Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of 4-[4-(ethoxycarbonyl)piperazin-1-yl]benzoic acid

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Received 21 June 2016
Accepted 2 August 2016

Edited by A. J. Lough, University of Toronto, Canada

Keywords: crystal structure; piperazine; hydrogen bonds; carboxylic acids; 4-fluorobenzoic acid; ethyl 1-piperazinecarboxylate.

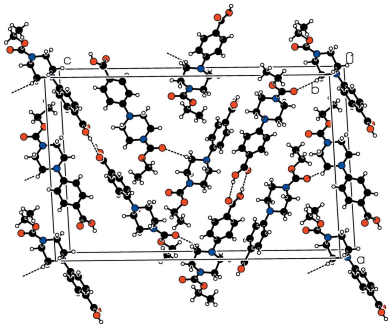
CCDC reference: 1497342

Supporting information: this article has supporting information at journals.iucr.org/e

The asymmetric unit of the title compound, $C_{14}H_{18}N_2O_4$, contains two independent molecules (*A* and *B*) which have essentially the same conformation. The piperazine rings adopts chair conformations with the N atoms out of plane. The dihedral angles formed by the four approximately planar C atoms of the piperazine ring and the benzene ring is 30.8 (5)° in molecule *A* and 30.6 (5)° in molecule *B*. In the crystal, molecules *A* and *B* are connected by a pair of O—H···O hydrogen bonds, forming a dimer with graph-set notation $R_2^2(8)$. Weak C—H···O hydrogen bonds connect the dimers, forming zigzag chains along [001].

1. Chemical context

Piperazines are among the most important building blocks in drug discovery today. The piperazine nucleus is capable of binding to multiple receptors with high affinity and therefore piperazine has been classified as a privileged structure (Dinsmore & Beshore, 2002). Piperazine and its derivatives are important pharmacores that can be found in biologically active compounds across a number of different therapeutic areas (Berkheij *et al.*, 2005), such as antifungal (Upadhayaya *et al.*, 2004), anti-bacterial, antimalarial, anti-psychotic agents (Chaudhary *et al.*, 2006), HIV protease inhibitors (Dorsey *et al.*, 1994), anti-depressant and anti-tumour activity against colon, prostate, breast, lung and leukemia tumors (Hulme & Cherrier, 1999). A review on the current pharmacological and toxicological information for piperazine derivatives is given by Elliott (2011). The title compound also contains a carboxylic group, which has been widely used in various fields such as coordination chemistry (Rueff *et al.*, 2001), pharmaceutical chemistry (Strachan *et al.*, 2007) and supramolecular chemistry (Desiraju, 2002). Recently, the main focus for carboxylic acids has been in crystal engineering *via* hydrogen-bonded assembly of organic acids and organic bases (Grossel *et al.*, 2006). In an attempt to further synthesis piperazine derivatives, the title compound was synthesized and the crystal structure is reported herein.



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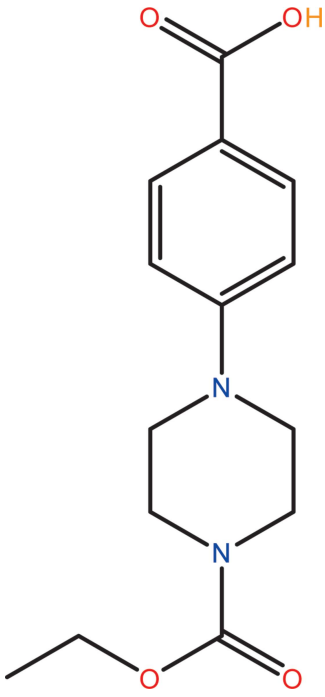
2. Structural commentary

The molecular structure of the asymmetric unit is shown in Fig. 1. The conformation of the two molecules (*A* and *B*) is essentially the same. The piperazine rings are in chair conformations with the N atoms (N1*A*/N2*A* and N1*B*/N2*B*)

out of plane of the essentially planar C atoms. The dihedral angles formed by the four approximately planar C atoms of the piperazine ring (C8*A*–C11*A* and C8*B*–C11*B*) and the benzene ring (C2*A*–C7*A* and C2*B*–C7*B*) is 30.8 (5)° in molecule *A* and 30.6 (5)° in molecule *B*.



3. Supramolecular features

In the crystal, molecules *A* and *B* are connected by a pair of O—H···O hydrogen bonds (Fig. 1, Table 1), forming a dimer with graph set $R_2^2(8)$. In addition, weak C—H···O hydrogen bonds connect the dimers, forming zigzag chains along [001] (Fig. 2).

