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ISSN 2414-3146

Methyl 1-[(6-methoxy-5-methylpyrimidin-4-yl)-methyl]-1*H*-benzo[*d*]imidazole-7-carboxylate: a combined X-ray and DFT study

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Received 5 January 2023
Accepted 10 January 2023

Edited by M. Bolte, Goethe-Universität Frankfurt, Germany

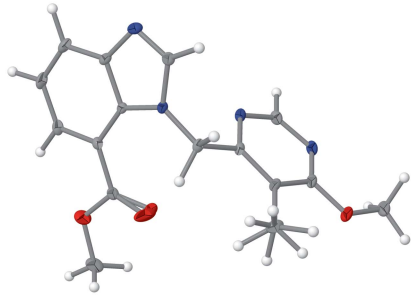
Keywords: crystal structure; DFT calculations; benzimidazole; pyrimidine; tuberculosis.

CCDC reference: 2235406

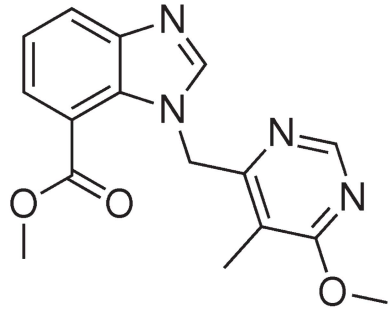
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{16}H_{16}N_4O_3$, was obtained as a side product during the synthesis of the previously reported antitubercular agent *N*-(2-fluoroethyl)-1-[(6-methoxy-5-methylpyrimidin-4-yl)methyl]-1*H*-benzo[*d*]imidazole-4-carboxamide and structurally characterized by X-ray crystallography and computational methods. In the crystal (space group $P2_1/n$, $Z = 4$), the title compound adopts a twisted conformation with a dihedral angle between the benzimidazole and pyrimidine mean planes of 84.11 (3)°. The carboxylate group and the 5-methyl group on the pyrimidine ring exhibit partial disorder. The DFT-optimized molecular structure resembles the structure of the minor component in the crystal.

3D view



Chemical scheme



Structure description

In the course of our studies on antimycobacterial agents, we synthesized and studied the compound *N*-(2-fluoroethyl)-1-[(6-methoxy-5-methylpyrimidin-4-yl)methyl]-1*H*-benzo-[*d*]imidazole-4-carboxamide (Richter *et al.*, 2022), a benzimidazole analogue of the 1,4-azaindole-based antituberculosis clinical drug candidate TBA-7371 (Shirude *et al.*, 2013, 2014), following the route published by Manjunatha *et al.* (2019). Therein, methyl 1*H*-benzo[*d*]imidazole-4-carboxylate (**1**) is *N*-alkylated with 4-(chloromethyl)-6-methoxy-5-methylpyrimidine to yield the desired methyl 1-[(6-methoxy-5-methylpyrimidin-4-yl)methyl]-1*H*-benzo[*d*]imidazole-4-carboxylate (**2**) and its structural isomer methyl 1-[(6-methoxy-5-methylpyrimidin-4-yl)methyl]-1*H*-benzo[*d*]imidazole-7-carboxylate (**3**), the title compound, as a side product (Fig. 1). After separation by flash chromatography,

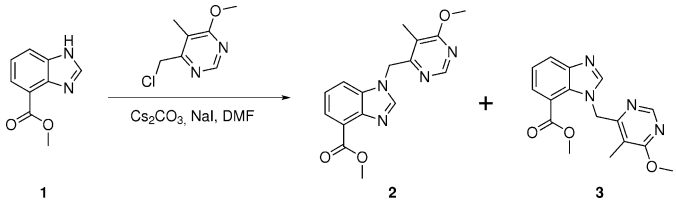


Figure 1
N-Alkylation of **1** with 4-(chloromethyl)-6-methoxy-5-methylpyrimidine to yield structural isomers **2** and **3**.

the ratio of **2** and **3** was approximately 3.75:1 (Richter *et al.*, 2022). We have now structurally characterized compound **3** by X-ray crystallography and computational methods.

