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Crystal structure of zwitterionic 4-(ammonio-methyl)benzoate: a simple molecule giving rise to a complex supramolecular structure

Ana María Atria,^{a*} María Teresa Garland^b and Ricardo Baggio^c

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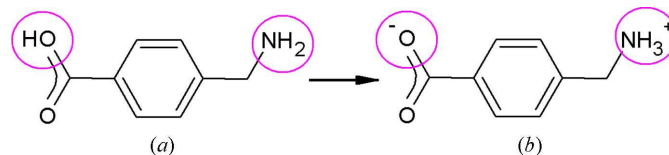
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^aFacultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile, ^bDepartamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago de Chile, Chile, and ^cDepartamento de Física, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina. *Correspondence e-mail: aatria@ciq.uchile.cl

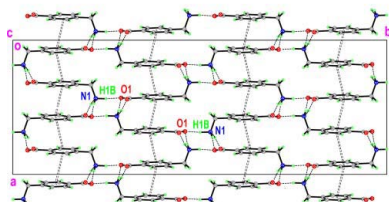
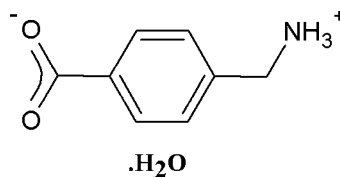
The asymmetric unit of the title compound, C₈H₉NO₂·H₂O consists of an isolated 4-(ammoniomethyl)benzoate zwitterion derived from 4-aminomethylbenzoic acid through the migration of the acidic proton, together with a water molecule of crystallization that is disordered over three sites with occupancy ratios (0.50:0.35:0.15). In the crystal structure, N—H...O hydrogen bonds together with π – π stacking of the benzene rings [centroid–centroid distance = 3.8602 (18) Å] result in a strongly linked, compact three-dimensional structure.

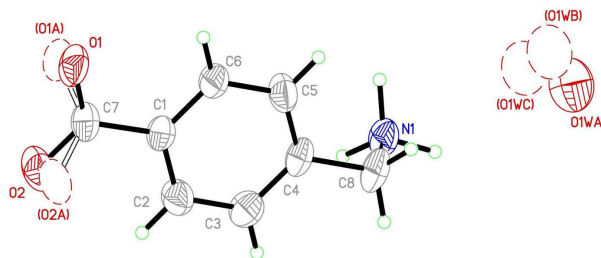
1. Chemical context

As part of a long-range project to find new transition-metal complexes of simple ligands such as carboxylates and amines, we have screened a number of derivatives of benzoic acid, in particular those that a search of the Cambridge Structural Database (CSD, Version 5.35, updated to May 2014; Groom & Allen, 2014) reveals to have formed few coordination complexes whose structures have been reported. The title compound was the unexpected product of an attempt to form a Co^{II} complex with 4-aminomethylbenzoic acid [HAMBA, (a) in scheme below], which has no entries in the CSD, and diaminopurine (DAP).



No coordination complex resulted, but the reaction provided, as an unexpected bonus, a crystalline phase of the monohydrate of the zwitterion of HAMBA (see scheme below), in which the acidic proton has migrated to the amino group resulting in COO[−] and CH₂NH₃⁺ substituents on the aromatic ring and forming 4-(ammoniomethyl)benzoate [(b) in scheme above]. In contrast to the utmost simplicity of its molecular structure, the zwitterion displays an extremely complex hydrogen-bonding scheme and concomitant supramolecular structure as reported herein.




Figure 1

The asymmetric unit of (I). The minor disorder component of the carboxylate group and those of the solvate water molecule are drawn with broken lines.

2. Structural commentary

Fig. 1 shows the asymmetric unit of the title compound, (I). The C–C₆–C backbone is essentially planar [maximum deviation of 0.005 (3) Å for C8], and subtends dihedral angles of 6.8 (2) and 83.9 (2)° with the O₂C–C (major disorder component) and C–CN planes, respectively. Bond lengths and angles are normal, with the C–O bond lengths of the carboxylate group close to equal, indicating extensive electron delocalization over the unit [C7–O1: 1.266 (4), C7–O2: 1.262 (4) Å].

