylate

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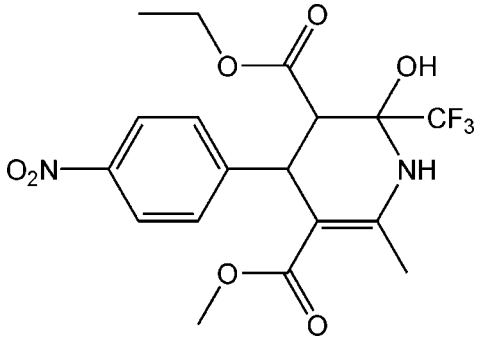
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.003 Å; disorder in main residue; $R$ factor = 0.053; $wR$ factor = 0.150; data-to-parameter ratio = 12.1.

In the title compound, $C_{18}H_{19}F_3N_2O_7$, the tetrahydropyridine ring adopts a half-chair conformation. The nitro group is disordered over two sites with occupancies of 0.780 (15) and 0.220 (15). An intramolecular N—H···F hydrogen bond is observed in the molecular structure. The molecules are linked into a two-dimensional network parallel to (100) by O—H···O, N—H···O and C—H···O hydrogen bonds.

## Related literature

For related literature, see: Achiwa & Kato (1999); Dubur *et al.* (1989); Hermann *et al.* (2003); Ulrich (2004).




## Experimental

### Crystal data

$C_{18}H_{19}F_3N_2O_7$
$M_r$ = 432.35
Monoclinic, $C2/c$
$a$ = 28.678 (6) Å
$b$ = 9.6678 (19) Å
$c$ = 14.120 (3) Å
$\beta$ = 95.72 (3)°
$V$ = 3895.1 (13) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.13 mm$^{-1}$
$T$ = 293 (2) K
0.16 × 0.16 × 0.04 mm

### Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2002)
$T_{min}$ = 0.979, $T_{max}$ = 0.995
11673 measured reflections
3438 independent reflections
2572 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.043

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.150
$S$ = 1.06
3438 reflections
284 parameters
14 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.20 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O7—H7···O5$^{i}$ | 0.82 | 1.98 | 2.783 (3) | 166 |
| N2—H2···O3$^{ii}$ | 0.86 | 2.20 | 3.030 (3) | 163 |
| N2—H2···F2 | 0.86 | 2.42 | 2.735 (2) | 102 |
| C5—H5···O2$^{iii}$ | 0.93 | 2.51 | 3.432 (4) | 171 |

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

Data collection: *CrystalClear* (Rigaku/MSC, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2642).

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# supporting information

*Acta Cryst.* (2008). E**64**, o1737 [doi:10.1107/S1600536808024835]

## 3-Ethyl 5-methyl 2-hydroxy-6-methyl-4-(4-nitrophenyl)-2-trifluoro-methyl-1,2,3,4-tetrahydropyridine-3,5-dicarboxylate

**Chen-Xia Yu, Pei-Li Qian, Jia-Jing Ping and Chang-Sheng Yao**

### S1. Comment

1,4-Dihydropyridines are well known compounds as a consequence of their pharmacological profile as the most important calcium channel modulators (Achiwa & Kato, 1999). 4-Aryl-2,6-dimethyl-1,4-dihydropyridine -3,5-di-carboxylate derivatives are widely used for the treatment of cardiovascular diseases such as hypertension, angina pectoris and infarction (Dubur *et al.*, 1989). In addition, compounds that contain fluorine have special bioactivity, for example, flumioxazin is a widely used herbicide (Hermann *et al.*, 2003; Ulrich,2004). This led us to pay much attention to the synthesis and bioactivity of these fluoro-compounds. During the synthesis of trifluoromethylated 1,4-dihydropyridine derivatives, an intermediate, the title compound, was isolated. We report here the crystal structure of the title compound.

In the title molecule (Fig.1), the pyridine ring adopts a half-chair conformation, with atoms C10 and C11 deviating from the N2/C7/C8/C9 plane by 0.261 (4) Å and -0.544 (4)Å, respectively. The dihedral angle between the N2/C7/C8/C9 and C1-C6 planes is 72.30 (9)°. The N atom of the nitro group adopts a planar configuration in the major disorder component, while pyramidal configuration in the minor disorder component. An intramolecular N2—H2···F2 hydrogen bond is observed in the molecular structure.

