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1-(2-Carboxyethyl)-3-(carboxylatomethyl)-2-ethylbenzimidazol-1-ium monohydrate

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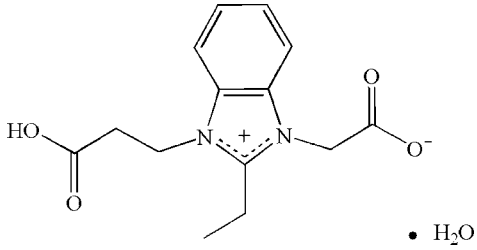
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.042; wR factor = 0.102; data-to-parameter ratio = 12.8.

In the title compound, $C_{14}H_{16}N_2O_4\cdot H_2O$, three substituent groups are located on the same side of the benzimidazole ring plane. In the crystal, O—H···O hydrogen bonds and π–π stacking between parallel imidazole rings [centroid–centroid distance = 3.858 (4) Å] link the molecules into a three-dimensional supramolecular structure.

Related literature

For general background to supramolecular coordination complexes, see: Chakrabarty *et al.* (2011); Cook *et al.* (2012); Wang *et al.* (2009, 2010). For related structures, see: Wei *et al.* (2012); Chen & Huang (2006); Wu *et al.* (2012).



Experimental

Crystal data

$C_{14}H_{16}N_2O_4\cdot H_2O$
M_r = 294.30
Triclinic, $P\overline{1}$
a = 8.286 (7) Å
b = 9.041 (8) Å
c = 10.629 (9) Å
α = 69.905 (7)°
β = 69.096 (7)°
γ = 79.082 (8)°
V = 696.6 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 296 K
0.26 × 0.23 × 0.22 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.973, T_{max} = 0.977
5039 measured reflections
2551 independent reflections
1888 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.102
S = 1.07
2551 reflections
200 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O1^{i}	0.82	1.69	2.474 (2)	160
O5—H1W···O4^{ii}	0.96 (3)	1.89 (3)	2.841 (3)	168 (2)
O5—H2W···O2^{i}	0.90 (3)	1.96 (3)	2.851 (3)	176 (3)

Symmetry codes: (i) $-x, -y+2, -z+1$; (ii) $-x+1, -y+1, -z+1$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5687).

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supplementary materials

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1-(2-Carboxyethyl)-3-(carboxylatomethyl)-2-ethylbenzimidazol-1-ium monohydrate

Hong Yao, Yong-Qiang Xie, Xiao-Qiang Yao, Yun-Xia Yang and You-Ming Zhang

Comment

Benzimidazole and its derivatives are strongly coordinating agents and form stable complexes with various metals, which find various application in supramolecular coordination complexes, catalytic systems and soft materials (Chakrabarty *et al.*, 2011; Cook *et al.*, 2012; Wang *et al.*, 2009; Wei *et al.*, 2012). Meanwhile, the coordination chemistry of dicarboxylates has gained great attention for a variety of reasons, such as good conformation freedom, various coordination modes and so on (Wang *et al.*, 2010; Wu *et al.*, 2012). Herein we report the crystal structure of 1-(2-acetoxy)-3-(3-propionyloxy)-2-ethyl-3*H*-benzimidazolium salt and the molecular structure is shown in Fig 1. In the imidazolium ring, the bond lenghs range from 1.338 (2) to 1.397 (2) Å, in good agreement with the presence of conjugated double bonds and indicating a zwitterionic structure (Chen & Huang, 2006). In the U-shaped molecule, the two carboxyl group run almost perpendicular to the benzimidazolium plane in the same orientation. The N1—C10—C11 and N2—C12—C13 angles are 112.57 (14) and 113.06 (15)°, respectively. A dimer is formed by benzimidazolium salt connected to neighboring molecule through O3—H3A ···O1 hydrogen bonds (Fig 2). In addition, the dimer makes full use of two water molecules as bridging molecules to form various O—H···O hydrogen bonds to generate the wide hydrogen-bond ribbon (Fig 3). Obviously, water molecules, as a kind of linking unit, play an important role in constructing this structure. The distance between the donor and acceptor of the hydrogen bond is in the range of 2.474 (2)–2.851 (3) Å. π-π stacking is observed between parallel imidazole rings of adjacent molecules [1-x, 2-y, -z], the centroids distance being 3.858 (4) Å.