3. Supramolecular features

As indicated previously, the most interesting features in the structure are those derived from the intermolecular interactions, presented in Table 1 (hydrogen bonds) and Table 2 (π – π contacts). Each ammonium group is bound through N–H···O hydrogen bonds to three different molecules of (I), with the carboxylate oxygen atoms as acceptors (Fig. 2*a*). In addition, the benzene rings stack almost parallel to each other in slanted columns (Fig. 2*b*). N1–H1A···O2 and N1–H1C···O1 hydrogen bonds link four molecules together, generating $R_4^4(24)$ ring motifs, Fig. 3*a*, while a second synthon with an $R_4^3(10)$ graph set motif is generated through contacts

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1A···O2 ⁱ	1.07 (3)	1.75 (3)	2.804 (4)	170 (3)
N1–H1B···O1 ⁱⁱ	1.07 (3)	1.73 (4)	2.768 (3)	162 (4)
N1–H1C···O1 ⁱⁱⁱ	1.07 (3)	1.87 (3)	2.901 (6)	161 (3)

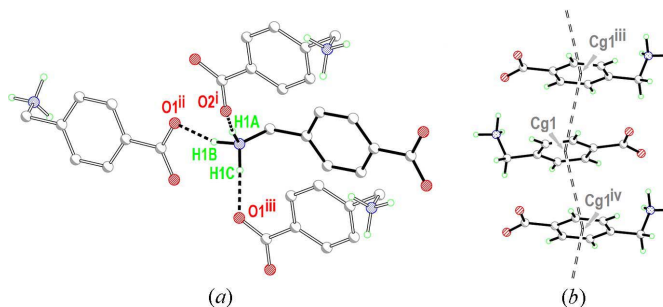
Symmetry codes: (i) $x - \frac{1}{4}, -y + \frac{7}{4}, z - \frac{3}{4}$; (ii) $-x + \frac{5}{4}, y - \frac{1}{4}, z - \frac{1}{4}$; (iii) $x - \frac{1}{4}, -y + \frac{7}{4}, z + \frac{1}{4}$.

Table 2
 π – π contacts (Å, °).

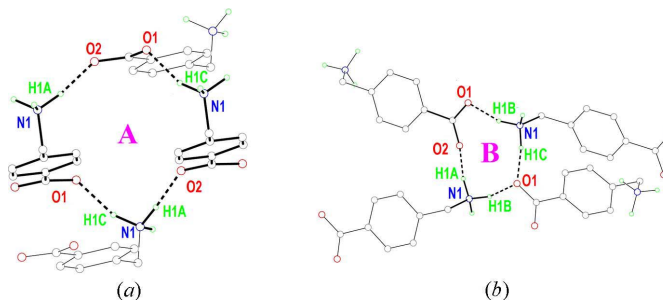
Cg1 is the centroid of atoms C1–C6. ccd is the centroid–centroid distance, da is the dihedral angle between rings and ipd is the interplanar distance, or (mean) distance from one plane to the neighbouring centroid. For details, see Janiak (2000).

Group 1···Group 2	ccd	da	ipd
Cg1···Cg1 ⁱⁱⁱ	3.8602 (18)	0.7 (2)	3.665 (5)

Symmetry code: (iii) $x - \frac{1}{4}, -y + 7/4, z + 1/4$.


Figure 2

(*a*) Hydrogen-bonding and (*b*) π – π interactions in (I). Symmetry codes: (i) $x - \frac{1}{4}, -y + \frac{7}{4}, z - \frac{3}{4}$; (ii) $-x + \frac{5}{4}, y - \frac{1}{4}, z - \frac{1}{4}$; (iii) $x - \frac{1}{4}, -y + \frac{7}{4}, z + \frac{1}{4}$; (iv) $x + \frac{1}{4}, -y + \frac{7}{4}, z - \frac{1}{4}$.

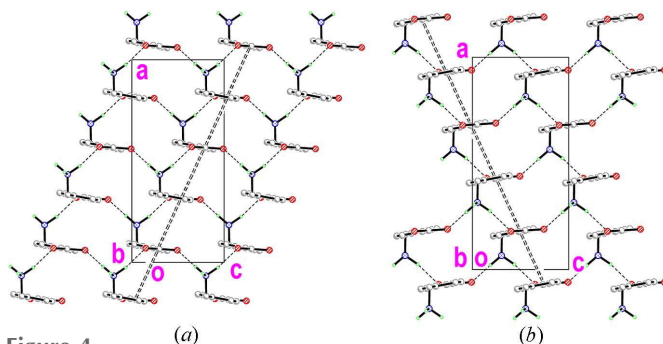

Figure 3

(*a*) $R_4^4(24)$ loops, A, formed by molecules of (I) through N1–H1A···O2 and N1–H1C···O1 hydrogen bonds. (*b*) $R_4^3(10)$ loops, B, formed by molecules of (I) through N–H···O contacts involving all three H atoms of the NH₃⁺ substituent.

involving all three hydrogens of the ammonium cation, Fig. 3*b* (for graph-set notation see, for example, Bernstein *et al.*, 1995).

