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Crystal structure of 4-(2-hydroxy-3-methoxybenzylamino)benzoic acid dimethylformamide monosolvate monohydrate

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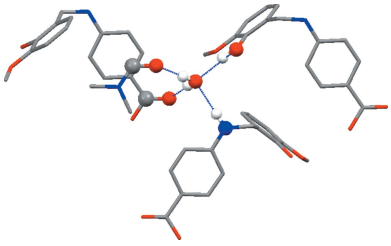
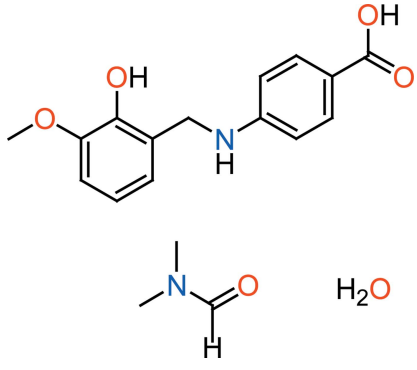
The title compound, $C_{15}H_{15}NO_4\cdot C_3H_7NO\cdot H_2O$, a secondary amine molecule, is accompanied by one equivalent of water and one equivalent of dimethylformamide (DMF) as solvents. The molecule is non-planar, with a $C_{aryl}—CH_2—NH—C_{aryl}$ torsion angle of −66.3 (3)°. In the crystal, O—H···O and N—H···O hydrogen-bonding interactions between the amine molecules and the two types of solvent molecule result in the formation of a layered structure extending parallel to (010).

1. Chemical context

Vanillin and vanillin derivatives are used in food and non-food applications, in fragrances and as flavouring agents for pharmaceutical products (Hocking, 1997; Walton *et al.*, 2003). Synthetic vanillin is used as an intermediate in the chemical and pharmaceutical industries for the production of herbicides, antifoaming agents and drugs, such as papaverine, L-dopa and L-methyldopa, as well as antimicrobial agents such as trimethoprim (Fitzgerald *et al.*, 2005), and as a bacterial co-factor involved in the synthesis of folic acid (Robinson, 1966). Another example is benzocaine, the ethyl ester of *p*-amino-benzoic acid, which is a local anaesthetic. The mechanism includes inhibiting voltage-dependent sodium channels on the nerve membrane, which results in stopping the signal propagation (Neumcke *et al.*, 1981). The title compound (1) was synthesized by reduction of reported (*E*)-4-(2-hydroxy-3-methoxybenzylideneamino)benzoic acid with sodium borohydride and crystallizes as a water and dimethylformamide solvate. The latter Schiff base is formed by condensation of 4-aminobenzoic acid with *o*-vanilline.





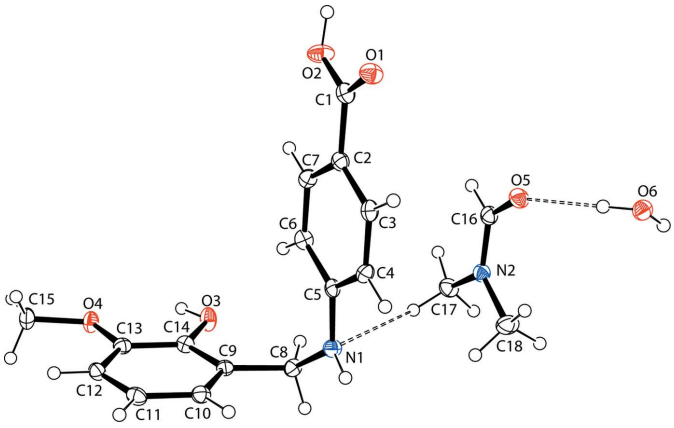


Figure 1
The structures of the molecular entities in the asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 40% probability level. Intermolecular $O-H_{water}\cdots O_{amide}$ and $C-H_{methyl}\cdots N_{amine}$ hydrogen bonds involving the water and dimethylformamide solvent molecules are shown as dashed lines (see Table 1 for numerical details).