Fig. 2 shows the molecular structure of **3** in the crystal. The molecule exhibits an angular shape, similar to the aforementioned *N*-(2-fluoroethyl)-1-[(6-methoxy-5-methylpyrimidin-4-yl)methyl]-1*H*-benzo[*d*]imidazole-4-carboxamide in the crystal (CSD refcode: DEVGEU; Richter *et al.*, 2022). In **3**, the angle between the mean planes through the benzimidazole moiety and the pyrimidine ring is 84.11 (3)°. The C2—N1—C10—C11 torsion angle is −87.61 (6)° in the chosen asymmetric unit, but the oppositely handed conformer is present in the centrosymmetric crystal structure. The methyl group on the pyrimidine ring and the carbonyl oxygen atom of the carboxylate group each were found to be partially disordered over two positions. The two orientations taken up by the methyl group of C16 may cause the carboxylate group to move slightly, hence the minor component O2′. To gain insight into the structural features of **3**, we optimized the structure of an isolated molecule by DFT calculations. An overlay of the molecular structures from X-ray crystallography and DFT structure optimization (Fig. 3) reveals that the conformation of the minor-disorder component in the crystal structure is very similar to the DFT-optimized structure. The latter exhibits a relatively short intramolecular C—H···O contact between oxygen atom of the carbonyl group and one of the

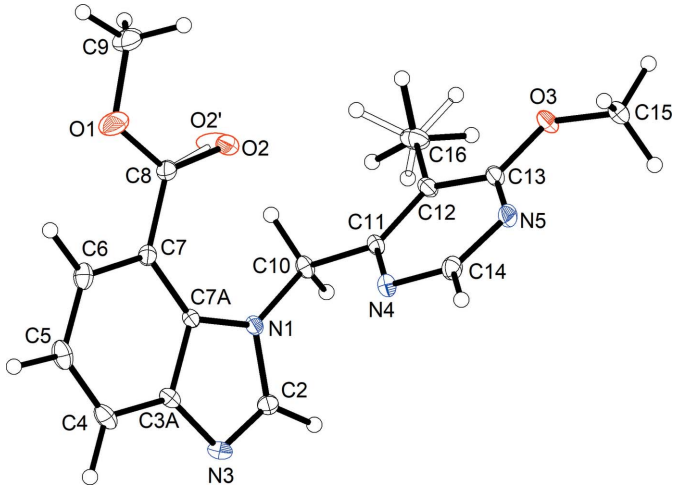


Figure 2
Displacement ellipsoid plot of **3** (50% probability level). Hydrogen atoms are represented by small spheres of arbitrary radius. Disordered parts with minor occupancy are drawn with empty bonds.

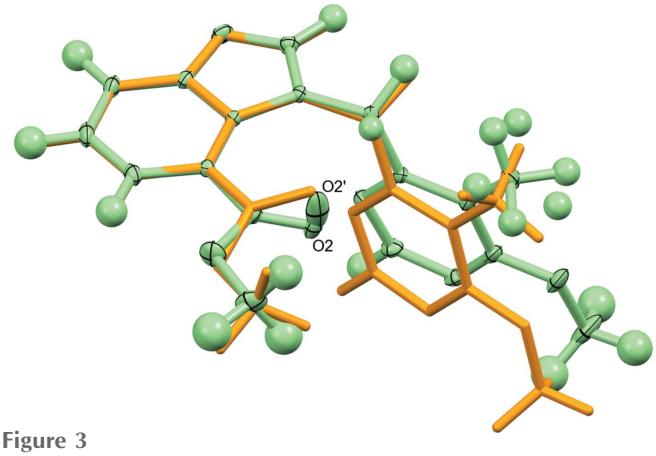


Figure 3
Structure overlay plot of the molecular structure of **3** in the crystal (green; displacement ellipsoids with 50% probability) and the DFT-optimized molecular structure (orange). The respective benzimidazole moieties were superimposed (r.m.s deviation for non-hydrogen atoms: 0.024 Å).

hydrogen atoms of the bridging methylene group (O···H = 2.13 Å).