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.37, update February 2015; Groom *et al.*, 2016) revealed 11 crystal structures containing the (ethoxycarbonyl)piperazin-1-yl group. Three of these also contain a benzene ring attached to the other piperazine N atom *viz*. ethyl 4-(5-bromo-2-formylphenyl)piperazine-1-carboxylate (EPEPUL; Nour *et al.*, 2011), ethyl 4-[4-nitro-2-(trifluoromethyl)phenyl]piperazine-1-carboxylate (OMOJAB; Lynch & McClenaghan, 2004) and ethyl 4-[2-nitro-4-(trifluoromethyl)phenyl]-piperazine-1-carboxylate (OMOJEF; Lynch & McClenaghan, 2004). The dihedral angles formed by the four essentially planar C atoms of the piperazine ring and the benzene ring are 48.4 (1)° for EPEPUL, 44.1 (1)° for OMOJAB and 43.2 (2) and 43.7 (2)° for the two independent molecules in OMOJEF.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O2*B*	0.84	2.14	2.973 (8)	170
C8*A*—H8*AB*···O3*B*^{i}	0.99	2.56	3.225 (11)	124
O1*B*—H1*B*···O2*A*	0.84	2.11	2.934 (8)	168

Symmetry code: (i) $-x+1, -y+1, z+\frac{1}{2}$.

5. Synthesis and crystallization

The title compound was prepared by a mixture of ethyl 1-piperazinecarboxylate (2.0 g, 12.6 mmol), 4-fluorobenzoic acid (1.7 g, 12.6 mmol), and K_2CO_3 (2.6 g, 18.9 mmol) in 10 mL of dry acetonitrile which was heated at 353 K for 12 h with constant stirring under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured slowly onto ice-cold water (100 ml) and acidified with glacial acetic acid (AcOH) to pH 3–5. After filtration, the product was obtained as a pale-white crystalline solid (70%). Crystals of the title compound used for X-ray analysis were obtained within three days by slow evaporation of the acetonitrile solvent.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were placed in calculated positions with C—H = 0.95–0.99 Å, O—H = 0.84 Å and included in the refinement in a riding-motion approximation with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(O, C_{methyl}). The crystal quality was generally poor and although the best crystal available was selected, the precision of the structure has been affected by the crystal quality.

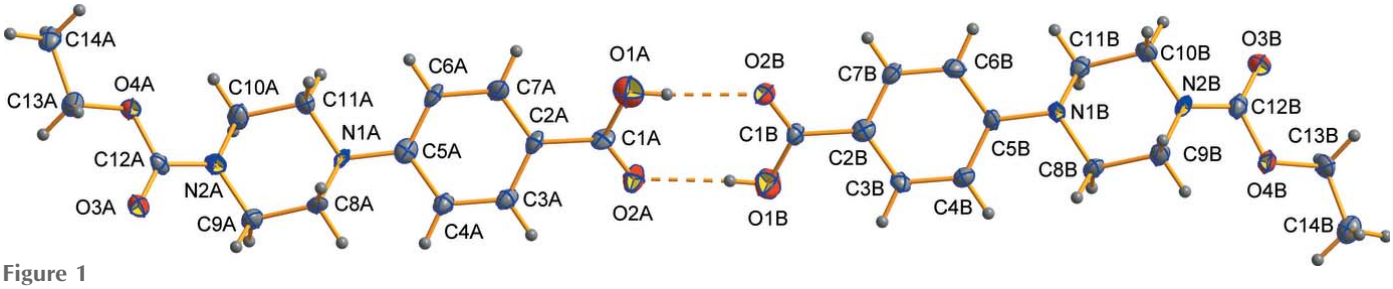


Figure 1
The molecular structures of the two crystallographically independent molecules (*A* and *B*) in the asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 40% probability level. Hydrogen bonds are shown as dashed lines.