In this context and as part of an ongoing structural study of Schiff bases and secondary amines for their utilization in the synthesis of new organic compounds and the application of excited-state proton transfer and fluorescent chemosensors (Faizi *et al.*, 2016*a*,*b*, 2018*a*,*b*; Kumar *et al.*, 2018; Mukherjee *et al.*, 2018), we report here the molecular and crystal structure of (1), $C_{15}H_{15}NO_4\cdot C_3H_7NO\cdot H_2O$.

2. Structural commentary

Compound (1) crystallizes in space group *Pbca* with one molecule of 4-(2-hydroxy-3-methoxybenzylamino)benzoic acid and one molecule each of DMF and water in the asymmetric unit (Fig. 1). The secondary amine has two substituted aromatic rings at either end of the $-CH_2-NH-$ linkage. As a result of the $C_{aryl}-CH_2-NH-C_{aryl}$ torsion angle of −66.3 (3)°, the molecular shape of the title compound is bent around the central C8—N1 bond. The secondary amine N atom (N1) has a practically trigonal-planar configuration deviating by 0.02 (1) Å from the mean plane of the adjacent atoms, and N1—C5 is apparently less conjugated with the C2–C7 benzenecarboxylic acid ring. For comparison, the reported C—N distance in the crystal structure of the ethyl 4-[(*E*)-(4-hydroxy-3-methoxybenzylidene)amino]benzoate Schiff base is 1.274 (2) Å (Ling *et al.*, 2016), and in the zwitterionic form it is 1.312 Å (Kamaal *et al.*, 2018). The benzene rings C2–C7 and C9–C14 are roughly perpendicular to each another, with a dihedral angle of 88.15 (10)° between them.

The C16═O5 bond length in the dimethylformamide solvent is 1.246 (2) Å, which is slightly longer than reported [1.2309 (17) Å (Fernandes *et al.*, 2007) or 1.2373 (18) Å (Elgemeie *et al.*, 2015)] for other dimethylformamide solvates. In (1), the C13—O4 bond length to the methoxy group is 1.366 (2) Å.

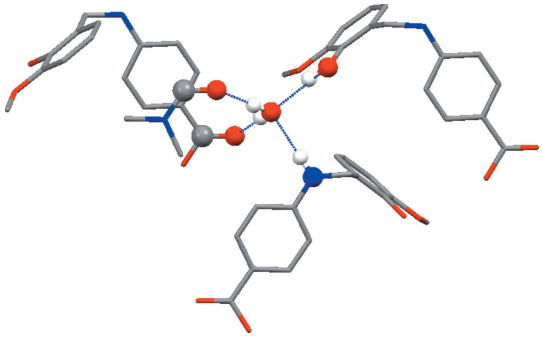


Figure 2
A view of hydrogen-bonding interactions around the water molecule in the title structure.

3. Supramolecular features

The water and dimethylformamide solvent molecules stabilize the packing within the crystal structure through hydrogen bonding. The molecules of dimethylformamide, 4-(2-hydroxy-3-methoxybenzylamino)benzoic acid and water are linked through $_{hydroxy}O3-H3\cdots O6_{water}$, $_{amine}N1-H1\cdots O6_{water}$, $_{water}O6-H6B\cdots O5_{amide}$, $_{water}O6-H6B\cdots O1_{carboxyate}$ and $O2-H2\cdots O5_{amide}$ hydrogen bonds (Table 1, Fig. 2) into a layered structure extending parallel to (010) (Fig. 3). Further C—H···O interactions (Table 1) between the methyl group of

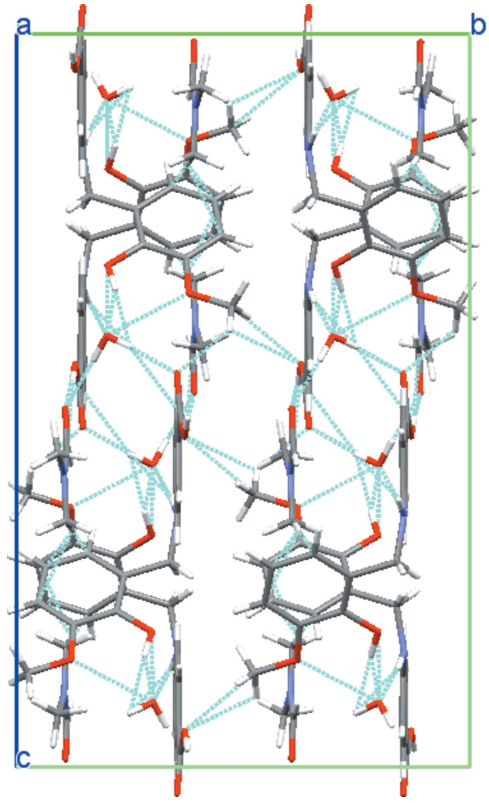


Figure 3
A partial view of the title structure projected along the *a* axis to emphasize the crystal packing. Dashed lines indicate hydrogen bonds (see Table 1 for numerical details).