The solid-state structure of **3** appears to be governed by close packing. The packing index calculated with *PLATON* (Spek, 2020) for the major disorder part is 73.8%, indicating a dense crystal packing (Kitaigorodskii, 1973). As shown in Fig. 4, face-to-face π–π stacking each between the benzimidazole and pyrimidine systems of adjacent molecules is a dominating structural motif. It is interesting to note that, in contrast to DEVGEU, the benzimidazole C2—H2 group does not form short C—H···*X* (*X* = N, O) contacts in the crystal structure of **3**.

Synthesis and crystallization

We obtained compound **3** as a side product in the deliberate synthesis of its structural isomer **2**, following the route

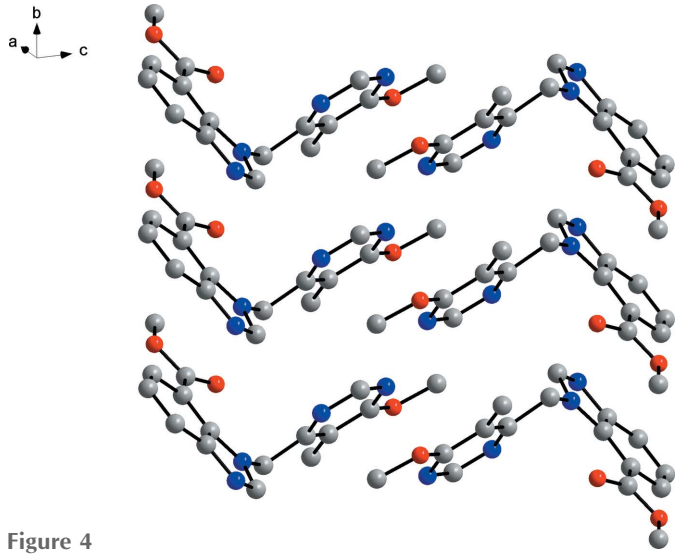


Figure 4
Section of the crystal structure of **3**. Colour scheme: carbon, grey; nitrogen, blue; oxygen, red. Hydrogen atoms and O2′ are omitted for clarity.

published by Manjunatha *et al.* (2019). The isomers were separated by flash chromatography (Richter *et al.*, 2022). Crystals of **3** suitable for X-ray crystallography were obtained as follows: Slow evaporation of a solution of the compound in chloroform-*d* to dryness yielded a powder, which was redissolved in methanol. The solution thus obtained was again set aside at room temperature, and the solvent was allowed to evaporate slowly. Colourless crystals appeared after the vessel had been left undisturbed for a couple of weeks.

Refinement

Crystal data, data collection and structure refinement details are listed in Table 1. Initial independent-atom model refinement was carried out with *SHELXL2018* (Sheldrick, 2015*b*). The final structure refinement was carried out by Hirshfeld atom refinement with non-spherical atomic form factors factors using *NoSpherA2* (Kleemiss *et al.*, 2021; Midgley *et al.*, 2021) partitioning in *OLEX2* (Dolomanov *et al.*, 2009) based on electron density from iterative single-determinant SCF single-point DFT calculations using *ORCA* (version 4.1.1; Neese *et al.*, 2020) with a B3LYP functional (Becke, 1993; Lee *et al.*, 1988) and a def2-TZVPP basis set (Weigend & Ahlrichs, 2005). The carbonyl oxygen atom (O2) and the methyl hydrogen atoms on C16 were found to be disordered over two positions in each case. Standard similar distance restraints were applied to the C8—O2 and C8—O2′ distances as well as on the 1,2- and 1,3-distances of the disordered methyl hydrogen atoms. The ratio of occupancy was refined by means of a free variable for each disordered group to give 0.63 (4):0.37 (4) for the carbonyl oxygen atom and 0.646 (12):0.354 (12) for the hydrogen atoms of the methyl group. U_{iso} values of hydrogen atoms were refined freely, except for those affected by disorder, for which $U_{iso}(H) = 1.5U_{eq}(C)$ was set.