The crystal packing is stabilized by O—H···O, N—H···O and C—H···O intermolecular hydrogen bonds (Table 1) which link the molecules into a two-dimensional network parallel to the (1 0 0) (Fig. 2).

### S2. Experimental

The title compound was synthesized by the reaction of 4-nitrobenzaldehyde (1 mmol), methyl 3-amino-but-2-enoate (1 mmol) and ethyl 4,4,4-trifluoro-3-oxobutanoate (1 mmol) catalyzed by triethylbenzylaminium chloride (0.02 g) in water (10 ml) at 363 K. After cooling, the reaction mixture was washed with water and recrystallized from ethanol, to obtain single crystals suitable for X-ray diffraction.

### S3. Refinement

All H atoms were placed in calculated positions (C-H = 0.93–0.98 Å, O-H = 0.82 Å and N-H = 0.86 Å) and included in the final cycles of refinement using a riding model, with $U_{iso}$(H) = 1.2$U_{eq}$(parent atom). Atom O1 is disordered over two positions with site-occupancy factors of 0.220 (15) and 0.780 (15), respectively. The $U^{ij}$ components of disordered atoms were restrained to an approximate isotropic behaviour. The N1—O1 and N1—O1′ bond lengths were restrained to 1.22 (2) Å.

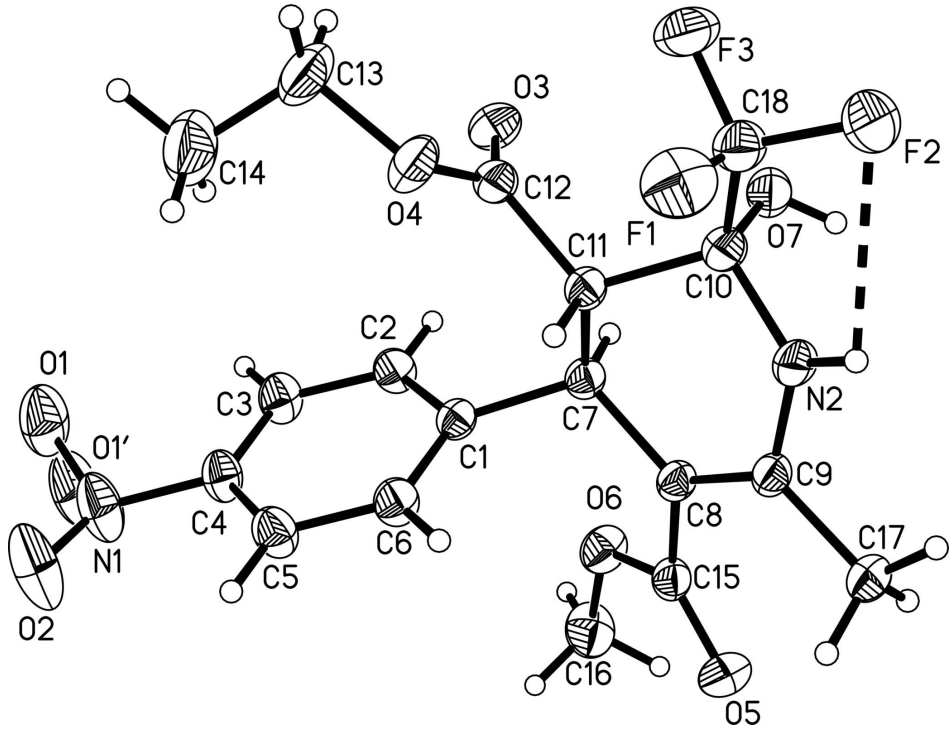


**Figure 1**

The molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme. Both disorder components are shown. The dashed line indicates a hydrogen bond.