The $R_4^4(24)$ synthons combine with the π – π stacking interactions to generate layers of molecules in the *ac* plane. The π – π contacts are inclined parallel to either the (101) plane for one set of contacts (Fig. 4*a*) or the ($\bar{1}01$) plane for the other (Fig. 4*b*).

Fig. 5 shows a view along the *c* axis, and reveals the ‘corrugated’ shape of these sheets, consisting of zigzag chains of molecules linked in a head-to-tail fashion and stacked roughly along the *a*-axis direction. Adjacent sheets are interconnected along *b* in an obverse fashion by N1–H1B···O1 hydrogen bonds.


Figure 4

Sheets of molecules of (I) in the *ac* plane linked by N–H···O hydrogen bonds (single dashed lines) and π – π interactions (double dashed lines).

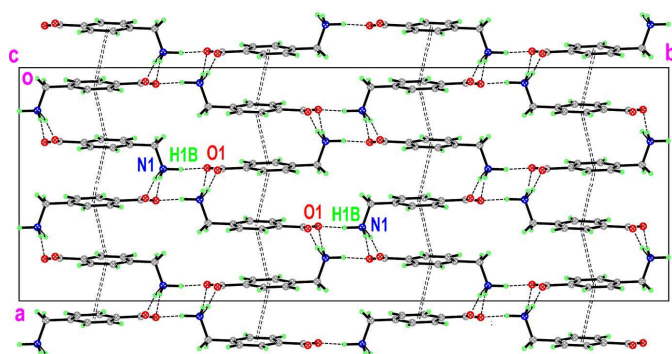


Figure 5
Chains of molecules of (I) linked by N—H...O hydrogen bonds to form a three-dimensional network.

Finally, Fig. 6 presents a view approximately along the *ac* diagonal displaying the two hydrogen-bonding synthons, A and B, together with the π – π interactions and demonstrates how they combine to generate the three-dimensional network.

4. Database survey

Neither 4-(ammoniomethyl)benzoate nor its zwitterionic form described here appear in the CSD (Version 5.35, updated to May 2014). The most closely related structures are those of a zwitterionic form of 4-ammoniomethylcyclohexane-1-carboxylic acid (IIa) (Shahzadi *et al.*, 2007; CSD refcode AMMCHC11) and its hemihydrated analogue (IIb) (Yamazaki *et al.*, 1981; CSD refcode AMCHCA), in which the phenyl ring is replaced by cyclohexane. This introduces some obvious differences with (I), for π – π contacts are clearly precluded and there are different relative orientations of the hydrogen-bonding donors and acceptors. In spite of this, the hydrogen-bonding schemes do show some striking similarities, leading to

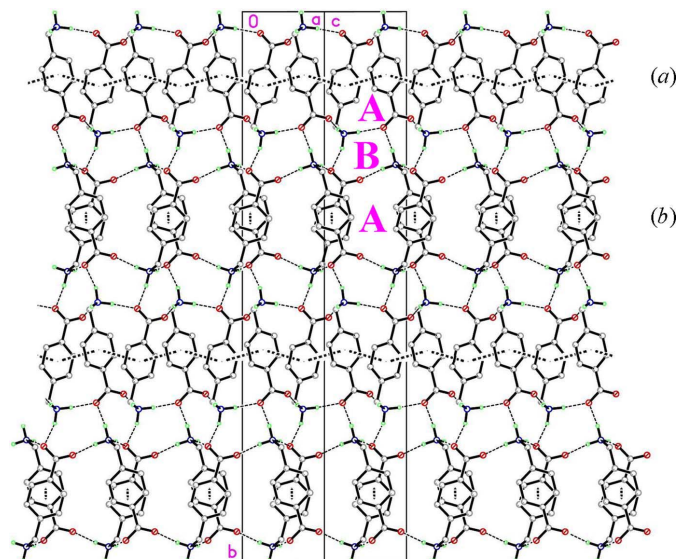


Figure 6
Overall packing for (I) showing how the A and B ring motifs combine with π – π stacking interactions to generate a three-dimensional network.