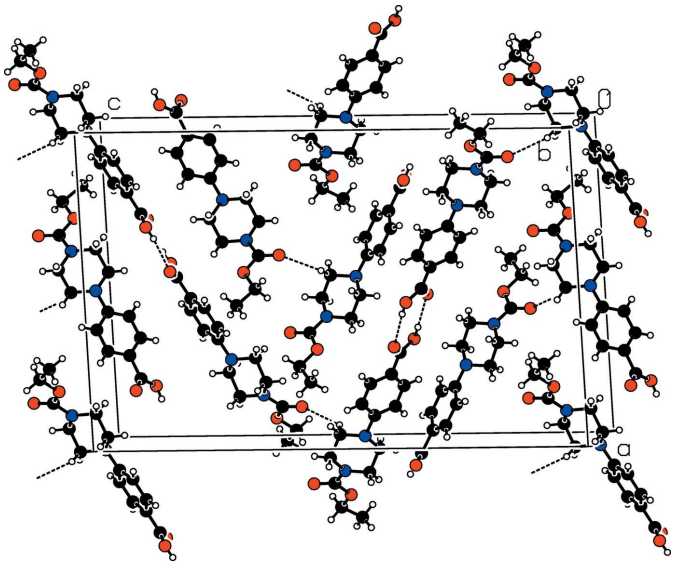


Figure 2
Part of the crystal structure with O—H···O and weak C—H···O hydrogen bonds shown as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{18}N_2O_4$
M_r	278.30
Crystal system, space group	Orthorhombic, $Pna2_1$
Temperature (K)	173
a, b, c (Å)	18.508 (5), 4.994 (5), 29.594 (5)
V (Å^3)	2735 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.29 × 0.21 × 0.15
Data collection	
Diffractometer	Bruker SMART APEX
Absorption correction	Multi-scan (*SADABS*; Bruker, 2003)
T_{min}, T_{max}	0.972, 0.985
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12918, 4042, 3100
R_{int}	0.068
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.077, 0.202, 1.08
No. of reflections	4042
No. of parameters	363
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.65, −0.47
Absolute structure parameter	0.2 (10)

Computer programs: *SMART* and *SAINT* (Bruker, 2003), *SIR97* (Altomare *et al.*, 1999), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg, 2006).

Acknowledgements

The authors are grateful to the Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, UP 208 016, India, for financial support.

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supporting information

Acta Cryst. (2016). E**72**, 1267-1269 [doi:10.1107/S2056989016012482]

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Computing details

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

4-[4-(Ethoxycarbonyl)piperazin-1-yl]benzoic acid

Crystal data

$C_{14}H_{18}N_2O_4$
M_r = 278.30
Orthorhombic, $Pna2_1$
a = 18.508 (5) Å
b = 4.994 (5) Å
c = 29.594 (5) Å
V = 2735 (3) Å^3
Z = 8
$F(000)$ = 1184
D_x = 1.352 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 999 reflections
θ = 2.2–25.5°
μ = 0.10 mm^{-1}
T = 173 K
Block, colorless
0.29 × 0.21 × 0.15 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
/w–scans
Absorption correction: multi-scan (SADABS; Bruker, 2003)
T_{min} = 0.972, T_{max} = 0.985
12918 measured reflections
4042 independent reflections
3100 reflections with $I > 2\sigma(I)$
R_{int} = 0.068
θ_{max} = 25.0°, θ_{min} = 2.2°
h = −22→21
k = −5→5
l = −35→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.202
S = 1.08
4042 reflections
363 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1131P)^2 + 0.9875P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}
Absolute structure: Flack x determined using 850 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.2 (10)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1A	0.6918 (3)	0.2291 (13)	0.3795 (3)	0.044 (2)
H1A	0.6528	0.2795	0.3678	0.065*
O2A	0.6971 (2)	0.6589 (12)	0.3981 (2)	0.0289 (13)
O3A	1.1546 (2)	−0.0268 (10)	0.61300 (19)	0.0282 (13)
O4A	1.1990 (3)	−0.2288 (9)	0.5501 (2)	0.0209 (14)
N1A	0.9933 (3)	0.2577 (10)	0.4888 (3)	0.0173 (18)
N2A	1.1101 (3)	0.0764 (13)	0.5433 (2)	0.0260 (15)
C1A	0.7243 (4)	0.4362 (14)	0.3986 (3)	0.0196 (16)
C2A	0.7949 (4)	0.3828 (13)	0.4214 (3)	0.0197 (16)
C3A	0.8164 (3)	0.5513 (14)	0.4560 (3)	0.0217 (16)
H3AA	0.7865	0.6969	0.4647	0.026*
C4A	0.8816 (3)	0.5082 (14)	0.4781 (3)	0.0219 (16)
H4AA	0.8957	0.6237	0.5021	0.026*
C5A	0.9277 (4)	0.2923 (16)	0.4653 (3)	0.0215 (19)
C6A	0.9066 (3)	0.1323 (14)	0.4308 (3)	0.0204 (16)
H6AA	0.9369	−0.0110	0.4216	0.024*
C7A	0.8404 (4)	0.1743 (18)	0.4086 (3)	0.0212 (16)
H7AA	0.8266	0.0591	0.3845	0.025*
C8A	0.9880 (4)	0.2484 (15)	0.5397 (3)	0.022 (2)
H8AA	0.9564	0.3955	0.5503	0.026*
H8AB	0.9658	0.0767	0.5490	0.026*
C9A	1.0603 (4)	0.2747 (17)	0.5609 (3)	0.027 (2)
H9AA	1.0797	0.4562	0.5551	0.033*
H9AB	1.0558	0.2519	0.5940	0.033*
C10A	1.1159 (4)	0.0718 (17)	0.4939 (3)	0.0285 (19)
H10A	1.1459	−0.0828	0.4846	0.034*
H10B	1.1402	0.2372	0.4834	0.034*
C11A	1.0420 (3)	0.0510 (15)	0.4721 (3)	0.0225 (17)
H11A	1.0470	0.0688	0.4389	0.027*
H11B	1.0211	−0.1275	0.4785	0.027*
C12A	1.1547 (3)	−0.0536 (14)	0.5723 (2)	0.0183 (16)
C13A	1.2448 (4)	−0.3858 (16)	0.5793 (3)	0.0301 (19)
H13A	1.2154	−0.4868	0.6014	0.036*
H13B	1.2788	−0.2686	0.5959	0.036*
C14A	1.2859 (4)	−0.5770 (15)	0.5485 (3)	0.0271 (18)
H14A	1.3186	−0.6875	0.5667	0.041*
H14B	1.3141	−0.4739	0.5265	0.041*
H14C	1.2516	−0.6926	0.5326	0.041*
O1B	0.5524 (3)	0.7761 (13)	0.3627 (3)	0.045 (2)

