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Ethane-1,2-diaminium bis(4-carboxy-2-propyl-1*H*-imidazole-5-carboxyate) monohydrate

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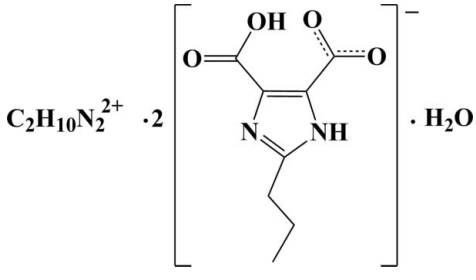
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.060; wR factor = 0.182; data-to-parameter ratio = 11.9.

In the title hydrated molecular salt, $C_2H_{10}N_2^{2+}\cdot 2C_8H_9N_2O_4^-\cdot H_2O$, an intramolecular O—H···O hydrogen bond occurs in the anion, forming an S(7) ring. The $-CO_2$ and $-CO_2H$ groups make dihedral angles of 3.2 (2) and 2.0 (3)°, respectively, with the five-membered ring. In the crystal, N—H···O, N—H···N and O—H···O hydrogen bonds lead to the formation of a three-dimensional supramolecular architecture. The methyl group in the anion is disordered over two sets of sites in a 0.716 (9):0.284 (9) ratio. The ethylenediamine cation is generated by symmetry and the water molecule lies on a twofold axis.

Related literature

For background to studies of supramolecular structures of co-crystals containing organic acids and organic bases resulting from hydrogen bonding, see: Wang & Wei (2005).



Experimental

Crystal data

$C_2H_{10}N_2^{2+}\cdot 2C_8H_9N_2O_4^-\cdot H_2O$
M_r = 474.48
Monoclinic, $C2/c$
a = 15.234 (4) Å
b = 16.859 (4) Å
c = 9.699 (3) Å
β = 112.991 (5)°
V = 2293.1 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 296 K
0.36 × 0.28 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.961, T_{max} = 0.983
5444 measured reflections
2011 independent reflections
1500 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.182
S = 1.05
2011 reflections
169 parameters
34 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O4^{i}	0.86	1.92	2.759 (3)	166
N3—H3A···N1	0.89	2.03	2.921 (3)	176
N3—H3A···O1	0.89	2.54	2.964 (3)	110
N3—H3B···O1^{ii}	0.89	1.94	2.792 (3)	160
N3—H3C···O1W^{iii}	0.89	2.08	2.917 (3)	157
O2—H2···O3	0.82	1.64	2.457 (3)	177
O1W—H1W···O3	0.85 (1)	1.96 (1)	2.795 (2)	169 (4)

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GG2081).

References

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supporting information

Acta Cryst. (2012). E**68**, o2327 [https://doi.org/10.1107/S1600536812029406]

Ethane-1,2-diaminium bis(4-carboxy-2-propyl-1*H*-imidazole-5-carboxyate) monohydrate

Yi-Mei Ying, Tong Zhang, Guang-Rui Yang and Ning Ma

S1. Comment

Currently, many groups are studying the supramolecular structures of co-crystals containing organic acids and organic bases resulting from hydrogen bonding (Wang & Wei, 2005).

The asymmetric unit of the title complex, (I), is composed of two 2-propyl-1*H*-imidazole-4-carboxylic acid-5-carboxyate anions, one diprotonated ethylenediaminium cation and one water molecule in general positions (Fig. 1). The C–O bond distances range from 1.221 (3)to 1.289 (3) Å, in which the C1–O1 [1.223 (3) Å], C4–O4 [1.221 (3) Å] and C4–O3 [1.266 (3) Å] are typical for C=O double bonds, whereas the C1–O2 bond length of 1.289 (3) Å indicates a C–O single bond. The elongation of the C4=O3 double bond is affected by the intra-molecular O2—H2···O3 hydrogen bonding interaction. Thus, the 5-carboxyl group of 2-propyl-1*H*-imidazole-4,5-dicarboxy acid is deprotonated, which must be balanced in charge terms by the presence of half of the diprotonated ethylenediamine. Furthermore, the acidic environment is propitious to the protonation of ethylenediamine.

In the crystal structure, intra-molecular hydrogen bonds are present, with O2–H2 acting as a hydrogen bond donor, and O3 atom as a hydrogen bond acceptor, thereby constructing S(7) rings. In addition, the diprotonated ethylenediaminium cations and 2-propyl-1*H*-imidazole-4-carboxylic acid-5-carboxyate anions together with water molecules are further linked into a three-dimensional supramolecular framework by multiple N—H···O, N—H···N and O—H···O hydrogen bonds (Fig. 2 and Table 1).

