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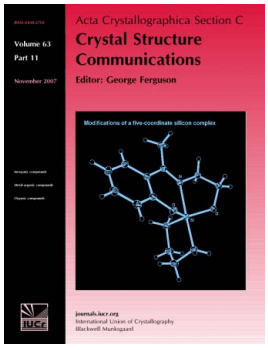

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The structural properties of a noncentrosymmetric polymorph of 4-aminobenzoic acid

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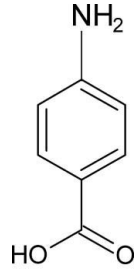
The crystal structure of a polymorph of 4-aminobenzoic acid (PABA), $C_7H_7NO_2$, at 100 K is noncentrosymmetric, as opposed to centrosymmetric in the structures of the other known polymorphs. The two crystallographically independent PABA molecules form pseudocentrosymmetric O—H···O hydrogen-bonded dimers that are further linked by N—H···O hydrogen bonds into a three-dimensional network. The benzene rings stack in the *b* direction. The CO_2 moieties are bent out slightly from the benzene ring plane.

Keywords: crystal structure; 4-aminobenzoic acid; PABA; polymorphism; noncentrosymmetric polymorph; hydrogen bonding; pharmaceuticals.

1. Introduction

Polymorphism and associated phenomena have been actively studied over the last few decades for both scientific aspects and industrial problems (Bernstein *et al.*, 1999; Brittain, 1999; Bernstein, 2002; Kitamura, 2002; Blagden & Davey, 2003). It is well established that different polymorphs have different structural and physical properties due to different crystal packing arrangements and/or molecular conformations. The control of such properties is one of the main challenges in crystal engineering and in quality control for the production of molecular materials, such as in pharmaceutical manufacturing (Herbstein, 2004). Although several studies highlight the effects of the competition between the nucleation–growth process and the transformation mechanism in the crystallization of polymorphous compounds, the conditions for the appearance and disappearance of polymorphs are still not completely understood. Among the most investigated systems are amino acids and their derivatives. These compounds have attracted major interest owing to their use in drug design based on hydrogen bonding and intermolecular interactions. Many of them are known to crystallize in polymorphic forms, for example, glutamic acid, asparagine, aspartic acid (Ono *et al.*, 2004; Ni *et al.*, 2004; Doki *et al.*, 2004; Bendeif & Jelsch, 2007) and 4-aminobenzoic acid (PABA). PABA is known for its biological properties and is well suited for use in medicine and is also used in the synthesis of esters, salts, folic acid, azo dyes and many other organic compounds. Because of its pharmaceutical and physical properties, the crystal structure of PABA has been studied since the early 1960s (Killean *et al.*, 1965; Alleaume *et al.*, 1966; Lai & Marsh, 1967). It has two known polymorphs, *viz.* the α and β forms. In the α form, PABA molecules are connected through alternating O—H···O and N—H···O interactions to form chains, while in the β form, PABA molecules are related *via* O—H···N and N—H···O hydrogen bonds to form a three-dimensional network. The crystal structures of the PABA polymorphs have been reinvestigated recently by various groups (Gracin & Rasmuson, 2004; Gracin & Fischer, 2005; Athimoolam & Natarajan, 2007). So far, four polymorphs of PABA are known in the literature, all of which are centrosymmetric. In the present study, the low-temperature structural properties of a new noncentrosymmetric PABA polymorph are discussed and compared with those of the polymorphs reported previously.