Experimental

1-(2-Acetoxy)-3-(3-propionyloxy)-2-ethyl-3*H*-benzimidazolium salt (0.2 mmol, 0.0552 g) was dissolved in distilled water. Colorless block crystals separated after several weeks.

Refinement

Water H atoms were located in a difference Fourier map and refined isotropically. Other H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 and O—H = 0.82 Å, U_{iso}(H) = 1.5U_{eq}(C,O).

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

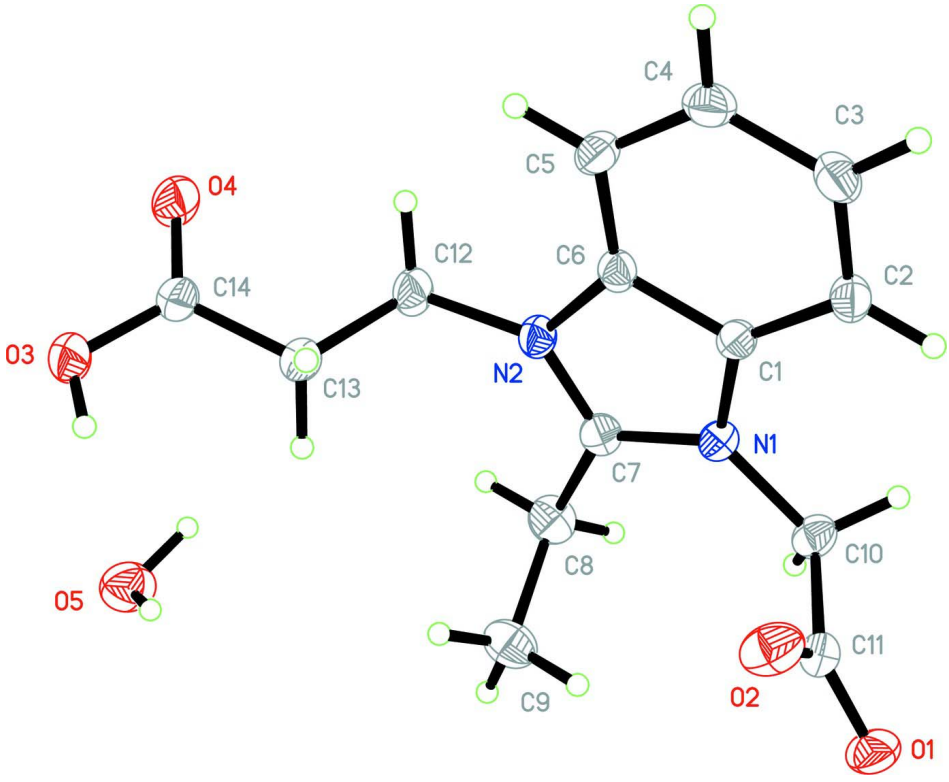

Figure 1

The molecular structure of the title compound with atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