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

D—H···A	D—H	H···A	D···A	D—H···A
C15—H15C···O1^{i}	0.96	2.50	3.329 (3)	145
N1—H1···O6^{iii}	0.89 (2)	2.05 (2)	2.936 (2)	175 (2)
O2—H2···O5^{iv}	0.90 (3)	1.70 (3)	2.591 (2)	171 (3)
O3—H3···O6^{v}	0.88 (3)	1.90 (3)	2.739 (2)	158 (3)
O6—H6A···O1^{vi}	0.85 (3)	1.94 (3)	2.776 (2)	172 (3)
O6—H6B···O5	0.88 (3)	1.91 (3)	2.785 (2)	178 (3)

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

the methoxy functionality and the carboxylate group consolidate the packing.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.39; Groom *et al.*, 2016) gave eleven hits for reduced Schiff bases containing a C_{aryl}—CH_2—NH— C_{aryl} moiety. In direct comparison with the title compound, there are two examples of very similar compounds reported in the literature: ethyl 4-{[(2-hydroxyphenyl)methyl]amino}benzoate, (**I**) (WEFQEG; Salman *et al.*, 2017), and ethyl 4-[(3,5-di-*tert*-butyl-2-hydroxybenzyl) amino]benzoate, (**II**) (VABTAV; Shakir *et al.*, 2010). There is also a related compound, *viz.* ethyl 4-[(2-hydroxybenzyl)amino]benzoate, in which the 3-methoxy group in the title compound is replaced by a hydrogen atom and the carboxylic acid is replaced by an ester. Other related structures based on a benzylidene–phenyl–amine moiety are *n*-propyl 4-[2-(4,6-dimethoxypyrimidin-2-yloxy)benzylamino]-benzoate, (**III**) (ILAGIL; Wu *et al.*, 2003), and [4-(2-hydroxybenzylamino)benzoato-κO]triphenyltin(IV), (**IV**) (WENXAP; Jiang *et al.*, 2006). The torsion angle C_{aryl}—CH_2—NH—C_{aryl} in the title compound [−66.3 (3)°] compares well to those in **I** (73.68°), **II** (77.38°) and **IV** (−87.28°), despite the difference in substituent groups.

5. Synthesis and crystallization

To a hot stirred solution of 4-aminobenzoic acid (PABA) (1.00 g, 7.2 mmol) in methanol (15 ml) was added vanillin (1.11 g, 7.2 mmol). The resultant mixture was then heated under reflux. After an hour, a precipitate was formed. The reaction mixture was heated for about a further 30 minutes for completion of the reaction, which was monitored through TLC. The reaction mixture was then cooled to room temperature, filtered and washed with hot methanol. It was then dried *in vacuo* to give (*E*)-4-(2-hydroxy-3-methoxybenzylideneamino) benzoic acid in 78% yield. The latter (1.00 g, 3.7 mmol) was dissolved in 25 ml of methanol and reduced by addition of excess sodium borohydride (0.28 g, 7.4 mmol). The solution was stirred until the yellow colour disappeared. Then the solution was diluted with 8–10 times the volume of water and the pH was adjusted to 6 by addition of 12%$_{wt}$ HCl. The white precipitate was collected and dried in air. Colourless single crystals of the title compound, suitable for X-ray analysis, were obtained by slow evaporation of a dimethylformamide solution.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{15}NO_4{\cdot}C_3H_7NO{\cdot}H_2O$
M_r	364.39
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	100
a, *b*, *c* (Å)	11.5504 (7), 13.8047 (7), 22.3899 (12)
V (Å^3)	3570.1 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.39 × 0.24 × 0.17
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40928, 3165, 2321
R_{int}	0.106
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.596
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.113, 1.05
No. of reflections	3165
No. of parameters	258
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.25

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2014), *SHELXT2015* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012), *WinGX* (Farrugia, 2012).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The N—H and O—H hydrogen atoms were located in difference-Fourier maps and were freely refined, while the C-bound H atoms were included in calculated positions and treated as riding, with fixed C—H = 0.93 Å, and U_{iso}(H) = 1.2U_{eq}(C,N).