PABA

2. Experimental

2.1. Synthesis and crystallization

The title compound crystallized during an attempt to prepare single crystals of 4-aminobenzoic acid/selenous acid. Single crystals grew rapidly in the form of long colourless needles from an aqueous solution containing a mixture of 4-aminobenzoic acid and selenous acid (H_2SeO_3).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms were clearly identified in difference Fourier maps and their atomic coordinates and isotropic displacement parameters were refined freely with the exception that the O1*A*—H1*A* distance was restrained to 0.96 (2) Å. The Flack (1983) parameter refined with 1654 Bijvoet pairs to the meaningless value of −0.1 (13).

 doi:10.1107/S2053229614002447

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_7H_7NO_2$
M_r	137.14
Crystal system, space group	Orthorhombic, $Pna2_1$
Temperature (K)	100
a, b, c (Å)	26.9945 (8), 3.7322 (3), 12.6731 (8)
V (Å^3)	1276.80 (14)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.11
Crystal size (mm)	0.12 × 0.05 × 0.04
Data collection	
Diffractometer	Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer
Absorption correction	Analytical [*CrysAlis PRO* (Agilent, 2012), based on expressions derived by Clark & Reid (1995)]
T_{min}, T_{max}	0.959, 0.997
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9638, 3604, 2986
R_{int}	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.704
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.130, 1.04
No. of reflections	3604
No. of parameters	237
No. of restraints	2
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.49, −0.21

Computer programs: *CrysAlis PRO* (Agilent, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008). *WinGX* (Farrugia, 2012), *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 2012) and *enCIFer* (Allen *et al.*, 2004).

3. Results and discussion

The asymmetric unit of this new polymorph of PABA comprises two structurally independent molecules, as shown in Fig. 1. The geometric parameters (Table 2) are in agreement with previously reported results (Lai & Marsh, 1967; Athimoolam & Natarajan, 2007). The aromatic C—C bond lengths

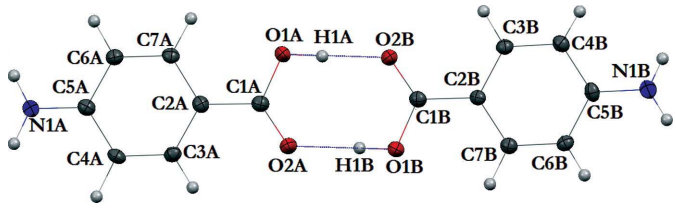


Figure 1
The asymmetric unit of PABA, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small grey spheres of arbitrary radius.

range from 1.377 (5) to 1.405 (5) Å, with average values of 1.392 (4) and 1.396 (4) Å for molecule *A* and *B*, respectively. It is worth noting that the C1*i*—C2*i* and C5*i*—N1*i* (*i* = *A* or *B*) bond lengths are significantly shorter (by about 0.07 Å) than classical single C—C and C—N bonds. This was also observed in the earliest work of Lai & Marsh (1967) and reveals the interesting quinoid structure of this polymorph. The molecular structure is also characterized by a slightly distorted planar geometry. The distortion from a perfect planar configuration is essentially due the different intermolecular interactions involving the amino and carboxylic acid groups. These groups are displaced, in the same direction, from the mean plan of the aromatic ring of each of the structurally distinct molecules, by 0.089 (3) and 0.100 (3) Å, respectively, for molecule *A*, and by 0.097 (3) and 0.127 (3) Å for molecule *B*. The bending out of the carboxylic acid group is commonly found in PABA compounds (Athimoolam & Natarajan, 2007) and the dihedral angles corresponding to this bending are 2.7 (4)° for molecule *A* and 4.3 (4)° for molecule *B*.

The crystal packing consists of pairs of PABA molecules linked together in a head-to-head fashion to form $(PABA)_2$ dimers *via* strong and pseudocentrosymmetric O—H···O hydrogen bonds [2.610 (2) and 2.631 (2) Å] (Fig. 2 and