DFT structure optimization of an isolated molecule of **3** was undertaken using *ORCA* (version 5.0; Neese *et al.*, 2020) with a B3LYP(G) (VWN1) hybrid functional (20% HF exchange) (Becke, 1993; Lee *et al.*, 1988; Hertwig & Koch, 1997), using a def2-TZVPP basis set (Weigend & Ahlrichs, 2005) utilizing the auxiliary basis def2/J (Weigend, 2006). The input structure was generated from the major disorder component in the crystal structure. Optimization of the structures used the BFGS method from an initial Hessian according to Almoef's model with a very tight self-consistent field convergence threshold (Fletcher, 2000). The optimized local minimum-energy structure exhibited only positive frequencies.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{16}N_4O_3$
M_r	312.33
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	9.3758 (7), 4.7862 (3), 32.764 (2)
β (°)	96.340 (3)
V (Å^3)	1461.28 (18)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.19 × 0.10 × 0.02
Data collection	
Diffractometer	Bruker AXS D8 VENTURE
Absorption correction	Gaussian (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.986, 0.998
No. of measured, independent and observed [$I \geq 2u(I)$] reflections	125687, 6375, 5698
R_{int}	0.047
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.814
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.061, 1.07
No. of reflections	6375
No. of parameters	289
No. of restraints	20
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.40

Computer programs: *APEX4* (Bruker, 2017), *SAINT* (Bruker, 2004), *SHELXT* (Sheldrick, 2015*a*), *OLEX2.refine* (Bourhis *et al.*, 2015), *DIAMOND* (Brandenburg, 2018) and *Mercury* (Macrae *et al.*, 2020), *publCIF* (Westrip, 2010).

Acknowledgements

We would like to thank Professor Christian W. Lehmann for providing access to the X-ray diffraction facility and Heike Schucht for technical assistance.

Funding information

Funding for this research was provided by: Deutsche Forschungsgemeinschaft (grant No. 432291016 to Adrian Richter); Mukoviszidose Institut gGmbH (Bonn, Germany), the research and development arm of the German Cystic Fibrosis Association Mukoviszidose e.V.; Open Access Publishing by the DFG.

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full crystallographic data

IUCrData (2023). **8**, x230025 [https://doi.org/10.1107/S2414314623000251]

Methyl 1-[(6-methoxy-5-methylpyrimidin-4-yl)methyl]-1*H*-benzo[*d*]imidazole-7-carboxylate: a combined X-ray and DFT study

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Methyl 1-[(6-methoxy-5-methylpyrimidin-4-yl)methyl]-1*H*-benzo[*d*]imidazole-7-carboxylate

Crystal data

$C_{16}H_{16}N_4O_3$
M_r = 312.33
Monoclinic, $P2_1/n$
a = 9.3758 (7) Å
b = 4.7862 (3) Å
c = 32.764 (2) Å
β = 96.340 (3)°
V = 1461.28 (18) Å^3
Z = 4
$F(000)$ = 656.464
D_x = 1.420 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9856 reflections
θ = 2.2–34.0°
μ = 0.10 mm^{-1}
T = 100 K
Needle
0.19 × 0.10 × 0.02 mm