H1B	0.5911	0.7222	0.3744	0.067*
O2B	0.5460 (2)	0.3407 (11)	0.34180 (19)	0.0242 (12)
O3B	0.0883 (3)	1.0119 (11)	0.12725 (19)	0.0296 (13)
O4B	0.0441 (3)	1.2149 (11)	0.1901 (2)	0.0222 (14)
N1B	0.2507 (3)	0.7383 (12)	0.2493 (3)	0.0208 (19)
N2B	0.1310 (3)	0.9039 (12)	0.1970 (2)	0.0219 (14)
C1B	0.5191 (3)	0.5682 (13)	0.3412 (3)	0.0182 (16)
C2B	0.4492 (4)	0.6208 (14)	0.3179 (3)	0.0194 (16)
C3B	0.4035 (4)	0.8309 (17)	0.3305 (3)	0.0202 (16)
H3BA	0.4176	0.9480	0.3543	0.024*
C4B	0.3379 (4)	0.8706 (15)	0.3089 (3)	0.0205 (16)
H4BA	0.3066	1.0094	0.3188	0.025*
C5B	0.3175 (3)	0.7085 (16)	0.2727 (3)	0.0179 (17)
C6B	0.3630 (4)	0.4965 (14)	0.2608 (3)	0.0237 (16)
H6BA	0.3492	0.3795	0.2369	0.028*
C7B	0.4273 (4)	0.4547 (15)	0.2829 (3)	0.0222 (17)
H7BA	0.4573	0.3093	0.2741	0.027*
C8B	0.2016 (3)	0.9471 (15)	0.2664 (3)	0.0237 (17)
H8BA	0.2210	1.1259	0.2586	0.028*
H8BB	0.1986	0.9348	0.2998	0.028*
C9B	0.1267 (4)	0.9150 (17)	0.2462 (3)	0.0260 (18)
H9BA	0.1043	0.7484	0.2578	0.031*
H9BB	0.0959	1.0677	0.2554	0.031*
C10B	0.1800 (4)	0.7025 (18)	0.1806 (3)	0.0238 (19)
H10C	0.1830	0.7130	0.1472	0.029*
H10D	0.1617	0.5226	0.1888	0.029*
C11B	0.2552 (4)	0.7435 (14)	0.2011 (3)	0.022 (2)
H11C	0.2881	0.6001	0.1905	0.026*
H11D	0.2751	0.9176	0.1910	0.026*
C12B	0.0880 (4)	1.0370 (15)	0.1678 (3)	0.0241 (18)
C13B	−0.0015 (4)	1.3737 (16)	0.1605 (3)	0.0266 (18)
H13C	−0.0346	1.2564	0.1433	0.032*
H13D	0.0285	1.4762	0.1389	0.032*
C14B	−0.0436 (4)	1.5605 (15)	0.1900 (3)	0.0276 (18)
H14E	−0.0708	1.6860	0.1711	0.041*
H14F	−0.0103	1.6605	0.2095	0.041*
H14G	−0.0772	1.4574	0.2088	0.041*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.047 (4)	0.052 (5)	0.033 (5)	0.000 (3)	0.003 (3)	0.007 (3)
O2A	0.025 (3)	0.024 (3)	0.038 (4)	0.001 (2)	−0.001 (2)	0.006 (3)
O3A	0.025 (3)	0.037 (3)	0.022 (3)	0.003 (2)	−0.005 (2)	−0.003 (3)
O4A	0.020 (3)	0.026 (3)	0.017 (4)	0.002 (2)	0.001 (2)	0.001 (2)
N1A	0.014 (3)	0.010 (4)	0.027 (5)	0.005 (2)	−0.001 (3)	0.000 (2)
N2A	0.025 (3)	0.035 (4)	0.018 (4)	0.004 (3)	−0.001 (3)	−0.003 (3)
C1A	0.024 (4)	0.007 (4)	0.028 (5)	−0.002 (3)	0.002 (3)	0.003 (3)