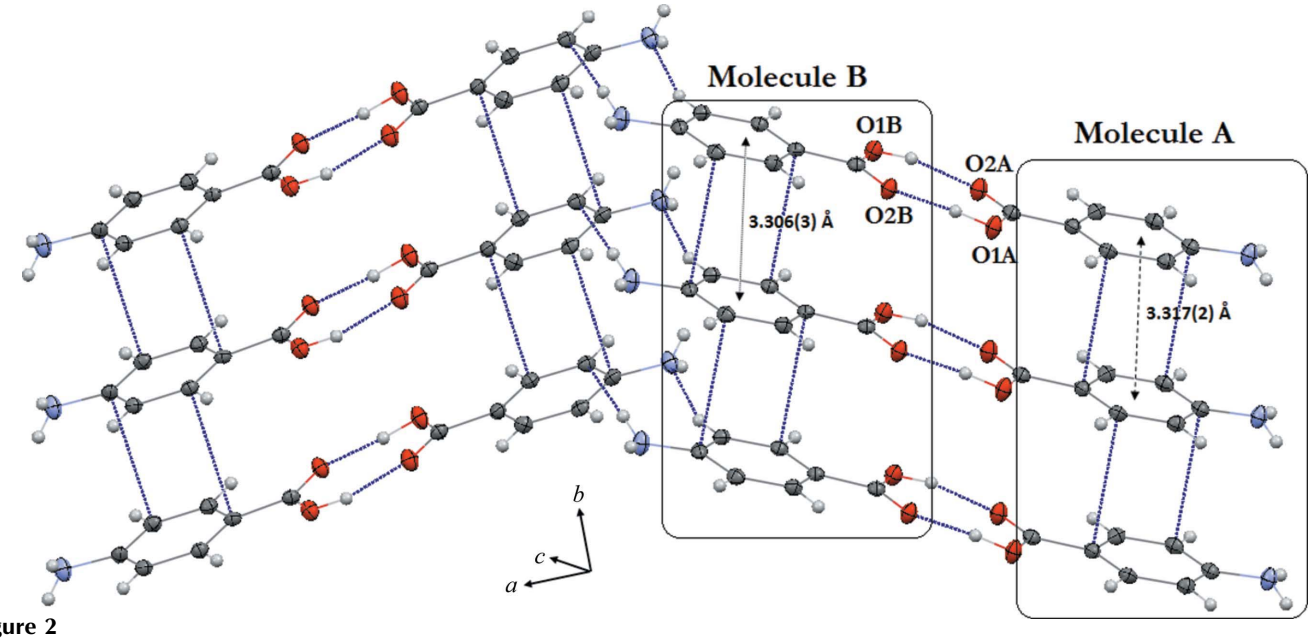


Figure 2
The molecular packing of PABA, showing the O—H···O and N—H···O hydrogen bonding (dotted lines) between molecules.

Table 2
Selected bond lengths (Å).

O1*A*—C1*A*	1.320 (4)	O1*B*—C1*B*	1.327 (4)
O2*A*—C1*A*	1.237 (4)	O2*B*—C1*B*	1.234 (4)
N1*A*—C5*A*	1.376 (4)	N1*B*—C5*B*	1.381 (4)
C1*A*—C2*A*	1.460 (4)	C1*B*—C2*B*	1.464 (4)
C2*A*—C3*A*	1.397 (5)	C2*B*—C3*B*	1.399 (5)
C2*A*—C7*A*	1.397 (5)	C2*B*—C7*B*	1.402 (5)
C3*A*—C4*A*	1.377 (5)	C3*B*—C4*B*	1.380 (5)
C4*A*—C5*A*	1.404 (5)	C4*B*—C5*B*	1.405 (5)
C5*A*—C6*A*	1.399 (4)	C5*B*—C6*B*	1.402 (4)
C6*A*—C7*A*	1.382 (4)	C6*B*—C7*B*	1.383 (4)

Table 3
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O2*B*	0.97 (3)	1.64 (4)	2.610 (2)	176 (5)
O1*B*—H1*B*···O2*A*	0.89 (3)	1.76 (4)	2.631 (2)	166 (4)
N1*A*—H1···O2*B*^{i}	0.96 (5)	2.00 (5)	2.958 (3)	171 (4)
N1*B*—H3···O2*A*^{ii}	0.83 (5)	2.59 (3)	3.305 (3)	143 (3)
N1*B*—H3···O2*A*^{iii}	0.83 (5)	2.73 (3)	3.312 (3)	128 (3)