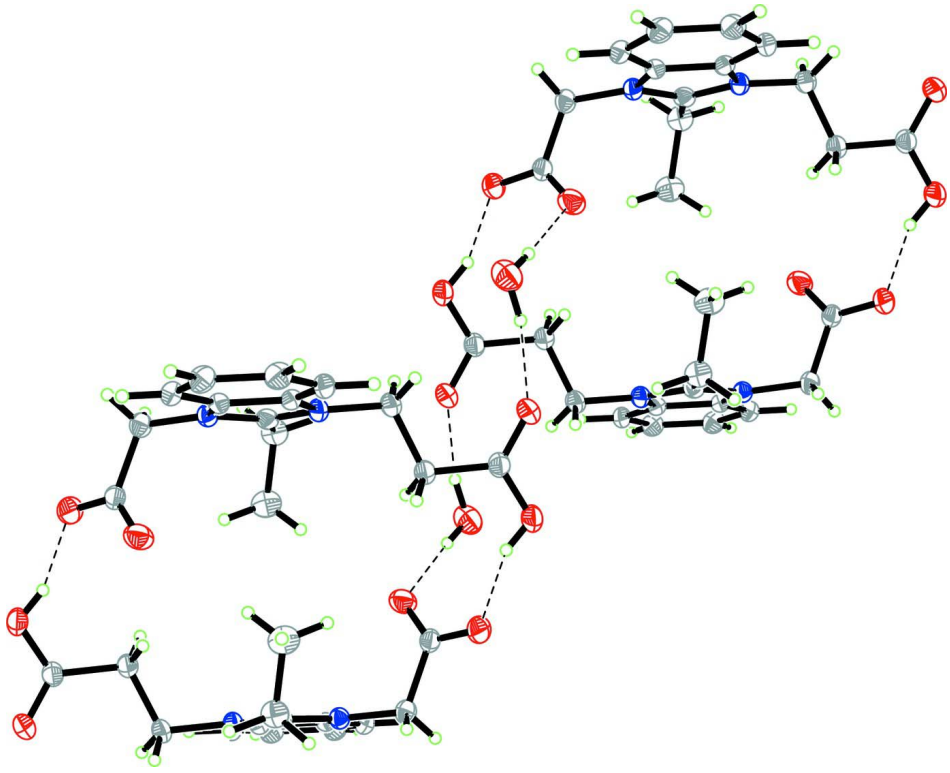

Figure 2

Hydrogen-bonded linking pattern of the wide hydrogen-bonded ribbon in the crystal structure of the title compound.

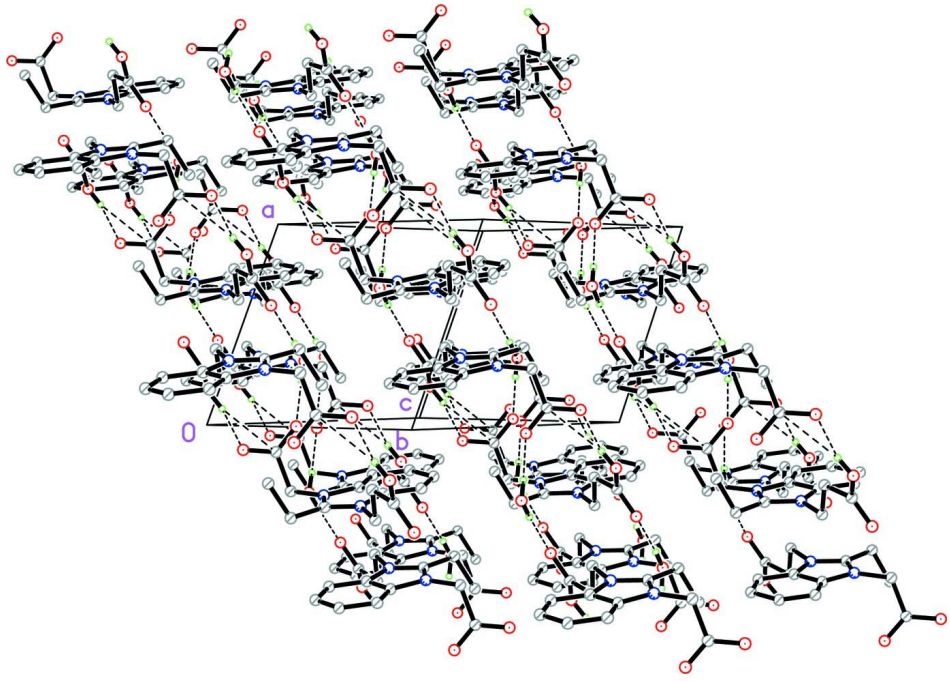

Figure 3

Packing diagram of the title compound. All hydrogen atoms bonded to carbon are omitted for clarity.

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Crystal data

$C_{14}H_{16}N_2O_4 \cdot H_2O$
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Hall symbol: -P 1
$a = 8.286$ (7) Å
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$c = 10.629$ (9) Å
$\alpha = 69.905$ (7)°
$\beta = 69.096$ (7)°
$\gamma = 79.082$ (8)°
$V = 696.6$ (10) Å^3
$Z = 2$
$F(000) = 312$
$D_x = 1.403$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1681 reflections
$\theta = 2.4$–$26.1°$
$\mu = 0.11$ mm^{-1}
$T = 296$ K
Block, colourless
0.26 × 0.23 × 0.22 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.973$, $T_{max} = 0.977$
5039 measured reflections
2551 independent reflections
1888 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.5°$, $\theta_{min} = 2.4°$
$h = -10 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.102$
$S = 1.07$
2551 reflections
200 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.0692P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

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.