C2A	0.017 (4)	0.014 (4)	0.028 (5)	0.004 (3)	0.001 (3)	0.004 (3)
C3A	0.018 (3)	0.019 (4)	0.029 (4)	0.000 (3)	0.004 (3)	−0.001 (3)
C4A	0.018 (3)	0.017 (4)	0.030 (4)	0.000 (3)	0.000 (3)	−0.001 (3)
C5A	0.019 (3)	0.018 (4)	0.027 (5)	−0.004 (3)	0.005 (3)	0.006 (4)
C6A	0.016 (3)	0.013 (4)	0.032 (5)	0.005 (3)	0.003 (3)	0.003 (3)
C7A	0.024 (4)	0.026 (4)	0.014 (4)	0.005 (4)	0.003 (3)	0.003 (4)
C8A	0.020 (4)	0.033 (6)	0.012 (5)	0.008 (3)	0.003 (3)	−0.005 (3)
C9A	0.021 (4)	0.034 (5)	0.027 (5)	0.003 (3)	0.001 (3)	−0.009 (4)
C10A	0.022 (4)	0.040 (5)	0.024 (5)	0.005 (3)	0.001 (3)	0.003 (4)
C11A	0.022 (4)	0.025 (4)	0.020 (4)	0.002 (3)	−0.005 (3)	−0.001 (3)
C12A	0.014 (3)	0.024 (4)	0.017 (5)	−0.006 (3)	0.000 (3)	−0.001 (3)
C13A	0.027 (4)	0.029 (5)	0.035 (5)	0.007 (3)	−0.006 (4)	−0.003 (4)
C14A	0.025 (4)	0.016 (4)	0.041 (5)	0.001 (3)	−0.004 (3)	0.000 (3)
O1B	0.032 (3)	0.037 (4)	0.065 (6)	−0.004 (3)	−0.007 (3)	−0.006 (3)
O2B	0.020 (2)	0.020 (3)	0.032 (3)	0.001 (2)	0.002 (2)	−0.001 (3)
O3B	0.029 (3)	0.038 (3)	0.022 (3)	0.007 (2)	−0.003 (2)	−0.005 (3)
O4B	0.020 (3)	0.026 (3)	0.021 (4)	0.008 (2)	−0.003 (2)	0.003 (2)
N1B	0.014 (3)	0.034 (5)	0.015 (4)	0.004 (2)	−0.001 (3)	−0.004 (2)
N2B	0.013 (3)	0.026 (3)	0.026 (4)	0.007 (2)	0.000 (3)	−0.001 (3)
C1B	0.013 (3)	0.018 (4)	0.024 (4)	−0.002 (3)	0.001 (3)	0.000 (3)
C2B	0.023 (4)	0.015 (4)	0.021 (4)	−0.002 (3)	0.004 (3)	0.005 (3)
C3B	0.020 (3)	0.017 (4)	0.024 (4)	−0.004 (3)	−0.004 (3)	−0.002 (3)
C4B	0.021 (3)	0.020 (4)	0.020 (4)	0.002 (3)	0.003 (3)	−0.001 (3)
C5B	0.012 (3)	0.028 (4)	0.014 (4)	0.001 (3)	0.001 (3)	0.000 (3)
C6B	0.025 (4)	0.020 (4)	0.026 (4)	−0.001 (3)	0.000 (3)	−0.007 (3)
C7B	0.019 (3)	0.018 (4)	0.030 (5)	0.005 (3)	0.002 (3)	−0.001 (3)
C8B	0.019 (3)	0.030 (5)	0.022 (4)	0.007 (3)	0.003 (3)	−0.004 (3)
C9B	0.018 (4)	0.035 (5)	0.025 (5)	0.005 (3)	0.000 (3)	−0.001 (3)
C10B	0.023 (4)	0.031 (4)	0.017 (5)	0.003 (3)	−0.001 (3)	−0.002 (4)
C11B	0.019 (4)	0.017 (5)	0.029 (6)	0.001 (3)	0.001 (3)	0.000 (3)
C12B	0.015 (3)	0.023 (4)	0.035 (6)	0.000 (3)	−0.003 (3)	0.000 (3)
C13B	0.030 (4)	0.030 (5)	0.020 (4)	0.006 (3)	−0.006 (3)	0.001 (3)
C14B	0.026 (4)	0.025 (4)	0.032 (5)	0.001 (3)	0.003 (3)	0.008 (3)