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

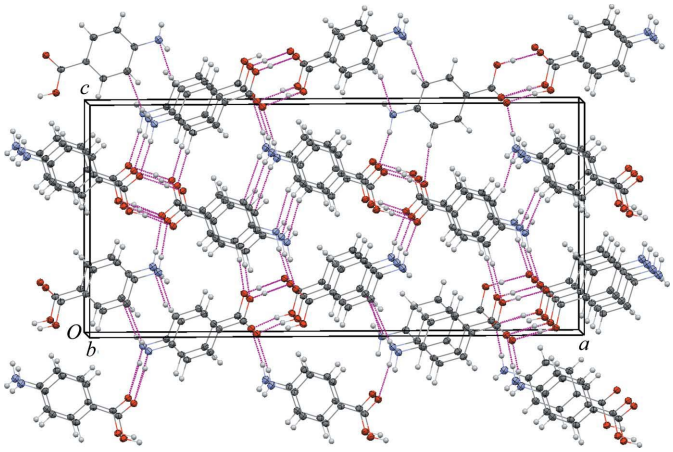


Figure 3
A projection of the three-dimensional network of intermolecular interactions (dotted lines) of PABA molecules.

Table 3). The dimers are themselves connected *via* a moderate N—H···O hydrogen bond [2.958 (3) Å] extending along the *c* axis. Moreover, the amino group of molecule *B* acts as a hydrogen-bond donor to two neighbouring carboxylic acid groups of *A* molecules lying one on top of the other through two weak N1*B*—H3···O2*A*^{ii,iii} interactions [3.305 (3) and 3.312 (3) Å; symmetry codes are as in Table 3] and therefore ensure the connection along the *b* axis.

Besides these hydrogen bonds, the crystal packing is also characterized by π–π stacking interactions and by additional C—H···N short contacts (Fig. 2), allowing the formation of a highly linked three-dimensional network of intermolecular interactions (Fig. 3). Furthermore, a detailed examination of the molecular packing reveals that the spacing between the *A* molecules [3.317 (2) Å] is slightly larger than that between the *B* molecules [3.306 (3) Å]. This may be explained by the twisting of the carboxylic acid group from the mean plane of the aromatic ring.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SK3526).

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supplementary materials

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The structural properties of a noncentrosymmetric polymorph of 4-amino-benzoic acid

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *WinGX* (Farrugia, 2012); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

4-Aminobenzoic acid

Crystal data

$C_7H_7NO_2$
M_r = 137.14
Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n
a = 26.9945 (8) Å
b = 3.7322 (3) Å
c = 12.6731 (8) Å
V = 1276.80 (14) Å^3
Z = 8
$F(000)$ = 576
D_x = 1.427 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2789 reflections
θ = 3.0–31.8°
μ = 0.11 mm^{-1}
T = 100 K
Needle, colorless
0.12 × 0.05 × 0.04 mm

Data collection

Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer
Radiation source: SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 8.1207 pixels mm^{-1}
ω scans
Absorption correction: analytical [*CrysAlis PRO* (Agilent, 2012), based on expressions derived by Clark & Reid (1995)]
T_{min} = 0.959, T_{max} = 0.997
9638 measured reflections
3604 independent reflections
2986 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 30.0°, θ_{min} = 3.0°
h = −38→38
k = −5→5
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.130
S = 1.04
3604 reflections
237 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 0.4328P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Experimental. Absorption correction: CrysAlisPro (2012), Agilent Technologies UK Ltd, Oxford, UK, Version 1.171.36.24 (release 03-12-2012 CrysAlis171 .NET) (compiled Dec 3 2012,18:21:49) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived byby Clark & Reid, 1995.