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Crystal structure of 4-(2-hydroxy-3-methoxybenzylamino)benzoic acid dimethylformamide monosolvate monohydrate

Md. Serajul Haque Faizi, Saima Kamaal, Arif Ali, Musheer Ahmad and Irina A. Golenya

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: SHELXT2015 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

4-(2-Hydroxy-3-methoxybenzylamino)benzoic acid dimethylformamide monosolvate monohydrate

Crystal data

$C_{15}H_{15}NO_4·C_3H_7NO·H_2O$
M_r = 364.39
Orthorhombic, *Pbca*
a = 11.5504 (7) Å
b = 13.8047 (7) Å
c = 22.3899 (12) Å
V = 3570.1 (3) Å^3
Z = 8
$F(000)$ = 1552
D_x = 1.356 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6409 reflections
θ = 2.3–28.2°
μ = 0.10 mm^{-1}
T = 100 K
Block, colorless
0.39 × 0.24 × 0.17 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
40928 measured reflections
3165 independent reflections
2321 reflections with $I > 2\sigma(I)$
R_{int} = 0.106
θ_{max} = 25.1°, θ_{min} = 2.9°
h = −13→13
k = −16→16
l = −26→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.113
S = 1.05
3165 reflections
258 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 2.7178P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.97909 (13)	0.64576 (11)	0.53644 (7)	0.0253 (4)
O2	1.07571 (14)	0.62871 (12)	0.45097 (7)	0.0283 (4)
O3	0.71716 (14)	0.70129 (10)	0.18430 (7)	0.0252 (4)
O4	0.76784 (13)	0.88000 (10)	0.14629 (6)	0.0225 (4)
N1	0.56965 (16)	0.64392 (13)	0.34340 (8)	0.0202 (4)
C1	0.97938 (19)	0.63895 (15)	0.48187 (10)	0.0203 (5)
C2	0.87414 (18)	0.64213 (15)	0.44484 (9)	0.0191 (5)
C3	0.76483 (19)	0.64465 (15)	0.47181 (10)	0.0205 (5)
H3A	0.759163	0.644607	0.513245	0.025*
C4	0.66632 (18)	0.64718 (15)	0.43802 (9)	0.0195 (5)
H4	0.594711	0.649520	0.456958	0.023*
C5	0.67081 (18)	0.64633 (14)	0.37540 (9)	0.0182 (5)
C6	0.78028 (18)	0.64468 (15)	0.34804 (9)	0.0209 (5)
H6	0.786010	0.645126	0.306608	0.025*
C7	0.87952 (18)	0.64238 (15)	0.38257 (10)	0.0204 (5)
H7	0.951416	0.640972	0.363889	0.024*
C8	0.56478 (18)	0.66082 (15)	0.27954 (9)	0.0198 (5)
H8A	0.487059	0.646580	0.265676	0.024*
H8B	0.617048	0.615927	0.259956	0.024*
C9	0.59608 (18)	0.76308 (15)	0.26052 (9)	0.0183 (5)
C10	0.54893 (18)	0.84270 (15)	0.29065 (9)	0.0204 (5)
H10	0.499734	0.832750	0.322951	0.024*
C11	0.57492 (18)	0.93582 (15)	0.27275 (9)	0.0216 (5)
H11	0.543392	0.988120	0.293264	0.026*
C12	0.64763 (18)	0.95228 (15)	0.22444 (9)	0.0204 (5)
H12	0.664327	1.015250	0.212442	0.024*
C13	0.69509 (18)	0.87437 (15)	0.19427 (9)	0.0184 (5)
C14	0.66910 (18)	0.77913 (15)	0.21267 (9)	0.0185 (5)
C15	0.8038 (2)	0.97495 (15)	0.12804 (10)	0.0246 (5)
H15A	0.838277	1.007996	0.161321	0.037*
H15B	0.737862	1.010846	0.114248	0.037*
H15C	0.859436	0.969537	0.096352	0.037*
O5	0.73401 (13)	0.39240 (11)	0.48915 (6)	0.0232 (4)
N2	0.63766 (15)	0.39534 (12)	0.40067 (8)	0.0197 (4)
C16	0.73235 (19)	0.38897 (15)	0.43356 (10)	0.0207 (5)
H16	0.802632	0.381408	0.413834	0.025*
C17	0.64116 (19)	0.39045 (16)	0.33595 (9)	0.0233 (5)
H17A	0.718785	0.376788	0.323146	0.035*
H17B	0.616637	0.451334	0.319537	0.035*