S2. Experimental

All reagents were commercially available and of analytical grade. The mixture of $DyCl_3.6H_2O$ (0.189 g, 0.50 mmol), 2-propyl-1*H*-imidazole-4,5-dicarboxylic acid (0.197 g, 1.00 mmol), and ethylenediamine (1 ml) was dissolved in 50 ml H_2O, and the mixture was stirred and heated to reflux at 80°C for two hours. The resulting solution was filtered, the filtrate was adjusted to pH = 7.5 using 4 *M* HCl solution, then was placed inside a programmable electric furnace at 130 °C for five days. After cooling the autoclave to room temperature, colorless block crystals of (I) were obtained.

S3. Refinement

H atoms were treated as riding, with C—H distances of 0.96 Å for methyl, 0.97 Å for methylene, N—H distances in the range of 0.96–0.89 Å and O—H distances of 0.82 Å for hydroxy group and 0.84 Å for water, and were refined as riding with $U_{iso}(H)=1.2U_{eq}(C_{methylene}$, O2 and N) and $U_{iso}(H)=1.5U_{eq}(O1W$ and $(C_{methyl}))$.

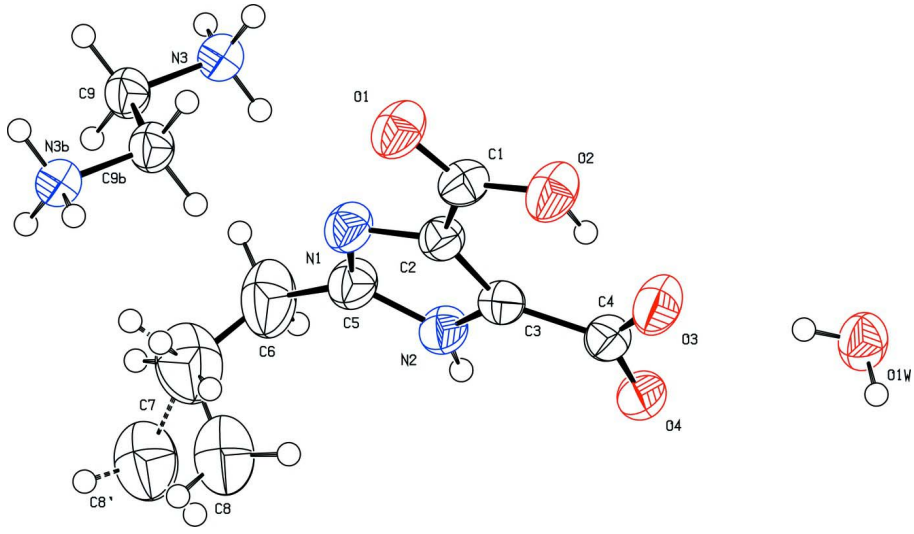

Figure 1

The molecular structure of (I), with displacement ellipsoids for the non-hydrogen atoms drawn at the 50% probability level.