Data collection

Bruker AXS D8 VENTURE diffractometer
Radiation source: IμS DIAMOND
Incoatec multilayer optics monochromator
Detector resolution: 7.391 pixels mm^{-1}
φ– and ω–scans
Absorption correction: gaussian (SADABS; Krause *et al.*, 2015)
T_{min} = 0.986, T_{max} = 0.998
125687 measured reflections
6375 independent reflections
5698 reflections with $I \geq 2u(I)$
R_{int} = 0.047
θ_{max} = 35.4°, θ_{min} = 2.2°
h = −15→15
k = −7→7
l = −53→52

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.061
S = 1.07
6375 reflections
289 parameters
20 restraints
8 constraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0015P)^2 + 0.4692P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Special details

Experimental. Crystal mounted on a MiTeGen loop using Perfluoropolyether PFO-XR75

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C2	0.41793 (7)	0.30578 (14)	0.347562 (19)	0.01418 (11)	
H2	0.3810 (9)	0.143 (2)	0.3663 (3)	0.030 (2)*	
C3A	0.43336 (6)	0.62087 (13)	0.302844 (18)	0.01290 (10)	
C4	0.40396 (7)	0.80361 (15)	0.269895 (19)	0.01730 (12)	
H4	0.2991 (10)	0.811 (2)	0.2534 (3)	0.036 (3)*	
C5	0.51499 (8)	0.96871 (15)	0.25906 (2)	0.01903 (12)	
H5	0.4962 (10)	1.114 (2)	0.2346 (3)	0.041 (3)*	
C6	0.65157 (7)	0.95258 (14)	0.280843 (19)	0.01600 (11)	
H6	0.7336 (10)	1.083 (2)	0.2723 (3)	0.038 (3)*	
C7	0.68523 (6)	0.77003 (13)	0.313947 (17)	0.01144 (10)	
C7A	0.57230 (6)	0.59893 (12)	0.324773 (17)	0.00994 (9)	
C8	0.83210 (7)	0.77743 (14)	0.336015 (19)	0.01473 (11)	
C9	1.06327 (8)	0.9716 (2)	0.33753 (3)	0.02662 (16)	
H9a	1.1186 (11)	0.774 (2)	0.3367 (3)	0.046 (3)*	
H9b	1.1135 (12)	1.129 (3)	0.3209 (3)	0.057 (3)*	
H9c	1.0648 (12)	1.029 (3)	0.3683 (4)	0.054 (3)*	
C10	0.65713 (7)	0.27497 (13)	0.385944 (18)	0.01206 (10)	
H10a	0.7645 (9)	0.270 (2)	0.3765 (3)	0.024 (2)*	
H10b	0.6245 (10)	0.064 (2)	0.3908 (3)	0.031 (2)*	
C11	0.65753 (6)	0.43198 (12)	0.426058 (17)	0.01067 (10)	
C12	0.75223 (6)	0.35346 (13)	0.459654 (18)	0.01303 (10)	
C13	0.73550 (7)	0.49763 (15)	0.496289 (18)	0.01579 (12)	
C14	0.55770 (7)	0.76028 (14)	0.464026 (19)	0.01531 (11)	
H14	0.4812 (10)	0.925 (2)	0.4657 (3)	0.034 (2)*	
C15	0.80160 (9)	0.5572 (3)	0.56782 (2)	0.0335 (2)	
H15a	0.8874 (11)	0.483 (2)	0.5890 (3)	0.048 (3)*	
H15b	0.8061 (12)	0.782 (3)	0.5644 (3)	0.053 (3)*	
H15c	0.7008 (12)	0.496 (3)	0.5774 (3)	0.053 (3)*	
C16	0.86532 (7)	0.13435 (16)	0.45806 (2)	0.02042 (13)	
H16a	0.8658 (17)	−0.003 (3)	0.4854 (4)	0.03063 (19)*	0.646 (12)
H16b	0.8514 (16)	0.001 (3)	0.4320 (4)	0.03063 (19)*	0.646 (12)