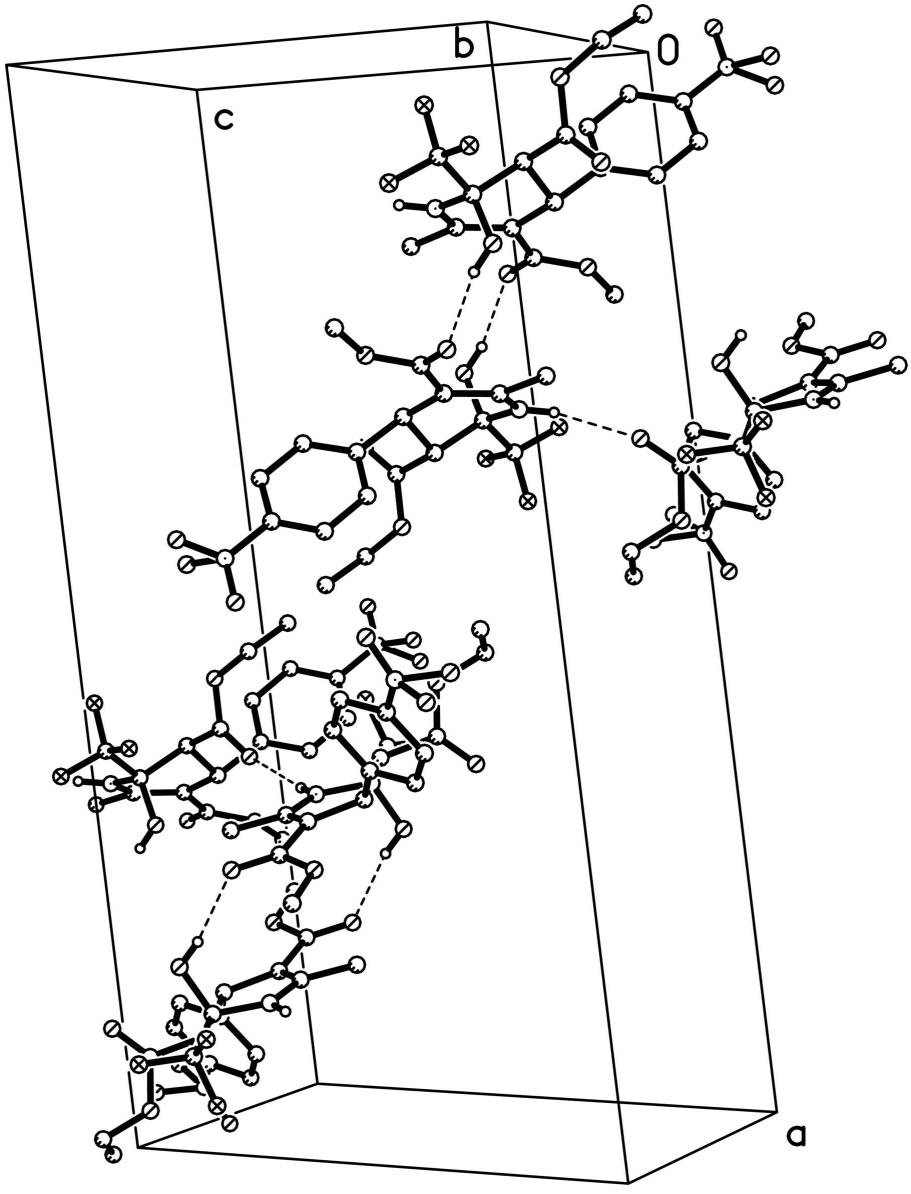


**Figure 2**

The packing diagram of the title compound. Intermolecular hydrogen bonds are shown as dashed lines and H atoms not involved in hydrogen bonding have been omitted for clarity.

## 3-Ethyl 5-methyl 2-hydroxy-6-methyl-4-(4-nitrophenyl)-2-trifluoromethyl- 1,2,3,4-tetrahydropyridine-3,5-dicarboxylate

*Crystal data*

$C_{18}H_{19}F_3N_2O_7$
$M_r = 432.35$
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
$a = 28.678\ (6)$ Å
$b = 9.6678\ (19)$ Å
$c = 14.120\ (3)$ Å
$\beta = 95.72\ (3)°$
$V = 3895.1\ (13)$ Å$^3$
$Z = 8$
$F(000) = 1792$
$D_x = 1.475$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3562 reflections

$\theta$ = 2.2–25.0°
$\mu$ = 0.13 mm$^{-1}$
$T$ = 293 K

Prism, colourless
0.16 × 0.16 × 0.04 mm

*Data collection*

Rigaku Saturn diffractometer
Radiation source: rotating anode
Confocal monochromator
Detector resolution: 7.31 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2002)
$T_{min}$ = 0.979, $T_{max}$ = 0.995