H17C	0.590384	0.340011	0.322353	0.035*
C18	0.52415 (19)	0.40815 (18)	0.42793 (10)	0.0287 (6)
H18A	0.533133	0.419569	0.469968	0.043*
H18B	0.478642	0.350798	0.421860	0.043*
H18C	0.485877	0.462530	0.409914	0.043*
O6	0.63671 (14)	0.30090 (13)	0.58799 (7)	0.0227 (4)
H1	0.506 (2)	0.6567 (16)	0.3644 (10)	0.025 (6)*
H2	1.138 (3)	0.623 (2)	0.4752 (13)	0.060 (10)*
H3	0.759 (2)	0.7170 (19)	0.1528 (12)	0.045 (8)*
H6A	0.607 (2)	0.250 (2)	0.5735 (12)	0.044 (9)*
H6B	0.667 (2)	0.329 (2)	0.5565 (13)	0.047 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0240 (9)	0.0326 (9)	0.0193 (9)	0.0028 (7)	−0.0005 (7)	0.0003 (7)
O2	0.0179 (9)	0.0423 (10)	0.0247 (9)	0.0061 (7)	0.0004 (7)	−0.0053 (7)
O3	0.0359 (10)	0.0164 (8)	0.0234 (9)	0.0002 (7)	0.0095 (7)	−0.0016 (7)
O4	0.0277 (9)	0.0182 (8)	0.0217 (8)	−0.0013 (6)	0.0070 (7)	0.0019 (6)
N1	0.0190 (10)	0.0251 (10)	0.0165 (10)	0.0002 (8)	0.0014 (8)	0.0014 (8)
C1	0.0243 (12)	0.0164 (11)	0.0202 (13)	0.0024 (9)	0.0011 (9)	−0.0017 (9)
C2	0.0218 (12)	0.0156 (11)	0.0199 (12)	0.0009 (9)	−0.0004 (9)	−0.0008 (9)
C3	0.0255 (12)	0.0185 (12)	0.0175 (11)	−0.0009 (9)	0.0026 (9)	0.0010 (9)
C4	0.0178 (11)	0.0206 (12)	0.0199 (12)	−0.0018 (9)	0.0038 (9)	0.0000 (9)
C5	0.0212 (12)	0.0117 (10)	0.0216 (12)	−0.0006 (9)	0.0001 (9)	0.0005 (8)
C6	0.0254 (12)	0.0204 (12)	0.0169 (11)	0.0017 (9)	0.0019 (9)	−0.0016 (9)
C7	0.0189 (11)	0.0182 (11)	0.0240 (12)	0.0013 (9)	0.0042 (9)	−0.0020 (9)
C8	0.0195 (11)	0.0225 (12)	0.0173 (11)	−0.0023 (9)	0.0003 (9)	−0.0003 (9)
C9	0.0171 (11)	0.0192 (11)	0.0185 (11)	−0.0019 (9)	−0.0053 (9)	0.0009 (9)
C10	0.0182 (11)	0.0233 (12)	0.0196 (12)	0.0014 (9)	0.0003 (9)	0.0006 (9)
C11	0.0215 (12)	0.0192 (12)	0.0242 (12)	0.0054 (9)	−0.0002 (9)	−0.0029 (9)
C12	0.0208 (11)	0.0157 (11)	0.0246 (12)	0.0013 (9)	−0.0031 (9)	0.0011 (9)
C13	0.0175 (11)	0.0223 (12)	0.0156 (11)	0.0003 (9)	−0.0020 (9)	0.0001 (9)
C14	0.0200 (11)	0.0184 (11)	0.0170 (11)	0.0013 (9)	−0.0009 (9)	−0.0029 (9)
C15	0.0290 (13)	0.0181 (12)	0.0265 (13)	−0.0025 (10)	0.0044 (10)	0.0042 (9)
O5	0.0247 (8)	0.0262 (9)	0.0188 (8)	0.0007 (7)	−0.0020 (6)	0.0019 (7)
N2	0.0198 (10)	0.0194 (10)	0.0198 (10)	0.0007 (7)	0.0014 (8)	0.0010 (7)
C16	0.0211 (12)	0.0169 (11)	0.0241 (13)	0.0006 (9)	0.0018 (9)	0.0011 (9)
C17	0.0246 (12)	0.0266 (13)	0.0186 (12)	0.0026 (10)	−0.0003 (9)	0.0006 (9)
C18	0.0207 (12)	0.0386 (14)	0.0267 (13)	0.0027 (10)	0.0038 (10)	0.0013 (11)
O6	0.0226 (8)	0.0265 (9)	0.0190 (9)	−0.0021 (7)	0.0003 (7)	0.0005 (7)