Table 3
Experimental details.

Crystal data	
Chemical formula	C ₈ H ₉ NO ₂ ·H ₂ O
<i>M_r</i>	169.18
Crystal system, space group	Orthorhombic, <i>Fdd2</i>
Temperature (K)	297
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.743 (3), 38.302 (7), 6.2686 (11)
<i>V</i> (Å ³)	3299.7 (11)
<i>Z</i>	16
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.11
Crystal size (mm)	0.48 × 0.30 × 0.22
Data collection	
Diffractometer	Bruker <i>SMART</i> CCD area detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2002)
<i>T_{min}</i> , <i>T_{max}</i>	0.94, 0.98
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	6720, 1827, 1555
<i>R_{int}</i>	0.021
(sin θ/λ) _{max} (Å ⁻¹)	0.659
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.046, 0.137, 1.04
No. of reflections	1827
No. of parameters	134
No. of restraints	13
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.21, -0.18
Absolute structure	Flack <i>x</i> determined using 616 quotients [(<i>I</i> ⁺) – (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons & Flack, 2004)
Absolute structure parameter	-1.2 (4)

Computer programs: *SMART* (Bruker, 2001) and *SAINT* (Bruker, 2002), *SHELXS97*, *SHELXL2014* and *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

similar (though differently connected) two-dimensional substructures. In particular, the same *R*₄⁴(24) and *R*₃³(10) synthons are present in both cases as in (I), and play predominant roles in the crystal packing. This is despite the presence of the water solvate in (IIb), which is not involved in classical hydrogen bonding to the zwitterion.

5. Synthesis and crystallization

To an aqueous solution of HAMBAs (1 mmol, 0.15116g) were added an aqueous solution of Co(Ac)₂·4H₂O (2 mmol, 0.49816g) and an ethanolic solution of DAP (1 mmol, 0.15009 g). The resulting mixture was heated at reflux for 4 h and left to cool down and evaporate at room temperature. After a few days, crystals suitable for X-ray diffraction of the (uncomplexed) zwitterion (I) appeared. These were used as grown.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

There are two disorder features in this structure. The oxygen atoms of the carboxylate group were disordered over

two positions that were refined with similarity restraints with occupancy factors 0.912 (13)/0.088 (13). Disorder involving the water molecule was more pronounced, with the oxygen atoms disordered over three distinct sites. When refined, the occupancies appeared to be strongly correlated with their displacement factors, showing an oscillating behaviour. In the final refinement cycles, occupancies were fixed to the mean values of these oscillation ranges with occupancy ratios 0.50:0.35:0.15.

All the H atoms (except for those of the disordered water molecules) were recognizable in an early difference Fourier map. Hydrogen atoms of the NH₃ group were refined with N–H distances restrained to be equal to within 0.01 Å [final $d(\text{N}–\text{H}) = 1.07 (3) \text{ \AA}$]. All H atoms bound to carbon were refined using a riding model with $d(\text{C}–\text{H}) = 0.93 \text{ \AA}$ and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for aromatic and 0.98 \AA , $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for methylene H atoms. The hydrogen atoms on the disordered water solvate were not identified.

When trying to calculate the Flack parameter of the inverted structure, it was recognised that the space group was one of the few (seven, in fact) where the structure cannot be inverted by simple inversion of the atomic coordinates. In the case of *Fdd2*, the ‘inversion rule’ to be applied is $\text{Inv}(x, y, z) = \frac{1}{4} - x, \frac{1}{4} - y, -z$. After this, the refinement proceeded smoothly without any change in the symmetry operators. Even so, the

resulting Flack Parameters were both disparate and high [$-1.2 (4)$ vs $2.2 (4)$ for the reported/inverted structures, respectively]. Hence, the absolute configuration could not be determined reliably.