Geometric parameters (Å, º)

O1A—C1A	1.324 (10)	O1B—C1B	1.365 (9)
O1A—H1A	0.8400	O1B—H1B	0.8400
O2A—C1A	1.221 (9)	O2B—C1B	1.241 (9)
O3A—C12A	1.212 (8)	O3B—C12B	1.207 (9)
O4A—C12A	1.367 (8)	O4B—C12B	1.372 (9)
O4A—C13A	1.441 (9)	O4B—C13B	1.451 (9)
N1A—C5A	1.409 (10)	N1B—C5B	1.425 (10)
N1A—C11A	1.457 (9)	N1B—C11B	1.430 (11)
N1A—C8A	1.510 (10)	N1B—C8B	1.473 (9)
N2A—C12A	1.357 (9)	N2B—C12B	1.351 (9)
N2A—C9A	1.450 (10)	N2B—C10B	1.439 (9)
N2A—C10A	1.464 (10)	N2B—C9B	1.460 (10)

C1A—C2A	1.494 (10)	C1B—C2B	1.490 (10)
C2A—C3A	1.384 (10)	C2B—C7B	1.387 (11)
C2A—C7A	1.392 (11)	C2B—C3B	1.399 (11)
C3A—C4A	1.390 (9)	C3B—C4B	1.388 (10)
C3A—H3AA	0.9500	C3B—H3BA	0.9500
C4A—C5A	1.427 (10)	C4B—C5B	1.394 (11)
C4A—H4AA	0.9500	C4B—H4BA	0.9500
C5A—C6A	1.352 (12)	C5B—C6B	1.399 (10)
C6A—C7A	1.406 (10)	C6B—C7B	1.376 (10)
C6A—H6AA	0.9500	C6B—H6BA	0.9500
C7A—H7AA	0.9500	C7B—H7BA	0.9500
C8A—C9A	1.485 (11)	C8B—C9B	1.519 (9)
C8A—H8AA	0.9900	C8B—H8BA	0.9900
C8A—H8AB	0.9900	C8B—H8BB	0.9900
C9A—H9AA	0.9900	C9B—H9BA	0.9900
C9A—H9AB	0.9900	C9B—H9BB	0.9900
C10A—C11A	1.517 (9)	C10B—C11B	1.532 (11)
C10A—H10A	0.9900	C10B—H10C	0.9900
C10A—H10B	0.9900	C10B—H10D	0.9900
C11A—H11A	0.9900	C11B—H11C	0.9900
C11A—H11B	0.9900	C11B—H11D	0.9900
C13A—C14A	1.523 (11)	C13B—C14B	1.496 (11)
C13A—H13A	0.9900	C13B—H13C	0.9900
C13A—H13B	0.9900	C13B—H13D	0.9900
C14A—H14A	0.9800	C14B—H14E	0.9800
C14A—H14B	0.9800	C14B—H14F	0.9800
C14A—H14C	0.9800	C14B—H14G	0.9800

C1A—O1A—H1A	109.5	C1B—O1B—H1B	109.5
C12A—O4A—C13A	114.4 (7)	C12B—O4B—C13B	114.2 (7)
C5A—N1A—C11A	116.8 (7)	C5B—N1B—C11B	115.9 (6)
C5A—N1A—C8A	116.1 (6)	C5B—N1B—C8B	116.2 (7)
C11A—N1A—C8A	110.9 (6)	C11B—N1B—C8B	111.5 (6)
C12A—N2A—C9A	119.0 (7)	C12B—N2B—C10B	119.9 (7)
C12A—N2A—C10A	125.4 (6)	C12B—N2B—C9B	126.0 (6)
C9A—N2A—C10A	114.7 (7)	C10B—N2B—C9B	113.5 (6)
O2A—C1A—O1A	121.2 (7)	O2B—C1B—O1B	120.6 (6)
O2A—C1A—C2A	122.0 (7)	O2B—C1B—C2B	121.1 (6)
O1A—C1A—C2A	116.8 (6)	O1B—C1B—C2B	118.3 (6)
C3A—C2A—C7A	118.9 (6)	C7B—C2B—C3B	118.2 (6)
C3A—C2A—C1A	118.4 (6)	C7B—C2B—C1B	119.7 (6)
C7A—C2A—C1A	122.7 (7)	C3B—C2B—C1B	122.2 (7)
C2A—C3A—C4A	120.3 (6)	C4B—C3B—C2B	120.8 (7)
C2A—C3A—H3AA	119.9	C4B—C3B—H3BA	119.6
C4A—C3A—H3AA	119.9	C2B—C3B—H3BA	119.6
C3A—C4A—C5A	120.7 (7)	C3B—C4B—C5B	120.6 (7)
C3A—C4A—H4AA	119.7	C3B—C4B—H4BA	119.7
C5A—C4A—H4AA	119.7	C5B—C4B—H4BA	119.7