H16c	0.9698 (13)	0.230 (3)	0.4614 (5)	0.03063 (19)*	0.646 (12)
H16d	0.932 (3)	0.191 (5)	0.4335 (7)	0.03063 (19)*	0.354 (12)
H16e	0.815 (2)	−0.059 (4)	0.4467 (8)	0.03063 (19)*	0.354 (12)
H16f	0.934 (3)	0.101 (6)	0.4846 (6)	0.03063 (19)*	0.354 (12)
N1	0.55809 (5)	0.38936 (11)	0.353175 (15)	0.01077 (9)	
N3	0.33883 (6)	0.43622 (13)	0.318270 (17)	0.01624 (10)	
N4	0.56045 (6)	0.63817 (11)	0.427757 (15)	0.01239 (9)	
N5	0.63968 (6)	0.69880 (13)	0.498873 (16)	0.01738 (11)	
O1	0.91869 (5)	0.94660 (12)	0.318121 (17)	0.02457 (11)	
O2	0.8667 (4)	0.6788 (12)	0.36899 (8)	0.0202 (7)	0.63 (4)
O2′	0.8822 (11)	0.606 (5)	0.3628 (6)	0.040 (3)	0.37 (4)
O3	0.82283 (5)	0.42339 (13)	0.529660 (14)	0.02307 (11)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0136 (2)	0.0155 (3)	0.0133 (2)	−0.0044 (2)	0.00101 (19)	0.0002 (2)
C3A	0.0127 (2)	0.0141 (2)	0.0112 (2)	0.0007 (2)	−0.00191 (18)	−0.0002 (2)
C4	0.0193 (3)	0.0185 (3)	0.0128 (3)	0.0042 (2)	−0.0039 (2)	0.0019 (2)
C5	0.0263 (3)	0.0176 (3)	0.0127 (3)	0.0036 (3)	0.0002 (2)	0.0053 (2)
C6	0.0215 (3)	0.0139 (3)	0.0131 (2)	−0.0006 (2)	0.0042 (2)	0.0028 (2)
C7	0.0132 (2)	0.0112 (2)	0.0101 (2)	−0.0013 (2)	0.00209 (18)	−0.00018 (19)
C7A	0.0108 (2)	0.0104 (2)	0.0083 (2)	−0.00019 (19)	−0.00006 (17)	−0.00010 (18)
C8	0.0137 (2)	0.0185 (3)	0.0121 (2)	−0.0046 (2)	0.00212 (19)	−0.0016 (2)
C9	0.0180 (3)	0.0330 (4)	0.0292 (4)	−0.0117 (3)	0.0044 (3)	−0.0039 (3)
C10	0.0158 (2)	0.0102 (2)	0.0099 (2)	0.0013 (2)	−0.00020 (19)	0.00046 (19)
C11	0.0137 (2)	0.0097 (2)	0.0083 (2)	−0.00153 (19)	−0.00023 (18)	0.00081 (18)
C12	0.0137 (2)	0.0140 (3)	0.0106 (2)	−0.0028 (2)	−0.00208 (19)	0.0020 (2)
C13	0.0158 (3)	0.0217 (3)	0.0094 (2)	−0.0077 (2)	−0.00081 (19)	0.0008 (2)
C14	0.0178 (3)	0.0158 (3)	0.0128 (2)	−0.0021 (2)	0.0038 (2)	−0.0032 (2)
C15	0.0198 (3)	0.0690 (7)	0.0109 (3)	−0.0133 (4)	−0.0013 (2)	−0.0033 (4)
C16	0.0153 (3)	0.0203 (3)	0.0242 (3)	0.0007 (2)	−0.0044 (2)	0.0051 (3)
N1	0.0120 (2)	0.0113 (2)	0.00872 (19)	−0.00109 (17)	0.00008 (15)	0.00024 (17)
N3	0.0110 (2)	0.0203 (3)	0.0166 (2)	−0.0027 (2)	−0.00210 (18)	−0.0011 (2)
N4	0.0158 (2)	0.0115 (2)	0.0099 (2)	0.00026 (18)	0.00143 (17)	−0.00015 (17)
N5	0.0189 (2)	0.0234 (3)	0.0101 (2)	−0.0071 (2)	0.00264 (18)	−0.0043 (2)
O1	0.0175 (2)	0.0267 (3)	0.0297 (3)	−0.0083 (2)	0.00328 (19)	0.0061 (2)
O2	0.0140 (6)	0.0305 (12)	0.0153 (9)	−0.0053 (6)	−0.0022 (4)	0.0069 (6)
O2′	0.0159 (15)	0.054 (5)	0.047 (3)	−0.014 (2)	−0.0119 (19)	0.030 (4)
O3	0.0194 (2)	0.0376 (3)	0.01085 (19)	−0.0088 (2)	−0.00411 (16)	0.0020 (2)