11673 measured reflections
3438 independent reflections
2572 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.043
$\theta_{max}$ = 25.0°, $\theta_{min}$ = 2.2°
$h$ = −33→34
$k$ = −11→11
$l$ = −16→12

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.150
$S$ = 1.06
3438 reflections
284 parameters
14 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
$w = 1/[\sigma^2(F_o^2) + (0.0873P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.21 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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| F1 | 0.08689 (6) | 0.58977 (17) | 0.93658 (13) | 0.0775 (5) | |
| F2 | 0.15032 (7) | 0.70065 (15) | 0.97856 (12) | 0.0800 (6) | |
| F3 | 0.12464 (6) | 0.68534 (15) | 0.83137 (11) | 0.0725 (5) | |
| O1 | 0.0452 (7) | −0.100 (2) | 0.5112 (8) | 0.086 (6) | 0.220 (15) |
| O1′ | 0.06713 (19) | −0.1837 (7) | 0.5322 (3) | 0.090 (2) | 0.780 (15) |
| O2 | 0.01478 (8) | −0.1793 (3) | 0.63009 (19) | 0.0972 (9) | |
| O3 | 0.13847 (6) | 0.44788 (18) | 0.67834 (12) | 0.0545 (5) | |
| O4 | 0.06795 (6) | 0.44145 (19) | 0.73469 (12) | 0.0594 (5) | |
| O5 | 0.21673 (6) | 0.00503 (18) | 1.01751 (13) | 0.0546 (5) | |
| O6 | 0.21490 (6) | 0.01870 (17) | 0.85947 (12) | 0.0512 (5) | |
| O7 | 0.19972 (6) | 0.52220 (18) | 0.86560 (12) | 0.0512 (5) | |
| H7 | 0.2218 | 0.5189 | 0.9071 | 0.077* | |
| N1 | 0.05038 (9) | −0.1349 (3) | 0.6024 (2) | 0.0738 (8) | |