Geometric parameters (Å, º)

O1—C1	1.225 (2)	C9—C10	1.400 (3)
O2—C1	1.318 (3)	C10—C11	1.380 (3)
O2—H2	0.90 (3)	C10—H10	0.9300
O3—C14	1.366 (2)	C11—C12	1.388 (3)

O3—H3	0.88 (3)	C11—H11	0.9300
O4—C13	1.366 (2)	C12—C13	1.383 (3)
O4—C15	1.434 (2)	C12—H12	0.9300
N1—C5	1.371 (3)	C13—C14	1.410 (3)
N1—C8	1.450 (3)	C15—H15A	0.9600
N1—H1	0.89 (2)	C15—H15B	0.9600
C1—C2	1.472 (3)	C15—H15C	0.9600
C2—C7	1.396 (3)	O5—C16	1.246 (2)
C2—C3	1.400 (3)	N2—C16	1.321 (3)
C3—C4	1.367 (3)	N2—C17	1.451 (3)
C3—H3A	0.9300	N2—C18	1.457 (3)
C4—C5	1.403 (3)	C16—H16	0.9300
C4—H4	0.9300	C17—H17A	0.9600
C5—C6	1.405 (3)	C17—H17B	0.9600
C6—C7	1.383 (3)	C17—H17C	0.9600
C6—H6	0.9300	C18—H18A	0.9600
C7—H7	0.9300	C18—H18B	0.9600
C8—C9	1.518 (3)	C18—H18C	0.9600
C8—H8A	0.9700	O6—H6A	0.85 (3)
C8—H8B	0.9700	O6—H6B	0.88 (3)
C9—C14	1.382 (3)		

C1—O2—H2	111.3 (19)	C9—C10—H10	119.8
C14—O3—H3	113.6 (18)	C10—C11—C12	120.70 (19)
C13—O4—C15	117.01 (16)	C10—C11—H11	119.6
C5—N1—C8	122.99 (18)	C12—C11—H11	119.6
C5—N1—H1	115.1 (15)	C13—C12—C11	119.53 (19)
C8—N1—H1	117.1 (15)	C13—C12—H12	120.2
O1—C1—O2	122.3 (2)	C11—C12—H12	120.2
O1—C1—C2	123.9 (2)	O4—C13—C12	125.70 (19)
O2—C1—C2	113.87 (18)	O4—C13—C14	114.44 (17)
C7—C2—C3	118.1 (2)	C12—C13—C14	119.87 (19)
C7—C2—C1	121.73 (19)	O3—C14—C9	118.85 (18)
C3—C2—C1	120.17 (19)	O3—C14—C13	120.74 (18)
C4—C3—C2	120.8 (2)	C9—C14—C13	120.40 (19)
C4—C3—H3A	119.6	O4—C15—H15A	109.5
C2—C3—H3A	119.6	O4—C15—H15B	109.5
C3—C4—C5	121.5 (2)	H15A—C15—H15B	109.5
C3—C4—H4	119.3	O4—C15—H15C	109.5
C5—C4—H4	119.3	H15A—C15—H15C	109.5
N1—C5—C4	119.40 (19)	H15B—C15—H15C	109.5
N1—C5—C6	122.59 (19)	C16—N2—C17	122.02 (18)
C4—C5—C6	118.0 (2)	C16—N2—C18	121.30 (18)
C7—C6—C5	120.2 (2)	C17—N2—C18	116.68 (18)
C7—C6—H6	119.9	O5—C16—N2	124.5 (2)
C5—C6—H6	119.9	O5—C16—H16	117.7
C6—C7—C2	121.4 (2)	N2—C16—H16	117.7
C6—C7—H7	119.3	N2—C17—H17A	109.5