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 $F^2 > 2\sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1A	0.32623 (9)	0.2235 (7)	0.1596 (2)	0.0207 (6)
O2A	0.34318 (8)	0.4714 (7)	0.0030 (2)	0.0205 (5)
N1A	0.11867 (10)	−0.0303 (8)	−0.0574 (2)	0.0205 (6)
C1A	0.31417 (11)	0.3118 (9)	0.0621 (3)	0.0156 (6)
C2A	0.26421 (12)	0.2071 (9)	0.0305 (3)	0.0155 (7)
C3A	0.24705 (12)	0.2927 (9)	−0.0704 (3)	0.0164 (7)
C4A	0.19931 (13)	0.2119 (9)	−0.1005 (3)	0.0161 (6)
C5A	0.16700 (11)	0.0401 (9)	−0.0299 (2)	0.0158 (6)
C6A	0.18435 (11)	−0.0478 (9)	0.0708 (2)	0.0159 (6)
C7A	0.23219 (11)	0.0357 (9)	0.1009 (2)	0.0158 (6)
O1B	0.42862 (9)	0.7458 (6)	0.0618 (2)	0.0189 (6)
O2B	0.41094 (8)	0.4964 (6)	0.21799 (19)	0.0187 (5)
N1B	0.63292 (10)	1.0268 (9)	0.2935 (3)	0.0232 (6)
C1B	0.43984 (11)	0.6638 (9)	0.1609 (3)	0.0150 (6)
C2B	0.48920 (12)	0.7752 (8)	0.1957 (3)	0.0133 (6)
C3B	0.50488 (12)	0.6946 (9)	0.2982 (3)	0.0162 (6)
C4B	0.55198 (13)	0.7817 (9)	0.3318 (3)	0.0168 (7)
C5B	0.58484 (10)	0.9554 (9)	0.2627 (2)	0.0161 (6)
C6B	0.56921 (11)	1.0398 (8)	0.1602 (3)	0.0155 (6)
C7B	0.52193 (11)	0.9513 (8)	0.1272 (2)	0.0154 (6)
H1	0.1118 (17)	−0.006 (12)	−0.131 (4)	0.039 (13)*
H2	0.1035 (17)	−0.193 (12)	−0.015 (4)	0.029 (12)*
H3	0.6389 (16)	1.003 (11)	0.358 (4)	0.029 (12)*
H4	0.6483 (19)	1.201 (14)	0.258 (4)	0.039 (14)*
H4A	0.1889 (17)	0.266 (11)	−0.183 (4)	0.032 (14)*
H4B	0.5636 (16)	0.729 (11)	0.397 (4)	0.021 (12)*
H1A	0.3571 (17)	0.34 (2)	0.182 (6)	0.10 (3)*
H1B	0.3975 (13)	0.685 (10)	0.046 (3)	0.008 (8)*
H3A	0.2683 (14)	0.412 (11)	−0.118 (3)	0.018 (10)*
H3B	0.4825 (15)	0.564 (12)	0.349 (3)	0.027 (11)*
H6A	0.1624 (14)	−0.176 (12)	0.123 (3)	0.019 (10)*