| | | | | |
|---|---|---|---|---|
| N2 | 0.16656 (7) | 0.42268 (18) | 0.99703 (13) | 0.0432 (5) |
| H2 | 0.1630 | 0.4725 | 1.0463 | 0.052* |
| C1 | 0.13495 (7) | 0.1409 (2) | 0.77500 (16) | 0.0353 (5) |
| C2 | 0.14347 (8) | 0.1173 (2) | 0.68116 (16) | 0.0424 (6) |
| H2A | 0.1683 | 0.1621 | 0.6565 | 0.051* |
| C3 | 0.11549 (9) | 0.0281 (2) | 0.62409 (18) | 0.0485 (6) |
| H3 | 0.1210 | 0.0132 | 0.5611 | 0.058* |
| C4 | 0.07957 (8) | −0.0378 (2) | 0.66212 (18) | 0.0469 (6) |
| C5 | 0.07026 (9) | −0.0190 (3) | 0.75489 (19) | 0.0502 (6) |
| H5 | 0.0458 | −0.0659 | 0.7793 | 0.060* |
| C6 | 0.09829 (8) | 0.0715 (2) | 0.81067 (17) | 0.0446 (6) |
| H6 | 0.0924 | 0.0860 | 0.8735 | 0.053* |
| C7 | 0.16340 (7) | 0.2485 (2) | 0.83367 (15) | 0.0365 (5) |
| H7A | 0.1902 | 0.2747 | 0.7996 | 0.044* |
| C8 | 0.18168 (7) | 0.2018 (2) | 0.93315 (15) | 0.0354 (5) |
| C9 | 0.18004 (7) | 0.2873 (2) | 1.00940 (15) | 0.0368 (5) |
| C10 | 0.15830 (8) | 0.4834 (2) | 0.90448 (17) | 0.0427 (6) |
| C11 | 0.13175 (8) | 0.3763 (2) | 0.83985 (16) | 0.0373 (5) |
| H11 | 0.1044 | 0.3473 | 0.8711 | 0.045* |
| C12 | 0.11414 (9) | 0.4275 (2) | 0.74130 (17) | 0.0418 (6) |
| C13 | 0.04231 (12) | 0.4735 (4) | 0.6429 (2) | 0.0755 (9) |
| H13A | 0.0637 | 0.5090 | 0.5997 | 0.091* |
| H13B | 0.0189 | 0.5439 | 0.6509 | 0.091* |
| C14 | 0.01957 (13) | 0.3484 (4) | 0.6032 (2) | 0.0918 (11) |
| H14A | 0.0430 | 0.2830 | 0.5884 | 0.138* |
| H14B | −0.0001 | 0.3712 | 0.5462 | 0.138* |
| H14C | 0.0008 | 0.3086 | 0.6488 | 0.138* |
| C15 | 0.20522 (8) | 0.0677 (2) | 0.94376 (17) | 0.0396 (5) |
| C16 | 0.23732 (10) | −0.1148 (3) | 0.8569 (2) | 0.0651 (8) |
| H16A | 0.2607 | −0.1231 | 0.9101 | 0.098* |
| H16B | 0.2518 | −0.1237 | 0.7987 | 0.098* |
| H16C | 0.2143 | −0.1864 | 0.8601 | 0.098* |
| C17 | 0.19319 (8) | 0.2520 (2) | 1.11186 (15) | 0.0460 (6) |
| H17A | 0.1907 | 0.3331 | 1.1502 | 0.069* |
| H17B | 0.2249 | 0.2184 | 1.1198 | 0.069* |
| H17C | 0.1725 | 0.1818 | 1.1313 | 0.069* |
| C18 | 0.12955 (10) | 0.6156 (2) | 0.91287 (19) | 0.0543 (7) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| F1 | 0.0761 (12) | 0.0770 (11) | 0.0819 (13) | 0.0222 (9) | 0.0199 (10) | −0.0030 (9) |
| F2 | 0.1242 (15) | 0.0509 (9) | 0.0612 (11) | 0.0076 (9) | −0.0094 (10) | −0.0176 (8) |
| F3 | 0.1081 (13) | 0.0524 (9) | 0.0544 (10) | 0.0161 (8) | −0.0046 (9) | 0.0094 (7) |
| O1 | 0.085 (8) | 0.118 (10) | 0.055 (7) | −0.032 (7) | 0.008 (5) | −0.026 (6) |
| O1′ | 0.093 (3) | 0.111 (4) | 0.069 (2) | −0.038 (3) | 0.023 (2) | −0.052 (2) |
| O2 | 0.0728 (14) | 0.1166 (18) | 0.1066 (19) | −0.0437 (14) | 0.0303 (14) | −0.0568 (16) |
| O3 | 0.0674 (11) | 0.0622 (11) | 0.0344 (10) | −0.0019 (8) | 0.0074 (9) | 0.0101 (8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O4 | 0.0528 (11) | 0.0799 (12) | 0.0425 (11) | 0.0022 (9) | −0.0094 (9) | 0.0098 (9) |
| O5 | 0.0621 (11) | 0.0555 (10) | 0.0458 (11) | 0.0078 (8) | 0.0028 (9) | 0.0114 (9) |