Acknowledgements

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Computing details

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE* (Bruker, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

4-(Ammoniomethyl)benzoate

Crystal data

$C_8H_9NO_2 \cdot H_2O$
 $M_r = 169.18$
 Orthorhombic, *Fdd2*
 $a = 13.743$ (3) Å
 $b = 38.302$ (7) Å
 $c = 6.2686$ (11) Å
 $V = 3299.7$ (11) Å³
 $Z = 16$
 $F(000) = 1440$

$D_x = 1.362$ Mg m⁻³
 Mo *K*α radiation, $\lambda = 0.71073$ Å
 Cell parameters from 1680 reflections
 $\theta = 3.1$ – 26.1°
 $\mu = 0.11$ mm⁻¹
 $T = 297$ K
 Block, pale pink
 0.48 × 0.30 × 0.22 mm

Data collection

Bruker SMART CCD area detector
 diffractometer
 CCD rotation images, thin slices scans
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2002)
 $T_{\min} = 0.94$, $T_{\max} = 0.98$
 6720 measured reflections

1827 independent reflections
 1555 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\text{max}} = 27.9^\circ$, $\theta_{\text{min}} = 2.1^\circ$
 $h = -16 \rightarrow 18$
 $k = -48 \rightarrow 47$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.137$
 $S = 1.04$
 1827 reflections
 134 parameters
 13 restraints
 Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0839P)^2 + 1.177P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³
 Absolute structure: Flack x determined using 616 quotients $[(I^-)-(I)]/[(I^+)+(I)]$ (Parsons & Flack, 2004)
 Absolute structure parameter: -1.2 (4)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.6801 (4)	0.96039 (6)	0.9009 (5)	0.0628 (10)	0.912 (13)
O2	0.6899 (4)	0.94439 (9)	1.2429 (5)	0.0759 (12)	0.912 (13)
O1A	0.641 (3)	0.9615 (6)	0.946 (6)	0.0628 (10)	0.088 (13)
O2A	0.736 (3)	0.9413 (8)	1.210 (5)	0.0759 (12)	0.088 (13)
C1	0.67898 (18)	0.89967 (7)	0.9810 (4)	0.0461 (6)	
C2	0.6919 (2)	0.87399 (7)	1.1326 (5)	0.0579 (7)	
H2	0.7033	0.8802	1.2738	0.069*	
C3	0.6881 (2)	0.83912 (7)	1.0764 (6)	0.0620 (8)	
H3	0.6974	0.8221	1.1800	0.074*	
C4	0.6705 (2)	0.82944 (6)	0.8686 (5)	0.0507 (7)	
C5	0.6570 (2)	0.85503 (7)	0.7172 (5)	0.0584 (7)	
H5	0.6449	0.8488	0.5764	0.070*	
C6	0.6612 (2)	0.89013 (7)	0.7727 (5)	0.0538 (7)	
H6	0.6521	0.9072	0.6691	0.065*	
C7	0.68372 (16)	0.93753 (7)	1.0465 (5)	0.0546 (7)	
C8	0.6665 (2)	0.79104 (7)	0.8069 (7)	0.0653 (9)	
H8A	0.6956	0.7880	0.6672	0.078*	
H8B	0.7040	0.7775	0.9085	0.078*	
N1	0.5655 (2)	0.77823 (6)	0.8030 (5)	0.0576 (6)	
H1A	0.524 (2)	0.7907 (12)	0.682 (7)	0.131 (18)*	
H1B	0.5636 (19)	0.7506 (9)	0.776 (8)	0.119 (16)*	
H1C	0.529 (2)	0.7830 (10)	0.951 (6)	0.16 (2)*	
O1WA	0.6665 (7)	0.73276 (19)	0.2872 (17)	0.100 (2)	0.5
O1WB	0.6438 (12)	0.7488 (3)	0.244 (3)	0.100 (2)	0.35
O1WC	0.647 (2)	0.7552 (7)	0.323 (5)	0.100 (2)	0.15

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.088 (3)	0.0314 (9)	0.0690 (15)	-0.0019 (11)	0.0092 (15)	-0.0041 (10)
O2	0.107 (3)	0.0553 (14)	0.0655 (15)	-0.0144 (17)	-0.0026 (16)	-0.0195 (12)
O1A	0.088 (3)	0.0314 (9)	0.0690 (15)	-0.0019 (11)	0.0092 (15)	-0.0041 (10)
O2A	0.107 (3)	0.0553 (14)	0.0655 (15)	-0.0144 (17)	-0.0026 (16)	-0.0195 (12)
C1	0.0512 (14)	0.0333 (12)	0.0537 (15)	-0.0039 (9)	0.0023 (11)	-0.0037 (10)
C2	0.0784 (19)	0.0426 (14)	0.0526 (16)	-0.0071 (13)	-0.0054 (16)	-0.0023 (12)
C3	0.0843 (19)	0.0379 (13)	0.0638 (19)	-0.0031 (14)	-0.0036 (14)	0.0076 (13)
C4	0.0527 (13)	0.0296 (11)	0.0697 (17)	-0.0005 (10)	0.0082 (12)	-0.0056 (12)
C5	0.083 (2)	0.0411 (14)	0.0511 (15)	-0.0050 (13)	0.0033 (14)	-0.0103 (12)
C6	0.0757 (18)	0.0318 (12)	0.0538 (16)	-0.0001 (11)	-0.0040 (13)	-0.0002 (11)