H6B	0.5897 (15)	1.155 (12)	0.115 (3)	0.024 (10)*
H7A	0.2443 (14)	−0.027 (10)	0.175 (3)	0.018 (10)*
H7B	0.5112 (14)	1.017 (11)	0.051 (3)	0.018 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.0178 (11)	0.0297 (15)	0.0147 (12)	−0.0060 (9)	−0.0030 (10)	0.0029 (10)
O2A	0.0177 (10)	0.0273 (14)	0.0164 (10)	−0.0036 (9)	0.0003 (8)	0.0021 (10)
N1A	0.0177 (12)	0.0272 (17)	0.0167 (12)	−0.0042 (11)	−0.0022 (10)	0.0021 (12)
C1A	0.0170 (13)	0.0149 (15)	0.0149 (13)	0.0020 (11)	0.0008 (11)	−0.0007 (13)
C2A	0.0155 (13)	0.0141 (16)	0.0168 (16)	0.0020 (11)	−0.0005 (11)	−0.0009 (12)
C3A	0.0181 (14)	0.0163 (16)	0.0146 (16)	−0.0008 (11)	0.0025 (12)	−0.0013 (12)
C4A	0.0198 (15)	0.0163 (16)	0.0124 (14)	0.0031 (11)	−0.0025 (11)	0.0012 (12)
C5A	0.0176 (13)	0.0144 (16)	0.0153 (13)	0.0030 (11)	−0.0003 (10)	−0.0009 (11)
C6A	0.0173 (13)	0.0152 (16)	0.0154 (13)	0.0004 (11)	0.0012 (11)	0.0005 (12)
C7A	0.0174 (13)	0.0134 (15)	0.0168 (13)	0.0025 (11)	−0.0004 (10)	0.0015 (12)
O1B	0.0184 (11)	0.0228 (14)	0.0155 (12)	−0.0035 (8)	−0.0024 (9)	0.0035 (9)
O2B	0.0174 (10)	0.0234 (12)	0.0154 (10)	−0.0046 (9)	−0.0001 (8)	0.0016 (9)
N1B	0.0183 (12)	0.0317 (18)	0.0194 (14)	−0.0025 (12)	−0.0026 (10)	0.0006 (13)
C1B	0.0175 (13)	0.0136 (14)	0.0139 (13)	0.0010 (12)	0.0010 (11)	−0.0023 (13)
C2B	0.0162 (13)	0.0111 (15)	0.0127 (14)	0.0005 (10)	−0.0001 (11)	−0.0008 (11)
C3B	0.0176 (14)	0.0147 (16)	0.0162 (15)	0.0008 (11)	0.0006 (12)	0.0011 (13)
C4B	0.0186 (14)	0.0160 (17)	0.0157 (16)	0.0014 (11)	−0.0009 (12)	−0.0014 (12)
C5B	0.0150 (13)	0.0157 (15)	0.0175 (13)	0.0015 (11)	−0.0017 (10)	−0.0058 (12)
C6B	0.0171 (13)	0.0131 (15)	0.0162 (12)	0.0002 (10)	0.0017 (11)	−0.0001 (13)
C7B	0.0173 (13)	0.0143 (15)	0.0145 (13)	0.0014 (11)	0.0007 (10)	−0.0014 (11)

Geometric parameters (Å, º)

O1A—C1A	1.320 (4)	O1B—C1B	1.327 (4)
O1A—H1A	0.97 (3)	O1B—H1B	0.89 (3)
O2A—C1A	1.237 (4)	O2B—C1B	1.234 (4)
N1A—C5A	1.376 (4)	N1B—C5B	1.381 (4)
N1A—H1	0.96 (5)	N1B—H3	0.83 (5)
N1A—H2	0.91 (5)	N1B—H4	0.89 (5)
C1A—C2A	1.460 (4)	C1B—C2B	1.464 (4)
C2A—C3A	1.397 (5)	C2B—C3B	1.399 (5)
C2A—C7A	1.397 (5)	C2B—C7B	1.402 (5)
C3A—C4A	1.377 (5)	C3B—C4B	1.380 (5)
C3A—H3A	0.95 (4)	C3B—H3B	1.01 (4)
C4A—C5A	1.404 (5)	C4B—C5B	1.405 (5)
C4A—H4A	1.10 (5)	C4B—H4B	0.91 (5)
C5A—C6A	1.399 (4)	C5B—C6B	1.402 (4)
C6A—C7A	1.382 (4)	C6B—C7B	1.383 (4)
C6A—H6A	1.01 (4)	C6B—H6B	0.91 (4)
C7A—H7A	1.02 (4)	C7B—H7B	1.04 (4)
C1A—O1A—H1A	112 (5)	C1B—O1B—H1B	111 (2)
C5A—N1A—H1	114 (3)	C5B—N1B—H3	116 (3)