| O6 | 0.0595 (11) | 0.0521 (10) | 0.0420 (10) | 0.0109 (8) | 0.0042 (9) | −0.0055 (8) |
| O7 | 0.0536 (10) | 0.0592 (10) | 0.0403 (10) | −0.0162 (9) | 0.0018 (8) | 0.0045 (8) |
| N1 | 0.0681 (16) | 0.0885 (18) | 0.0668 (18) | −0.0311 (14) | 0.0167 (14) | −0.0349 (15) |
| N2 | 0.0620 (13) | 0.0418 (10) | 0.0254 (10) | 0.0000 (9) | 0.0027 (9) | −0.0041 (8) |
| C1 | 0.0372 (12) | 0.0379 (11) | 0.0307 (12) | 0.0012 (9) | 0.0025 (10) | −0.0011 (9) |
| C2 | 0.0468 (13) | 0.0470 (13) | 0.0348 (13) | −0.0064 (11) | 0.0109 (11) | −0.0042 (11) |
| C3 | 0.0543 (15) | 0.0555 (14) | 0.0368 (14) | −0.0044 (12) | 0.0099 (12) | −0.0133 (11) |
| C4 | 0.0476 (14) | 0.0504 (13) | 0.0425 (14) | −0.0070 (11) | 0.0032 (12) | −0.0148 (11) |
| C5 | 0.0478 (14) | 0.0553 (14) | 0.0487 (15) | −0.0135 (12) | 0.0103 (12) | −0.0045 (12) |
| C6 | 0.0506 (14) | 0.0524 (13) | 0.0318 (13) | −0.0075 (11) | 0.0097 (11) | −0.0045 (11) |
| C7 | 0.0392 (12) | 0.0414 (11) | 0.0291 (11) | −0.0038 (9) | 0.0047 (10) | 0.0004 (10) |
| C8 | 0.0356 (11) | 0.0421 (11) | 0.0286 (12) | −0.0036 (9) | 0.0028 (9) | 0.0022 (9) |
| C9 | 0.0360 (11) | 0.0447 (12) | 0.0294 (12) | −0.0058 (10) | 0.0008 (9) | 0.0023 (10) |
| C10 | 0.0536 (14) | 0.0420 (12) | 0.0320 (13) | −0.0026 (10) | 0.0022 (11) | 0.0012 (10) |
| C11 | 0.0420 (12) | 0.0408 (11) | 0.0291 (12) | −0.0032 (10) | 0.0030 (10) | 0.0001 (9) |
| C12 | 0.0521 (14) | 0.0390 (12) | 0.0338 (13) | −0.0027 (10) | 0.0016 (12) | 0.0007 (10) |
| C13 | 0.076 (2) | 0.095 (2) | 0.0499 (18) | 0.0053 (18) | −0.0195 (16) | 0.0128 (17) |
| C14 | 0.091 (2) | 0.114 (3) | 0.065 (2) | −0.019 (2) | −0.0149 (19) | −0.008 (2) |
| C15 | 0.0373 (12) | 0.0449 (12) | 0.0363 (13) | −0.0063 (10) | 0.0015 (10) | −0.0001 (11) |
| C16 | 0.0681 (18) | 0.0536 (15) | 0.072 (2) | 0.0125 (13) | 0.0009 (16) | −0.0161 (14) |
| C17 | 0.0544 (14) | 0.0520 (13) | 0.0309 (13) | −0.0051 (11) | 0.0000 (11) | 0.0020 (11) |
| C18 | 0.0761 (19) | 0.0455 (14) | 0.0403 (15) | 0.0047 (13) | 0.0008 (14) | −0.0029 (12) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| F1—C18 | 1.324 (3) | C5—C6 | 1.380 (3) |
| F2—C18 | 1.335 (3) | C5—H5 | 0.93 |
| F3—C18 | 1.329 (3) | C6—H6 | 0.93 |
| O1—N1 | 1.325 (13) | C7—C8 | 1.518 (3) |
| O1′—N1 | 1.237 (4) | C7—C11 | 1.541 (3) |
| O2—N1 | 1.208 (3) | C7—H7A | 0.98 |
| O3—C12 | 1.200 (3) | C8—C9 | 1.362 (3) |
| O4—C12 | 1.326 (3) | C8—C15 | 1.462 (3) |
| O4—C13 | 1.458 (3) | C9—C17 | 1.498 (3) |
| O5—C15 | 1.221 (3) | C10—C18 | 1.532 (3) |
| O6—C15 | 1.336 (3) | C10—C11 | 1.532 (3) |
| O6—C16 | 1.444 (3) | C11—C12 | 1.515 (3) |
| O7—C10 | 1.408 (3) | C11—H11 | 0.98 |
| O7—H7 | 0.82 | C13—C14 | 1.459 (5) |
| N1—C4 | 1.467 (3) | C13—H13A | 0.97 |
| N2—C9 | 1.371 (3) | C13—H13B | 0.97 |
| N2—C10 | 1.431 (3) | C14—H14A | 0.96 |
| N2—H2 | 0.86 | C14—H14B | 0.96 |
| C1—C6 | 1.384 (3) | C14—H14C | 0.96 |
| C1—C2 | 1.390 (3) | C16—H16A | 0.96 |
| C1—C7 | 1.516 (3) | C16—H16B | 0.96 |