C6A—C5A—N1A	123.3 (7)	C4B—C5B—C6B	118.1 (7)
C6A—C5A—C4A	118.3 (7)	C4B—C5B—N1B	123.2 (7)
N1A—C5A—C4A	118.4 (7)	C6B—C5B—N1B	118.5 (7)
C5A—C6A—C7A	121.1 (7)	C7B—C6B—C5B	121.0 (7)
C5A—C6A—H6AA	119.4	C7B—C6B—H6BA	119.5
C7A—C6A—H6AA	119.4	C5B—C6B—H6BA	119.5
C2A—C7A—C6A	120.7 (7)	C6B—C7B—C2B	121.2 (7)
C2A—C7A—H7AA	119.6	C6B—C7B—H7BA	119.4
C6A—C7A—H7AA	119.6	C2B—C7B—H7BA	119.4
C9A—C8A—N1A	111.2 (7)	N1B—C8B—C9B	110.7 (6)
C9A—C8A—H8AA	109.4	N1B—C8B—H8BA	109.5
N1A—C8A—H8AA	109.4	C9B—C8B—H8BA	109.5
C9A—C8A—H8AB	109.4	N1B—C8B—H8BB	109.5
N1A—C8A—H8AB	109.4	C9B—C8B—H8BB	109.5
H8AA—C8A—H8AB	108.0	H8BA—C8B—H8BB	108.1
N2A—C9A—C8A	111.1 (7)	N2B—C9B—C8B	110.2 (6)
N2A—C9A—H9AA	109.4	N2B—C9B—H9BA	109.6
C8A—C9A—H9AA	109.4	C8B—C9B—H9BA	109.6
N2A—C9A—H9AB	109.4	N2B—C9B—H9BB	109.6
C8A—C9A—H9AB	109.4	C8B—C9B—H9BB	109.6
H9AA—C9A—H9AB	108.0	H9BA—C9B—H9BB	108.1
N2A—C10A—C11A	111.1 (6)	N2B—C10B—C11B	110.2 (6)
N2A—C10A—H10A	109.4	N2B—C10B—H10C	109.6
C11A—C10A—H10A	109.4	C11B—C10B—H10C	109.6
N2A—C10A—H10B	109.4	N2B—C10B—H10D	109.6
C11A—C10A—H10B	109.4	C11B—C10B—H10D	109.6
H10A—C10A—H10B	108.0	H10C—C10B—H10D	108.1
N1A—C11A—C10A	111.4 (6)	N1B—C11B—C10B	109.8 (7)
N1A—C11A—H11A	109.4	N1B—C11B—H11C	109.7
C10A—C11A—H11A	109.4	C10B—C11B—H11C	109.7
N1A—C11A—H11B	109.4	N1B—C11B—H11D	109.7
C10A—C11A—H11B	109.4	C10B—C11B—H11D	109.7
H11A—C11A—H11B	108.0	H11C—C11B—H11D	108.2
O3A—C12A—N2A	125.1 (7)	O3B—C12B—N2B	125.6 (7)
O3A—C12A—O4A	123.3 (7)	O3B—C12B—O4B	123.2 (7)
N2A—C12A—O4A	111.5 (6)	N2B—C12B—O4B	111.1 (7)
O4A—C13A—C14A	106.1 (7)	O4B—C13B—C14B	107.0 (6)
O4A—C13A—H13A	110.5	O4B—C13B—H13C	110.3
C14A—C13A—H13A	110.5	C14B—C13B—H13C	110.3
O4A—C13A—H13B	110.5	O4B—C13B—H13D	110.3
C14A—C13A—H13B	110.5	C14B—C13B—H13D	110.3
H13A—C13A—H13B	108.7	H13C—C13B—H13D	108.6
C13A—C14A—H14A	109.5	C13B—C14B—H14E	109.5
C13A—C14A—H14B	109.5	C13B—C14B—H14F	109.5
H14A—C14A—H14B	109.5	H14E—C14B—H14F	109.5
C13A—C14A—H14C	109.5	C13B—C14B—H14G	109.5
H14A—C14A—H14C	109.5	H14E—C14B—H14G	109.5
H14B—C14A—H14C	109.5	H14F—C14B—H14G	109.5