Geometric parameters (Å, º)

C2—H2	1.071 (9)	C10—H10b	1.074 (10)
C2—N1	1.3666 (8)	C10—C11	1.5136 (8)
C2—N3	1.3052 (8)	C10—N1	1.4472 (7)
C3A—C4	1.3931 (9)	C11—C12	1.3876 (8)
C3A—C7A	1.4204 (8)	C11—N4	1.3478 (8)
C3A—N3	1.3860 (8)	C12—C13	1.4082 (9)
C4—H4	1.069 (9)	C12—C16	1.4963 (10)
C4—C5	1.3841 (10)	C13—N5	1.3259 (9)
C5—H5	1.062 (10)	C13—O3	1.3395 (8)
C5—C6	1.3975 (10)	C14—H14	1.073 (10)
C6—H6	1.051 (10)	C14—N4	1.3271 (8)
C6—C7	1.4013 (8)	C14—N5	1.3368 (8)
C7—C7A	1.4143 (8)	C15—H15a	1.064 (11)
C7—C8	1.4834 (9)	C15—H15b	1.084 (13)
C7A—N1	1.3846 (7)	C15—H15c	1.070 (11)
C8—O1	1.3280 (8)	C15—O3	1.4381 (10)
C8—O2	1.191 (4)	C16—H16a	1.111 (11)
C8—O2′	1.255 (8)	C16—H16b	1.060 (11)

C9—H9a	1.080 (12)	C16—H16c	1.076 (11)
C9—H9b	1.069 (12)	C16—H16d	1.105 (15)
C9—H9c	1.043 (11)	C16—H16e	1.085 (15)
C9—O1	1.4374 (9)	C16—H16f	1.035 (15)
C10—H10a	1.085 (9)		