| | | | |
|---|---|---|---|
| C2—C3 | 1.381 (3) | C16—H16C | 0.96 |
| C2—H2A | 0.93 | C17—H17A | 0.96 |
| C3—C4 | 1.366 (3) | C17—H17B | 0.96 |
| C3—H3 | 0.93 | C17—H17C | 0.96 |
| C4—C5 | 1.375 (4) | | |

| | | | |
|---|---|---|---|
| C12—O4—C13 | 119.7 (2) | N2—C10—C11 | 107.09 (18) |
| C15—O6—C16 | 118.2 (2) | C18—C10—C11 | 111.8 (2) |
| C10—O7—H7 | 109.5 | C12—C11—C10 | 115.27 (18) |
| O2—N1—O1′ | 122.1 (3) | C12—C11—C7 | 110.74 (18) |
| O1′—N1—C4 | 117.4 (2) | C10—C11—C7 | 108.39 (18) |
| O2—N1—C4 | 119.6 (2) | C12—C11—H11 | 107.4 |
| O2—N1—O1 | 112.9 (7) | C10—C11—H11 | 107.4 |
| O1—N1—C4 | 113.5 (6) | C7—C11—H11 | 107.4 |
| C9—N2—C10 | 121.81 (19) | O3—C12—O4 | 125.6 (2) |
| C9—N2—H2 | 119.1 | O3—C12—C11 | 124.7 (2) |
| C10—N2—H2 | 119.1 | O4—C12—C11 | 109.7 (2) |
| C6—C1—C2 | 118.6 (2) | O4—C13—C14 | 109.4 (3) |
| C6—C1—C7 | 121.39 (19) | O4—C13—H13A | 109.8 |
| C2—C1—C7 | 119.82 (19) | C14—C13—H13A | 109.8 |
| C3—C2—C1 | 120.8 (2) | O4—C13—H13B | 109.8 |
| C3—C2—H2A | 119.6 | C14—C13—H13B | 109.8 |
| C1—C2—H2A | 119.6 | H13A—C13—H13B | 108.2 |
| C4—C3—C2 | 118.6 (2) | C13—C14—H14A | 109.5 |
| C4—C3—H3 | 120.7 | C13—C14—H14B | 109.5 |
| C2—C3—H3 | 120.7 | H14A—C14—H14B | 109.5 |
| C3—C4—C5 | 122.6 (2) | C13—C14—H14C | 109.5 |
| C3—C4—N1 | 118.8 (2) | H14A—C14—H14C | 109.5 |
| C5—C4—N1 | 118.6 (2) | H14B—C14—H14C | 109.5 |
| C4—C5—C6 | 118.0 (2) | O5—C15—O6 | 121.4 (2) |
| C4—C5—H5 | 121.0 | O5—C15—C8 | 127.6 (2) |
| C6—C5—H5 | 121.0 | O6—C15—C8 | 111.0 (2) |
| C5—C6—C1 | 121.3 (2) | O6—C16—H16A | 109.5 |
| C5—C6—H6 | 119.3 | O6—C16—H16B | 109.5 |
| C1—C6—H6 | 119.3 | H16A—C16—H16B | 109.5 |
| C1—C7—C8 | 114.77 (17) | O6—C16—H16C | 109.5 |
| C1—C7—C11 | 107.06 (17) | H16A—C16—H16C | 109.5 |
| C8—C7—C11 | 109.70 (17) | H16B—C16—H16C | 109.5 |
| C1—C7—H7A | 108.4 | C9—C17—H17A | 109.5 |
| C8—C7—H7A | 108.4 | C9—C17—H17B | 109.5 |
| C11—C7—H7A | 108.4 | H17A—C17—H17B | 109.5 |
| C9—C8—C15 | 120.6 (2) | C9—C17—H17C | 109.5 |
| C9—C8—C7 | 121.00 (19) | H17A—C17—H17C | 109.5 |
| C15—C8—C7 | 118.15 (19) | H17B—C17—H17C | 109.5 |
| C8—C9—N2 | 120.7 (2) | F1—C18—F3 | 107.1 (2) |
| C8—C9—C17 | 126.9 (2) | F1—C18—F2 | 107.5 (2) |
| N2—C9—C17 | 112.41 (19) | F3—C18—F2 | 106.9 (2) |
| O7—C10—N2 | 113.3 (2) | F1—C18—C10 | 112.3 (2) |

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| O7—C10—C18 | 106.83 (19) | F3—C18—C10 | 111.6 (2) |
| N2—C10—C18 | 108.25 (19) | F2—C18—C10 | 111.2 (2) |
| O7—C10—C11 | 109.64 (18) | | |