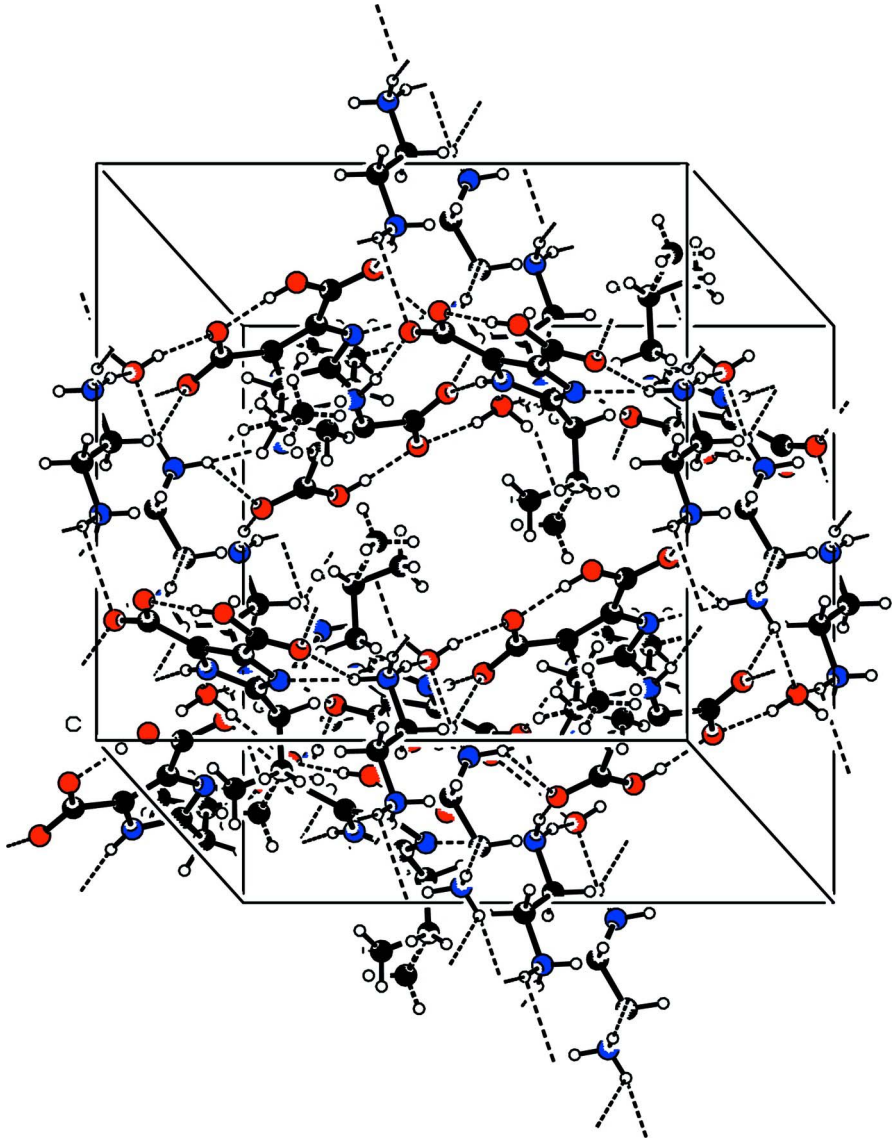

Figure 2

Three-dimensional structure of (I), with H-bonds indicated by dashed lines. Displacement ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

Ethane-1,2-diaminium bis(4-carboxy-2-propyl-1*H*-imidazole-5-carboxyate) monohydrate

Crystal data

$C_2H_{10}N_2^{2+}\cdot 2C_8H_9N_2O_4^-\cdot H_2O$
$M_r = 474.48$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 15.234\ (4)$ Å
$b = 16.859\ (4)$ Å
$c = 9.699\ (3)$ Å
$\beta = 112.991\ (5)°$
$V = 2293.1\ (10)$ Å^3
$Z = 4$
$F(000) = 1008$
$D_x = 1.374$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 356 reflections
$\theta = 2.5–14.8°$
$\mu = 0.11$ mm^{-1}
$T = 296$ K
Block, colorless
0.36 × 0.28 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.961, T_{max} = 0.983
5444 measured reflections
2011 independent reflections
1500 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 25.0°, θ_{min} = 1.9°
h = −18→17
k = −19→20
l = −11→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.182
S = 1.05
2011 reflections
169 parameters
34 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
$w = 1/[\sigma^2(F_o^2) + (0.1098P)^2 + 0.4118P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
N1	0.21377 (15)	0.37000 (13)	0.0929 (2)	0.0456 (6)	
N2	0.35960 (14)	0.32244 (13)	0.1911 (2)	0.0433 (6)	
H2A	0.4125	0.3057	0.2578	0.052*	
N3	0.00885 (15)	0.38982 (11)	0.0087 (2)	0.0402 (5)	
H3A	0.0712	0.3859	0.0313	0.048*	
H3B	−0.0229	0.3808	−0.0887	0.048*	
H3C	−0.0083	0.3542	0.0613	0.048*	
O1	0.10537 (13)	0.39974 (12)	−0.2035 (2)	0.0555 (6)	
O2	0.21678 (14)	0.35742 (13)	−0.2760 (2)	0.0566 (6)	
H2	0.2714	0.3404	−0.2372	0.068*	
O3	0.37886 (14)	0.30257 (13)	−0.1635 (2)	0.0578 (6)	
O4	0.48440 (12)	0.27422 (11)	0.0614 (2)	0.0509 (5)	
O1W	0.5000	0.20888 (16)	−0.2500	0.0544 (7)	
H1W	0.460 (2)	0.2394 (18)	−0.236 (4)	0.082*	
C1	0.18526 (18)	0.37268 (15)	−0.1732 (3)	0.0420 (6)	