C2—C7—H7	119.3	N2—C17—H17B	109.5
N1—C8—C9	114.65 (17)	H17A—C17—H17B	109.5
N1—C8—H8A	108.6	N2—C17—H17C	109.5
C9—C8—H8A	108.6	H17A—C17—H17C	109.5
N1—C8—H8B	108.6	H17B—C17—H17C	109.5
C9—C8—H8B	108.6	N2—C18—H18A	109.5
H8A—C8—H8B	107.6	N2—C18—H18B	109.5
C14—C9—C10	119.03 (19)	H18A—C18—H18B	109.5
C14—C9—C8	120.80 (19)	N2—C18—H18C	109.5
C10—C9—C8	120.15 (19)	H18A—C18—H18C	109.5
C11—C10—C9	120.5 (2)	H18B—C18—H18C	109.5
C11—C10—H10	119.8	H6A—O6—H6B	103 (2)

O1—C1—C2—C7	174.4 (2)	C14—C9—C10—C11	0.1 (3)
O2—C1—C2—C7	−5.1 (3)	C8—C9—C10—C11	−178.52 (19)
O1—C1—C2—C3	−5.8 (3)	C9—C10—C11—C12	0.4 (3)
O2—C1—C2—C3	174.68 (19)	C10—C11—C12—C13	−0.5 (3)
C7—C2—C3—C4	0.1 (3)	C15—O4—C13—C12	4.2 (3)
C1—C2—C3—C4	−179.70 (19)	C15—O4—C13—C14	−175.82 (18)
C2—C3—C4—C5	0.7 (3)	C11—C12—C13—O4	−179.86 (19)
C8—N1—C5—C4	168.25 (18)	C11—C12—C13—C14	0.1 (3)
C8—N1—C5—C6	−14.0 (3)	C10—C9—C14—O3	178.43 (18)
C3—C4—C5—N1	176.67 (19)	C8—C9—C14—O3	−3.0 (3)
C3—C4—C5—C6	−1.2 (3)	C10—C9—C14—C13	−0.4 (3)
N1—C5—C6—C7	−176.78 (19)	C8—C9—C14—C13	178.20 (19)
C4—C5—C6—C7	1.0 (3)	O4—C13—C14—O3	1.5 (3)
C5—C6—C7—C2	−0.3 (3)	C12—C13—C14—O3	−178.52 (19)
C3—C2—C7—C6	−0.2 (3)	O4—C13—C14—C9	−179.71 (18)
C1—C2—C7—C6	179.53 (19)	C12—C13—C14—C9	0.3 (3)
C5—N1—C8—C9	−66.3 (3)	C17—N2—C16—O5	−179.74 (19)
N1—C8—C9—C14	135.2 (2)	C18—N2—C16—O5	0.6 (3)
N1—C8—C9—C10	−46.3 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15*C*···O1^{i}	0.96	2.50	3.329 (3)	145
C15—H15*C*···O2^{ii}	0.96	2.55	3.094 (3)	116
N1—H1···O6^{iii}	0.89 (2)	2.05 (2)	2.936 (2)	175 (2)
O2—H2···O5^{iv}	0.90 (3)	1.70 (3)	2.591 (2)	171 (3)
O3—H3···O6^{v}	0.88 (3)	1.90 (3)	2.739 (2)	158 (3)
O6—H6*A*···O1^{vi}	0.85 (3)	1.94 (3)	2.776 (2)	172 (3)
O6—H6*B*···O5	0.88 (3)	1.91 (3)	2.785 (2)	178 (3)

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