N1—C2—H2	120.2 (5)	C16—C12—C11	123.78 (6)
N3—C2—H2	125.1 (5)	C16—C12—C13	121.28 (6)
N3—C2—N1	114.76 (6)	N5—C13—C12	123.39 (6)
C7A—C3A—C4	122.03 (6)	O3—C13—C12	116.75 (6)
N3—C3A—C4	127.10 (6)	O3—C13—N5	119.86 (6)
N3—C3A—C7A	110.86 (5)	N4—C14—H14	116.8 (5)
H4—C4—C3A	120.3 (5)	N5—C14—H14	116.2 (5)
C5—C4—C3A	117.85 (6)	N5—C14—N4	126.99 (6)
C5—C4—H4	121.9 (5)	H15b—C15—H15a	111.3 (9)
H5—C5—C4	120.1 (5)	H15c—C15—H15a	110.2 (8)
C6—C5—C4	120.68 (6)	H15c—C15—H15b	110.5 (9)
C6—C5—H5	119.2 (5)	O3—C15—H15a	104.5 (6)
H6—C6—C5	119.1 (5)	O3—C15—H15b	109.9 (6)
C7—C6—C5	123.02 (6)	O3—C15—H15c	110.2 (6)
C7—C6—H6	117.9 (5)	H16a—C16—C12	109.1 (8)
C7A—C7—C6	116.38 (5)	H16b—C16—C12	115.1 (8)
C8—C7—C6	118.68 (6)	H16b—C16—H16a	106.4 (10)
C8—C7—C7A	124.88 (5)	H16c—C16—C12	109.8 (8)
C7—C7A—C3A	120.03 (5)	H16c—C16—H16a	104.3 (10)
N1—C7A—C3A	104.04 (5)	H16c—C16—H16b	111.6 (10)
N1—C7A—C7	135.91 (5)	H16d—C16—C12	108.1 (13)
O1—C8—C7	112.29 (6)	H16d—C16—H16a	141.4 (15)
O2—C8—C7	125.30 (16)	H16d—C16—H16b	65.9 (14)
O2—C8—O1	121.60 (15)	H16d—C16—H16c	52.4 (13)
O2′—C8—C7	125.5 (3)	H16e—C16—C12	109.2 (13)
O2′—C8—O1	120.6 (3)	H16e—C16—H16a	74.6 (14)
H9b—C9—H9a	111.2 (8)	H16e—C16—H16c	138.8 (16)
H9c—C9—H9a	107.4 (9)	H16e—C16—H16d	102.6 (15)
H9c—C9—H9b	110.5 (9)	H16f—C16—C12	117.2 (13)
O1—C9—H9a	110.4 (6)	H16f—C16—H16b	126.2 (16)
O1—C9—H9b	106.2 (6)	H16f—C16—H16c	60.3 (14)
O1—C9—H9c	111.2 (6)	H16f—C16—H16d	107.5 (15)
H10b—C10—H10a	108.2 (7)	H16f—C16—H16e	111.2 (17)
C11—C10—H10a	110.1 (5)	C7A—N1—C2	106.50 (5)
C11—C10—H10b	108.1 (5)	C10—N1—C2	121.18 (5)
N1—C10—H10a	109.6 (5)	C10—N1—C7A	132.16 (5)
N1—C10—H10b	107.3 (5)	C3A—N3—C2	103.82 (5)
N1—C10—C11	113.34 (5)	C14—N4—C11	116.07 (5)
C12—C11—C10	119.63 (5)	C14—N5—C13	115.79 (5)
N4—C11—C10	117.55 (5)	C9—O1—C8	116.61 (6)
N4—C11—C12	122.78 (5)	C15—O3—C13	117.44 (7)
C13—C12—C11	114.94 (6)		

C2—N1—C7A—C3A	−1.20 (5)	C6—C7—C8—O2	163.8 (3)
C2—N1—C7A—C7	−179.47 (5)	C6—C7—C8—O2′	−171.1 (18)
C2—N1—C10—C11	−87.61 (6)	C7—C7A—N1—C10	5.16 (9)
C2—N3—C3A—C4	177.48 (5)	C7—C8—O1—C9	179.13 (6)
C2—N3—C3A—C7A	−1.12 (6)	C7A—N1—C10—C11	87.20 (7)
C3A—C4—C5—C6	−0.44 (8)	C10—C11—C12—C13	−174.93 (6)
C3A—C7A—C7—C6	−0.92 (7)	C10—C11—C12—C16	5.43 (7)
C3A—C7A—C7—C8	176.33 (5)	C10—C11—N4—C14	176.03 (5)
C3A—C7A—N1—C10	−176.57 (4)	C11—C12—C13—N5	−1.68 (7)
C4—C5—C6—C7	0.90 (8)	C11—C12—C13—O3	178.54 (5)
C5—C6—C7—C7A	−0.18 (8)	C11—N4—C14—N5	−0.65 (7)
C5—C6—C7—C8	−177.62 (6)	C12—C13—N5—C14	−0.16 (7)
C6—C7—C7A—N1	177.14 (5)	C12—C13—O3—C15	−176.49 (6)
C6—C7—C8—O1	−5.89 (6)	C13—N5—C14—N4	1.46 (7)