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|---|---|---|---|
| C6—C1—C2—C3 | 1.0 (3) | O7—C10—C11—C12 | −64.1 (3) |
| C7—C1—C2—C3 | −174.7 (2) | N2—C10—C11—C12 | 172.51 (19) |
| C1—C2—C3—C4 | −0.7 (4) | C18—C10—C11—C12 | 54.1 (3) |
| C2—C3—C4—C5 | −0.2 (4) | O7—C10—C11—C7 | 60.6 (2) |
| C2—C3—C4—N1 | −178.7 (2) | N2—C10—C11—C7 | −62.8 (2) |
| O2—N1—C4—C3 | −169.9 (3) | C18—C10—C11—C7 | 178.84 (19) |
| O1′—N1—C4—C3 | 20.9 (6) | C1—C7—C11—C12 | −56.5 (2) |
| O1—N1—C4—C3 | −32.6 (13) | C8—C7—C11—C12 | 178.39 (18) |
| O2—N1—C4—C5 | 11.5 (4) | C1—C7—C11—C10 | 176.15 (17) |
| O1′—N1—C4—C5 | −157.7 (5) | C8—C7—C11—C10 | 51.0 (2) |
| O1—N1—C4—C5 | 148.8 (12) | C13—O4—C12—O3 | 5.3 (4) |
| C3—C4—C5—C6 | 0.7 (4) | C13—O4—C12—C11 | −172.6 (2) |
| N1—C4—C5—C6 | 179.3 (2) | C10—C11—C12—O3 | 74.1 (3) |
| C4—C5—C6—C1 | −0.4 (4) | C7—C11—C12—O3 | −49.4 (3) |
| C2—C1—C6—C5 | −0.4 (3) | C10—C11—C12—O4 | −108.0 (2) |
| C7—C1—C6—C5 | 175.2 (2) | C7—C11—C12—O4 | 128.5 (2) |
| C6—C1—C7—C8 | 50.4 (3) | C12—O4—C13—C14 | 102.9 (3) |
| C2—C1—C7—C8 | −134.0 (2) | C16—O6—C15—O5 | 3.2 (3) |
| C6—C1—C7—C11 | −71.6 (3) | C16—O6—C15—C8 | −178.7 (2) |
| C2—C1—C7—C11 | 104.0 (2) | C9—C8—C15—O5 | 16.0 (3) |
| C1—C7—C8—C9 | −137.4 (2) | C7—C8—C15—O5 | −169.7 (2) |
| C11—C7—C8—C9 | −16.9 (3) | C9—C8—C15—O6 | −161.96 (19) |
| C1—C7—C8—C15 | 48.4 (2) | C7—C8—C15—O6 | 12.3 (3) |
| C11—C7—C8—C15 | 168.92 (18) | O7—C10—C18—F1 | 171.4 (2) |
| C15—C8—C9—N2 | 166.91 (19) | N2—C10—C18—F1 | −66.2 (3) |
| C7—C8—C9—N2 | −7.1 (3) | C11—C10—C18—F1 | 51.5 (3) |
| C15—C8—C9—C17 | −11.1 (3) | O7—C10—C18—F3 | 51.2 (3) |
| C7—C8—C9—C17 | 174.88 (19) | N2—C10—C18—F3 | 173.5 (2) |
| C10—N2—C9—C8 | −6.4 (3) | C11—C10—C18—F3 | −68.8 (3) |
| C10—N2—C9—C17 | 171.9 (2) | O7—C10—C18—F2 | −68.1 (3) |
| C9—N2—C10—O7 | −79.4 (3) | N2—C10—C18—F2 | 54.3 (3) |
| C9—N2—C10—C18 | 162.2 (2) | C11—C10—C18—F2 | 172.0 (2) |
| C9—N2—C10—C11 | 41.6 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O7—H7···O5$^{i}$ | 0.82 | 1.98 | 2.783 (3) | 166 |
| N2—H2···O3$^{ii}$ | 0.86 | 2.20 | 3.030 (3) | 163 |
| N2—H2···F2 | 0.86 | 2.42 | 2.735 (2) | 102 |
| C5—H5···O2$^{iii}$ | 0.93 | 2.51 | 3.432 (4) | 171 |

Symmetry codes: (i) −*x*+1/2, −*y*+1/2, −*z*+2; (ii) *x*, −*y*+1, *z*+1/2; (iii) −*x*, *y*, −*z*+3/2.