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2641 (2)	1.08245 (19)	0.06635 (18)	0.0295 (4)
C2	0.2190 (2)	1.1649 (2)	−0.05422 (18)	0.0358 (4)
H2	0.2043	1.2747	−0.0837	0.043*

C3	0.1973 (2)	1.0757 (2)	−0.12773 (19)	0.0420 (5)
H3	0.1676	1.1265	−0.2096	0.050*
C4	0.2185 (3)	0.9111 (2)	−0.0833 (2)	0.0423 (5)
H4	0.2019	0.8555	−0.1363	0.051*
C5	0.2629 (2)	0.8285 (2)	0.03621 (19)	0.0388 (5)
H5	0.2767	0.7188	0.0657	0.047*
C6	0.2861 (2)	0.91826 (19)	0.11035 (17)	0.0309 (4)
C7	0.3413 (2)	1.0071 (2)	0.26096 (19)	0.0333 (4)
C8	0.3829 (3)	1.0131 (2)	0.3834 (2)	0.0455 (5)
H8A	0.4589	1.0970	0.3522	0.055*
H8B	0.4449	0.9142	0.4195	0.055*
C9	0.2221 (3)	1.0414 (3)	0.5024 (2)	0.0526 (6)
H9A	0.1572	1.1366	0.4663	0.079*
H9B	0.2565	1.0516	0.5760	0.079*
H9C	0.1513	0.9539	0.5396	0.079*
C10	0.2867 (2)	1.2987 (2)	0.1588 (2)	0.0375 (5)
H10A	0.3267	1.3640	0.0613	0.045*
H10B	0.3618	1.3096	0.2067	0.045*
C11	0.1029 (3)	1.3575 (2)	0.22808 (19)	0.0371 (4)
C12	0.3833 (2)	0.7124 (2)	0.30663 (19)	0.0417 (5)
H12A	0.4830	0.7123	0.3342	0.050*
H12B	0.4172	0.6495	0.2422	0.050*
C13	0.2397 (2)	0.63694 (19)	0.43592 (19)	0.0370 (4)
H13A	0.2173	0.6898	0.5066	0.044*
H13B	0.1347	0.6500	0.4113	0.044*
C14	0.2846 (3)	0.4640 (2)	0.4969 (2)	0.0388 (5)
N1	0.29992 (18)	1.13350 (15)	0.16246 (15)	0.0312 (4)
N2	0.33392 (18)	0.87598 (16)	0.23231 (15)	0.0334 (4)
O1	0.09505 (19)	1.48021 (15)	0.26178 (15)	0.0534 (4)
O2	−0.01868 (18)	1.28600 (16)	0.24520 (16)	0.0548 (4)
O3	0.1787 (2)	0.38995 (15)	0.61738 (15)	0.0562 (4)
H3A	0.0996	0.4523	0.6453	0.084*
O4	0.41378 (18)	0.39251 (15)	0.43815 (15)	0.0523 (4)
O5	0.3224 (3)	0.5657 (2)	0.8276 (2)	0.0651 (5)
H1W	0.405 (4)	0.594 (3)	0.734 (3)	0.097 (10)*
H2W	0.230 (4)	0.614 (4)	0.800 (3)	0.114 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0273 (10)	0.0276 (9)	0.0312 (9)	−0.0028 (7)	−0.0062 (7)	−0.0088 (7)
C2	0.0375 (11)	0.0312 (9)	0.0334 (10)	−0.0035 (8)	−0.0093 (8)	−0.0047 (8)
C3	0.0484 (13)	0.0456 (11)	0.0298 (10)	−0.0060 (9)	−0.0126 (9)	−0.0072 (8)
C4	0.0490 (13)	0.0449 (11)	0.0365 (11)	−0.0089 (9)	−0.0086 (9)	−0.0187 (9)
C5	0.0426 (11)	0.0280 (9)	0.0412 (11)	−0.0042 (8)	−0.0047 (9)	−0.0129 (8)
C6	0.0280 (10)	0.0293 (9)	0.0294 (9)	−0.0021 (7)	−0.0054 (7)	−0.0055 (7)
C7	0.0268 (10)	0.0361 (10)	0.0349 (10)	0.0004 (7)	−0.0099 (8)	−0.0094 (8)
C8	0.0450 (12)	0.0533 (12)	0.0434 (11)	−0.0027 (9)	−0.0218 (10)	−0.0133 (9)
C9	0.0569 (14)	0.0669 (14)	0.0397 (11)	−0.0077 (11)	−0.0166 (10)	−0.0200 (10)
C10	0.0400 (11)	0.0311 (9)	0.0450 (11)	−0.0064 (8)	−0.0130 (9)	−0.0141 (8)