C5A—N1A—H2	114 (3)	C5B—N1B—H4	116 (3)
H1—N1A—H2	124 (4)	H3—N1B—H4	119 (5)
O2A—C1A—O1A	122.1 (3)	O2B—C1B—O1B	121.8 (3)
O2A—C1A—C2A	123.2 (3)	O2B—C1B—C2B	122.9 (3)
O1A—C1A—C2A	114.7 (3)	O1B—C1B—C2B	115.3 (3)
C3A—C2A—C7A	118.9 (3)	C3B—C2B—C7B	119.0 (3)
C3A—C2A—C1A	119.8 (3)	C3B—C2B—C1B	119.6 (3)
C7A—C2A—C1A	121.3 (3)	C7B—C2B—C1B	121.4 (3)
C4A—C3A—C2A	120.9 (3)	C4B—C3B—C2B	121.0 (3)
C4A—C3A—H3A	120 (2)	C4B—C3B—H3B	118 (2)
C2A—C3A—H3A	119 (2)	C2B—C3B—H3B	121 (2)
C3A—C4A—C5A	120.3 (3)	C3B—C4B—C5B	119.9 (3)
C3A—C4A—H4A	118 (2)	C3B—C4B—H4B	123 (3)
C5A—C4A—H4A	122 (2)	C5B—C4B—H4B	117 (3)
N1A—C5A—C6A	120.3 (3)	N1B—C5B—C6B	120.1 (3)
N1A—C5A—C4A	121.0 (3)	N1B—C5B—C4B	120.4 (3)
C6A—C5A—C4A	118.7 (3)	C6B—C5B—C4B	119.4 (3)
C7A—C6A—C5A	120.8 (3)	C7B—C6B—C5B	120.3 (3)
C7A—C6A—H6A	118 (2)	C7B—C6B—H6B	119 (3)
C5A—C6A—H6A	121 (2)	C5B—C6B—H6B	121 (3)
C6A—C7A—C2A	120.4 (3)	C6B—C7B—C2B	120.4 (3)
C6A—C7A—H7A	120 (2)	C6B—C7B—H7B	119 (2)
C2A—C7A—H7A	119 (2)	C2B—C7B—H7B	121 (2)
O2A—C1A—C2A—C3A	−1.0 (5)	O2B—C1B—C2B—C3B	−0.7 (5)
O1A—C1A—C2A—C3A	178.8 (3)	O1B—C1B—C2B—C3B	−178.7 (3)
O2A—C1A—C2A—C7A	−178.2 (3)	O2B—C1B—C2B—C7B	177.2 (3)
O1A—C1A—C2A—C7A	1.6 (5)	O1B—C1B—C2B—C7B	−0.8 (5)
C7A—C2A—C3A—C4A	0.3 (5)	C7B—C2B—C3B—C4B	−0.8 (5)
C1A—C2A—C3A—C4A	−177.0 (3)	C1B—C2B—C3B—C4B	177.1 (3)
C2A—C3A—C4A—C5A	−0.2 (5)	C2B—C3B—C4B—C5B	0.3 (5)
C3A—C4A—C5A—N1A	177.5 (3)	C3B—C4B—C5B—N1B	−176.5 (3)
C3A—C4A—C5A—C6A	−0.2 (5)	C3B—C4B—C5B—C6B	0.3 (5)
N1A—C5A—C6A—C7A	−177.2 (3)	N1B—C5B—C6B—C7B	176.5 (3)
C4A—C5A—C6A—C7A	0.6 (5)	C4B—C5B—C6B—C7B	−0.3 (5)
C5A—C6A—C7A—C2A	−0.5 (5)	C5B—C6B—C7B—C2B	−0.3 (5)
C3A—C2A—C7A—C6A	0.1 (5)	C3B—C2B—C7B—C6B	0.8 (5)
C1A—C2A—C7A—C6A	177.3 (3)	C1B—C2B—C7B—C6B	−177.1 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O2*B*	0.97 (3)	1.64 (4)	2.610 (2)	176 (5)
O1*B*—H1*B*···O2*A*	0.89 (3)	1.76 (4)	2.631 (2)	166 (4)
N1*A*—H1···O2*B*^{i}	0.96 (5)	2.00 (5)	2.958 (3)	171 (4)
N1*B*—H3···O2*A*^{ii}	0.83 (5)	2.59 (3)	3.305 (3)	143 (3)
N1*B*—H3···O2*A*^{iii}	0.83 (5)	2.73 (3)	3.312 (3)	128 (3)

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