C7	0.0639 (16)	0.0372 (13)	0.0626 (18)	-0.0062 (11)	0.0025 (13)	-0.0113 (13)
C8	0.0710 (18)	0.0320 (12)	0.093 (2)	0.0035 (12)	0.0091 (17)	-0.0108 (14)
N1	0.0777 (15)	0.0303 (10)	0.0648 (15)	-0.0039 (10)	-0.0015 (12)	-0.0033 (11)
O1WA	0.102 (4)	0.086 (5)	0.110 (6)	-0.028 (5)	0.013 (4)	-0.009 (5)
O1WB	0.102 (4)	0.086 (5)	0.110 (6)	-0.028 (5)	0.013 (4)	-0.009 (5)
O1WC	0.102 (4)	0.086 (5)	0.110 (6)	-0.028 (5)	0.013 (4)	-0.009 (5)

Geometric parameters (\AA , $^\circ$)

O1—C7	1.266 (4)	C4—C5	1.377 (4)
O2—C7	1.262 (4)	C4—C8	1.521 (4)
O1A—C7	1.259 (13)	C5—C6	1.390 (4)
O2A—C7	1.256 (13)	C5—H5	0.9300
C1—C6	1.378 (4)	C6—H6	0.9300
C1—C2	1.379 (4)	C8—N1	1.472 (4)
C1—C7	1.509 (4)	C8—H8A	0.9700
C2—C3	1.382 (4)	C8—H8B	0.9700
C2—H2	0.9300	N1—H1A	1.07 (3)
C3—C4	1.376 (5)	N1—H1B	1.07 (3)
C3—H3	0.9300	N1—H1C	1.07 (3)
C6—C1—C2	119.1 (2)	O2A—C7—O1A	126.0 (16)
C6—C1—C7	121.4 (2)	O2—C7—O1	124.2 (3)
C2—C1—C7	119.5 (3)	O2A—C7—C1	111.0 (15)
C1—C2—C3	120.6 (3)	O1A—C7—C1	123.0 (14)
C1—C2—H2	119.7	O2—C7—C1	118.0 (3)
C3—C2—H2	119.7	O1—C7—C1	117.8 (3)
C4—C3—C2	120.6 (3)	N1—C8—C4	111.1 (2)
C4—C3—H3	119.7	N1—C8—H8A	109.4
C2—C3—H3	119.7	C4—C8—H8A	109.4
C3—C4—C5	119.0 (2)	N1—C8—H8B	109.4
C3—C4—C8	120.5 (3)	C4—C8—H8B	109.4
C5—C4—C8	120.5 (3)	H8A—C8—H8B	108.0
C4—C5—C6	120.7 (3)	C8—N1—H1A	111.9 (15)
C4—C5—H5	119.6	C8—N1—H1B	110.8 (15)
C6—C5—H5	119.6	H1A—N1—H1B	109 (4)
C1—C6—C5	120.1 (3)	C8—N1—H1C	111.6 (16)
C1—C6—H6	120.0	H1A—N1—H1C	107 (2)
C5—C6—H6	120.0	H1B—N1—H1C	107 (2)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots O2 ⁱ	1.07 (3)	1.75 (3)	2.804 (4)	170 (3)
N1—H1B \cdots O1 ⁱⁱ	1.07 (3)	1.73 (4)	2.768 (3)	162 (4)
N1—H1C \cdots O1 ⁱⁱⁱ	1.07 (3)	1.87 (3)	2.901 (6)	161 (3)

Symmetry codes: (i) $x-1/4, -y+7/4, z-3/4$; (ii) $-x+5/4, y-1/4, z-1/4$; (iii) $x-1/4, -y+7/4, z+1/4$.