C11	0.0427 (12)	0.0296 (10)	0.0349 (10)	−0.0028 (9)	−0.0103 (9)	−0.0069 (8)
C12	0.0397 (11)	0.0323 (10)	0.0416 (11)	0.0075 (8)	−0.0123 (9)	−0.0030 (8)
C13	0.0397 (11)	0.0306 (10)	0.0382 (10)	0.0002 (8)	−0.0121 (9)	−0.0090 (8)
C14	0.0432 (12)	0.0324 (10)	0.0389 (11)	0.0001 (9)	−0.0140 (9)	−0.0091 (8)
N1	0.0322 (8)	0.0284 (8)	0.0343 (8)	−0.0022 (6)	−0.0113 (7)	−0.0101 (6)
N2	0.0350 (9)	0.0286 (8)	0.0322 (8)	0.0015 (6)	−0.0116 (7)	−0.0050 (6)
O1	0.0616 (10)	0.0376 (8)	0.0585 (9)	−0.0083 (7)	−0.0041 (7)	−0.0246 (7)
O2	0.0385 (9)	0.0531 (9)	0.0754 (11)	−0.0040 (7)	−0.0103 (7)	−0.0303 (8)
O3	0.0669 (11)	0.0318 (7)	0.0469 (8)	0.0043 (7)	−0.0031 (8)	−0.0036 (6)
O4	0.0472 (9)	0.0376 (8)	0.0580 (9)	0.0093 (7)	−0.0098 (7)	−0.0111 (7)
O5	0.0661 (12)	0.0636 (11)	0.0644 (12)	0.0109 (9)	−0.0241 (11)	−0.0227 (9)

Geometric parameters (Å, º)

C1—C2	1.385 (3)	C9—H9C	0.9600
C1—N1	1.392 (2)	C10—N1	1.464 (2)
C1—C6	1.392 (3)	C10—C11	1.518 (3)
C2—C3	1.372 (3)	C10—H10A	0.9700
C2—H2	0.9300	C10—H10B	0.9700
C3—C4	1.395 (3)	C11—O2	1.225 (2)
C3—H3	0.9300	C11—O1	1.262 (2)
C4—C5	1.373 (3)	C12—N2	1.475 (2)
C4—H4	0.9300	C12—C13	1.505 (3)
C5—C6	1.387 (3)	C12—H12A	0.9700
C5—H5	0.9300	C12—H12B	0.9700
C6—N2	1.397 (2)	C13—C14	1.503 (3)
C7—N2	1.338 (2)	C13—H13A	0.9700
C7—N1	1.344 (2)	C13—H13B	0.9700
C7—C8	1.481 (3)	C14—O4	1.221 (2)
C8—C9	1.527 (3)	C14—O3	1.300 (2)
C8—H8A	0.9700	O3—H3A	0.8200
C8—H8B	0.9700	O5—H1W	0.96 (3)
C9—H9A	0.9600	O5—H2W	0.90 (3)
C9—H9B	0.9600		