C2	0.24741 (17)	0.35651 (13)	−0.0175 (3)	0.0381 (6)	
C3	0.33827 (17)	0.32705 (13)	0.0420 (3)	0.0383 (6)	
C4	0.40669 (18)	0.29940 (14)	−0.0224 (3)	0.0427 (6)	
C5	0.28372 (19)	0.34863 (17)	0.2174 (3)	0.0483 (7)	
C6	0.2826 (3)	0.3534 (2)	0.3692 (4)	0.0794 (11)	
H6A	0.2221	0.3324	0.3638	0.095*	
H6B	0.3321	0.3185	0.4343	0.095*	
C7	0.2958 (4)	0.4296 (3)	0.4395 (5)	0.1099 (14)	
H7A	0.2500	0.4671	0.3743	0.132*	0.716 (9)
H7B	0.2863	0.4261	0.5325	0.132*	0.716 (9)
H7C	0.2345	0.4451	0.4399	0.132*	0.284 (9)
H7D	0.3065	0.4642	0.3676	0.132*	0.284 (9)
C8	0.3826 (5)	0.4534 (3)	0.4659 (8)	0.095 (2)	0.716 (9)
H8A	0.3969	0.4436	0.3794	0.142*	0.716 (9)
H8B	0.4268	0.4248	0.5500	0.142*	0.716 (9)
H8C	0.3879	0.5091	0.4877	0.142*	0.716 (9)
C8′	0.3712 (10)	0.4585 (7)	0.5926 (14)	0.074 (4)	0.284 (9)
H8′A	0.4097	0.4994	0.5756	0.111*	0.284 (9)
H8′B	0.4110	0.4147	0.6435	0.111*	0.284 (9)
H8′C	0.3393	0.4791	0.6529	0.111*	0.284 (9)
C9	−0.0132 (2)	0.46962 (15)	0.0454 (3)	0.0439 (6)	
H9A	0.0219	0.4798	0.1513	0.053*	
H9B	−0.0807	0.4735	0.0245	0.053*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0374 (12)	0.0566 (13)	0.0414 (12)	0.0062 (10)	0.0139 (10)	0.0008 (10)
N2	0.0337 (11)	0.0519 (12)	0.0387 (12)	0.0060 (9)	0.0081 (9)	0.0002 (9)
N3	0.0384 (12)	0.0418 (12)	0.0415 (12)	0.0015 (9)	0.0168 (9)	0.0007 (8)
O1	0.0392 (11)	0.0788 (13)	0.0444 (11)	0.0144 (9)	0.0120 (8)	0.0084 (9)
O2	0.0443 (11)	0.0833 (14)	0.0414 (11)	0.0144 (10)	0.0160 (9)	0.0085 (9)
O3	0.0480 (11)	0.0825 (15)	0.0470 (12)	0.0123 (10)	0.0230 (9)	0.0021 (9)
O4	0.0334 (10)	0.0600 (11)	0.0520 (12)	0.0067 (8)	0.0088 (8)	−0.0088 (8)
O1W	0.0606 (19)	0.0557 (17)	0.0575 (17)	0.000	0.0347 (15)	0.000
C1	0.0373 (14)	0.0487 (14)	0.0387 (14)	−0.0001 (11)	0.0134 (11)	0.0057 (10)
C2	0.0347 (13)	0.0398 (13)	0.0390 (14)	0.0000 (10)	0.0135 (11)	0.0001 (10)
C3	0.0362 (13)	0.0375 (12)	0.0401 (13)	−0.0014 (10)	0.0137 (11)	−0.0004 (10)
C4	0.0388 (15)	0.0417 (13)	0.0482 (16)	−0.0007 (11)	0.0176 (12)	−0.0028 (11)
C5	0.0401 (14)	0.0608 (16)	0.0419 (15)	0.0049 (12)	0.0138 (12)	−0.0007 (12)
C6	0.070 (2)	0.121 (3)	0.0458 (18)	0.025 (2)	0.0207 (16)	−0.0054 (18)
C7	0.118 (3)	0.114 (3)	0.086 (3)	0.023 (3)	0.027 (3)	−0.003 (2)
C8	0.130 (4)	0.069 (3)	0.109 (5)	0.012 (3)	0.073 (4)	−0.005 (3)
C8′	0.108 (9)	0.052 (6)	0.061 (7)	0.002 (6)	0.030 (6)	−0.002 (5)
C9	0.0491 (15)	0.0442 (14)	0.0442 (14)	−0.0007 (11)	0.0245 (12)	−0.0034 (10)

Geometric parameters (Å, º)