O2A—C1A—C2A—C3A	24.7 (11)	O2B—C1B—C2B—C7B	−24.7 (11)
O1A—C1A—C2A—C3A	−154.3 (7)	O1B—C1B—C2B—C7B	156.3 (7)
O2A—C1A—C2A—C7A	−154.0 (8)	O2B—C1B—C2B—C3B	153.9 (7)
O1A—C1A—C2A—C7A	27.0 (11)	O1B—C1B—C2B—C3B	−25.1 (11)
C7A—C2A—C3A—C4A	−1.4 (11)	C7B—C2B—C3B—C4B	0.4 (11)
C1A—C2A—C3A—C4A	179.8 (6)	C1B—C2B—C3B—C4B	−178.3 (7)
C2A—C3A—C4A—C5A	0.7 (11)	C2B—C3B—C4B—C5B	−2.8 (12)
C11A—N1A—C5A—C6A	4.9 (11)	C3B—C4B—C5B—C6B	3.7 (11)
C8A—N1A—C5A—C6A	−129.0 (8)	C3B—C4B—C5B—N1B	179.7 (7)
C11A—N1A—C5A—C4A	−174.5 (7)	C11B—N1B—C5B—C4B	131.7 (8)
C8A—N1A—C5A—C4A	51.5 (9)	C8B—N1B—C5B—C4B	−2.2 (11)
C3A—C4A—C5A—C6A	0.4 (11)	C11B—N1B—C5B—C6B	−52.3 (9)
C3A—C4A—C5A—N1A	179.9 (7)	C8B—N1B—C5B—C6B	173.8 (7)
N1A—C5A—C6A—C7A	179.7 (7)	C4B—C5B—C6B—C7B	−2.3 (11)
C4A—C5A—C6A—C7A	−0.9 (12)	N1B—C5B—C6B—C7B	−178.6 (7)
C3A—C2A—C7A—C6A	1.0 (12)	C5B—C6B—C7B—C2B	0.1 (12)
C1A—C2A—C7A—C6A	179.7 (7)	C3B—C2B—C7B—C6B	0.9 (11)
C5A—C6A—C7A—C2A	0.1 (12)	C1B—C2B—C7B—C6B	179.6 (7)
C5A—N1A—C8A—C9A	−166.9 (6)	C5B—N1B—C8B—C9B	−166.6 (7)
C11A—N1A—C8A—C9A	56.5 (8)	C11B—N1B—C8B—C9B	57.6 (8)
C12A—N2A—C9A—C8A	−137.3 (8)	C12B—N2B—C9B—C8B	−134.8 (7)
C10A—N2A—C9A—C8A	53.3 (9)	C10B—N2B—C9B—C8B	54.0 (8)
N1A—C8A—C9A—N2A	−54.1 (9)	N1B—C8B—C9B—N2B	−53.1 (9)
C12A—N2A—C10A—C11A	139.4 (7)	C12B—N2B—C10B—C11B	132.7 (7)
C9A—N2A—C10A—C11A	−52.0 (9)	C9B—N2B—C10B—C11B	−55.6 (9)
C5A—N1A—C11A—C10A	168.5 (6)	C5B—N1B—C11B—C10B	165.3 (6)
C8A—N1A—C11A—C10A	−55.3 (8)	C8B—N1B—C11B—C10B	−58.8 (8)
N2A—C10A—C11A—N1A	52.7 (9)	N2B—C10B—C11B—N1B	57.2 (9)
C9A—N2A—C12A—O3A	3.5 (11)	C10B—N2B—C12B—O3B	−3.5 (11)
C10A—N2A—C12A—O3A	171.6 (7)	C9B—N2B—C12B—O3B	−174.1 (7)
C9A—N2A—C12A—O4A	−178.7 (6)	C10B—N2B—C12B—O4B	178.4 (6)
C10A—N2A—C12A—O4A	−10.5 (10)	C9B—N2B—C12B—O4B	7.7 (10)
C13A—O4A—C12A—O3A	1.5 (9)	C13B—O4B—C12B—O3B	−0.8 (10)
C13A—O4A—C12A—N2A	−176.4 (6)	C13B—O4B—C12B—N2B	177.4 (6)
C12A—O4A—C13A—C14A	176.7 (6)	C12B—O4B—C13B—C14B	−178.3 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O2*B*	0.84	2.14	2.973 (8)	170
C8*A*—H8*AB*···O3*B*^{i}	0.99	2.56	3.225 (11)	124
O1*B*—H1*B*···O2*A*	0.84	2.11	2.934 (8)	168

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