C2—C1—N1	131.62 (16)	N1—C10—C11	112.57 (14)
C2—C1—C6	121.81 (16)	N1—C10—H10A	109.1
N1—C1—C6	106.55 (15)	C11—C10—H10A	109.1
C3—C2—C1	116.25 (17)	N1—C10—H10B	109.1
C3—C2—H2	121.9	C11—C10—H10B	109.1
C1—C2—H2	121.9	H10A—C10—H10B	107.8
C2—C3—C4	121.97 (18)	O2—C11—O1	127.11 (18)
C2—C3—H3	119.0	O2—C11—C10	119.49 (17)
C4—C3—H3	119.0	O1—C11—C10	113.39 (17)
C5—C4—C3	122.09 (18)	N2—C12—C13	113.06 (15)
C5—C4—H4	119.0	N2—C12—H12A	109.0
C3—C4—H4	119.0	C13—C12—H12A	109.0
C4—C5—C6	116.14 (17)	N2—C12—H12B	109.0
C4—C5—H5	121.9	C13—C12—H12B	109.0
C6—C5—H5	121.9	H12A—C12—H12B	107.8

C5—C6—C1	121.74 (17)	C14—C13—C12	111.66 (16)
C5—C6—N2	131.85 (16)	C14—C13—H13A	109.3
C1—C6—N2	106.40 (15)	C12—C13—H13A	109.3
N2—C7—N1	108.99 (16)	C14—C13—H13B	109.3
N2—C7—C8	125.90 (16)	C12—C13—H13B	109.3
N1—C7—C8	125.09 (17)	H13A—C13—H13B	107.9
C7—C8—C9	112.83 (17)	O4—C14—O3	119.89 (17)
C7—C8—H8A	109.0	O4—C14—C13	122.94 (17)
C9—C8—H8A	109.0	O3—C14—C13	117.17 (17)
C7—C8—H8B	109.0	C7—N1—C1	109.03 (15)
C9—C8—H8B	109.0	C7—N1—C10	126.07 (16)
H8A—C8—H8B	107.8	C1—N1—C10	124.85 (14)
C8—C9—H9A	109.5	C7—N2—C6	109.03 (14)
C8—C9—H9B	109.5	C7—N2—C12	126.86 (16)
H9A—C9—H9B	109.5	C6—N2—C12	123.88 (15)
C8—C9—H9C	109.5	C14—O3—H3A	109.5
H9A—C9—H9C	109.5	H1W—O5—H2W	95 (2)
H9B—C9—H9C	109.5		

N1—C1—C2—C3	178.24 (17)	C8—C7—N1—C1	−178.25 (16)
C6—C1—C2—C3	0.0 (3)	N2—C7—N1—C10	177.63 (15)
C1—C2—C3—C4	0.3 (3)	C8—C7—N1—C10	−0.7 (3)
C2—C3—C4—C5	−0.3 (3)	C2—C1—N1—C7	−178.66 (18)
C3—C4—C5—C6	−0.2 (3)	C6—C1—N1—C7	−0.20 (18)
C4—C5—C6—C1	0.5 (3)	C2—C1—N1—C10	3.8 (3)
C4—C5—C6—N2	−178.59 (18)	C6—C1—N1—C10	−177.77 (15)
C2—C1—C6—C5	−0.4 (3)	C11—C10—N1—C7	−94.1 (2)
N1—C1—C6—C5	−179.05 (15)	C11—C10—N1—C1	83.0 (2)
C2—C1—C6—N2	178.87 (16)	N1—C7—N2—C6	0.06 (19)
N1—C1—C6—N2	0.23 (17)	C8—C7—N2—C6	178.38 (16)
N2—C7—C8—C9	−100.2 (2)	N1—C7—N2—C12	174.64 (15)
N1—C7—C8—C9	77.8 (2)	C8—C7—N2—C12	−7.0 (3)
N1—C10—C11—O2	−19.1 (2)	C5—C6—N2—C7	178.99 (18)
N1—C10—C11—O1	161.19 (15)	C1—C6—N2—C7	−0.18 (19)
N2—C12—C13—C14	171.70 (16)	C5—C6—N2—C12	4.2 (3)
C12—C13—C14—O4	−7.5 (3)	C1—C6—N2—C12	−174.96 (15)
C12—C13—C14—O3	172.71 (17)	C13—C12—N2—C7	85.2 (2)
N2—C7—N1—C1	0.09 (19)	C13—C12—N2—C6	−101.0 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O1^{i}	0.82	1.69	2.474 (2)	160
O5—H1*W*···O4^{ii}	0.96 (3)	1.89 (3)	2.841 (3)	168 (2)
O5—H2*W*···O2^{i}	0.90 (3)	1.96 (3)	2.851 (3)	176 (3)

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