N1—C5	1.311 (3)	C6—C7	1.433 (6)
N1—C2	1.375 (3)	C6—H6A	0.9700
N2—C5	1.351 (3)	C6—H6B	0.9700
N2—C3	1.355 (3)	C7—C8	1.309 (7)
N2—H2A	0.8600	C7—C8′	1.558 (13)
N3—C9	1.464 (3)	C7—H7A	0.9700
N3—H3A	0.8900	C7—H7B	0.9700
N3—H3B	0.8900	C7—H7C	0.9699
N3—H3C	0.8900	C7—H7D	0.9698
O1—C1	1.223 (3)	C8—H7D	1.1934
O2—C1	1.289 (3)	C8—H8A	0.9600
O2—H2	0.8200	C8—H8B	0.9600
O3—C4	1.266 (3)	C8—H8C	0.9600
O4—C4	1.221 (3)	C8′—H8′A	0.9600
O1W—H1W	0.849 (10)	C8′—H8′B	0.9600
C1—C2	1.461 (4)	C8′—H8′C	0.9600
C2—C3	1.368 (3)	C9—C9^{i}	1.505 (5)
C3—C4	1.484 (4)	C9—H9A	0.9700
C5—C6	1.481 (4)	C9—H9B	0.9700
C5—N1—C2	104.8 (2)	C6—C7—H7A	110.1
C5—N2—C3	108.4 (2)	C8′—C7—H7A	119.5
C5—N2—H2A	125.8	C8—C7—H7B	110.1
C3—N2—H2A	125.8	C6—C7—H7B	110.1
C9—N3—H3A	109.5	C8′—C7—H7B	57.0
C9—N3—H3B	109.5	H7A—C7—H7B	108.4
H3A—N3—H3B	109.5	C8—C7—H7C	144.9
C9—N3—H3C	109.5	C6—C7—H7C	106.7
H3A—N3—H3C	109.5	C8′—C7—H7C	105.3
H3B—N3—H3C	109.5	H7A—C7—H7C	51.7
C1—O2—H2	109.5	H7B—C7—H7C	61.3
O1—C1—O2	121.7 (2)	C8—C7—H7D	61.0
O1—C1—C2	120.0 (2)	C6—C7—H7D	103.2
O2—C1—C2	118.4 (2)	C8′—C7—H7D	103.3
C3—C2—N1	110.8 (2)	H7A—C7—H7D	54.6
C3—C2—C1	130.1 (2)	H7B—C7—H7D	146.5
N1—C2—C1	119.1 (2)	H7C—C7—H7D	105.9
N2—C3—C2	104.6 (2)	C7—C8—H7D	45.3
N2—C3—C4	121.1 (2)	C7—C8—H8A	109.5
C2—C3—C4	134.3 (2)	H7D—C8—H8A	79.0
O4—C4—O3	124.2 (2)	C7—C8—H8B	109.5
O4—C4—C3	119.2 (2)	H7D—C8—H8B	153.6
O3—C4—C3	116.6 (2)	C7—C8—H8C	109.5
N1—C5—N2	111.3 (2)	H7D—C8—H8C	89.9
N1—C5—C6	125.5 (3)	C7—C8′—H8′A	109.5
N2—C5—C6	123.2 (3)	C7—C8′—H8′B	109.5

C7—C6—C5	117.9 (4)	H8′A—C8′—H8′B	109.5
C7—C6—H6A	107.8	C7—C8′—H8′C	109.5
C5—C6—H6A	107.8	H8′A—C8′—H8′C	109.5
C7—C6—H6B	107.8	H8′B—C8′—H8′C	109.5
C5—C6—H6B	107.8	N3—C9—C9^{i}	110.1 (2)
H6A—C6—H6B	107.2	N3—C9—H9A	109.6
C8—C7—C6	108.1 (5)	C9^{i}—C9—H9A	109.6
C8—C7—C8′	53.5 (6)	N3—C9—H9B	109.6
C6—C7—C8′	130.3 (6)	C9^{i}—C9—H9B	109.6
C8—C7—H7A	110.1	H9A—C9—H9B	108.2

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O4^{ii}	0.86	1.92	2.759 (3)	166
N3—H3*A*···N1	0.89	2.03	2.921 (3)	176
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N3—H3*C*···O1*W*^{iv}	0.89	2.08	2.917 (3)	157
O2—H2···O3	0.82	1.64	2.457 (3)	177
O1*W*—H1*W*···O3	0.85 (1)	1.96 (1)	2.795 (2)	169 (4)

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