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Bis(2,3-diaminopyridinium) phthalate dihydrate

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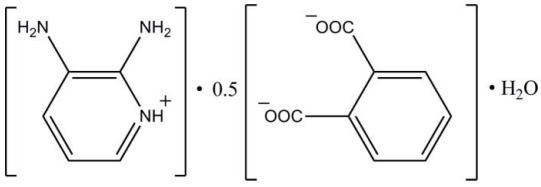
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.043; wR factor = 0.125; data-to-parameter ratio = 16.1.

The complete anion of the title hydrated molecular salt, $2C_5H_8N_3^+\cdot C_8H_4O_4^-\cdot 2H_2O$, is generated by a crystallographic twofold axis. In the crystal, the cations, anions and water molecules are connected by N—H···O, O—H···O and C—H···O hydrogen bonds, forming a three-dimensional network. The crystal structure also features C—H···π interactions.

Related literature

For background to hydrogen-bonding patterns of 2-aminopyridine derivatives, see: Gellert & Hsu (1988); Banerjee & Murugavel (2004). For related structures, see: Hemamalini & Fun (2010*a*,*b*,*c*). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$2C_5H_8N_3^+\cdot C_8H_4O_4^-\cdot 2H_2O$
M_r = 420.43
Monoclinic, $C2/c$
a = 15.795 (5) Å
b = 13.083 (4) Å
c = 11.012 (4) Å
β = 115.194 (5)°
V = 2059.2 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 100 K
0.42 × 0.36 × 0.03 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.958, T_{max} = 0.997
10343 measured reflections
2955 independent reflections
2148 reflections with $I > 2\sigma(I)$
R_{int} = 0.042

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.125
S = 1.04
2955 reflections
184 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

*Cg*1 and *Cg*2 are the centroids of the C6–C8/C6A–C8A and N1/C1–C5 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
N2—H5···O2^{i}	0.90 (2)	2.03 (2)	2.9155 (19)	169.0 (18)
N1—H6···O2^{ii}	0.98 (2)	1.790 (19)	2.7565 (18)	170.3 (19)
N2—H7···O1^{ii}	0.92 (2)	1.99 (2)	2.8976 (19)	168.1 (19)
N3—H9···O1W^{iii}	0.89 (2)	2.09 (2)	2.978 (2)	179 (3)
N3—H10···O2^{i}	0.89 (2)	2.23 (2)	3.078 (2)	158.8 (17)
O1W—H11···O1^{iv}	0.95 (3)	1.86 (3)	2.7878 (18)	165 (3)
O1W—H12···O1^{v}	0.92 (2)	1.99 (2)	2.8641 (18)	158.2 (19)
C3—H2···O1W^{vi}	0.984 (17)	2.516 (18)	3.369 (2)	145.0 (14)
C4—H8···*Cg*1^{iii}	1.01 (2)	2.76 (2)	3.629 (2)	144.3 (15)
C6—H3···*Cg*2^{vii}	0.959 (18)	2.568 (18)	3.497 (2)	163.4 (14)

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6574).

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Bis(2,3-diaminopyridinium) phthalate dihydrate

Madhukar Hemamalini, Jia Hao Goh and Hoong-Kun Fun

S1. Comment

2-Aminopyridine and its derivatives are amomg the most frequently used synthons in supramolecular chemistry based on hydrogen bonds (Gellert & Hsu, 1988; Banerjee & Murugavel, 2004). A series of similar complexes formed from 2-aminopyridine and carboxylates has been reported previously (Hemamalini & Fun, 2010*a,b,c*). The present work, 2,3-diaminopyridinium phthalate dihydrate, (2/1/1) (I), is a continuation of our structural study of complexes of the 2,3-diaminopyridinium system.

The asymmetric unit of the title compound, (I), contains one 2,3-diamino- pyridinium cation, a half of phthalate anion (which lies on a twofold axis; -x+1, y, -z+1/2) and a water molecule as shown in Fig. 1. The dihedral angle between the pyridine (N1/C1–C5) and benzene (C6–C8/ C6A–C8A) ring is 80.61 (7)°.

In the crystal structure (Fig. 2), the ion pairs and water molecules are connected *via* N—H···O, O—H···O and C—H···O (Table 1) hydrogen bonds forming a three-dimensional network. The crystal structure is further stabilized by C—H···π interactions involving the centroids of the C6–C8/C6A–C8A (Cg1) and N1/C1–C5 (Cg2) rings.

S2. Experimental

A hot methanol solution (20 ml) of 2,3-diaminopyridine (27 mg, Aldrich) and phthalic acid (42 mg, Merck) were mixed and warmed over a magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and brown plates of the title compound appeared after a few days.

S3. Refinement

All hydrogen atoms were located from a difference Fourier maps and refined freely [N–H = 0.89 (2)–0.98 (2)Å; O–H = 0.91 (2)– 0.95 (3) Å and C–H = 0.959 (18)–1.01 (2) Å]. The highest residual electron density peak is located at 0.73 Å from C9 and the deepest hole is located at 0.78 Å from C9.

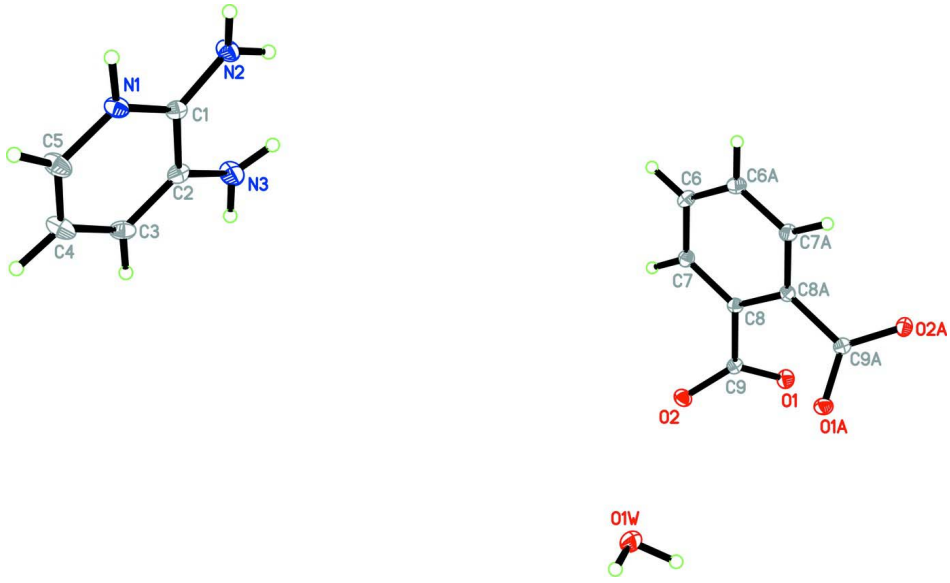

Figure 1

The molecule of (I) with 30% probability displacement ellipsoids. Atoms labelled A are generated by -x+1, y, -z+1/2.

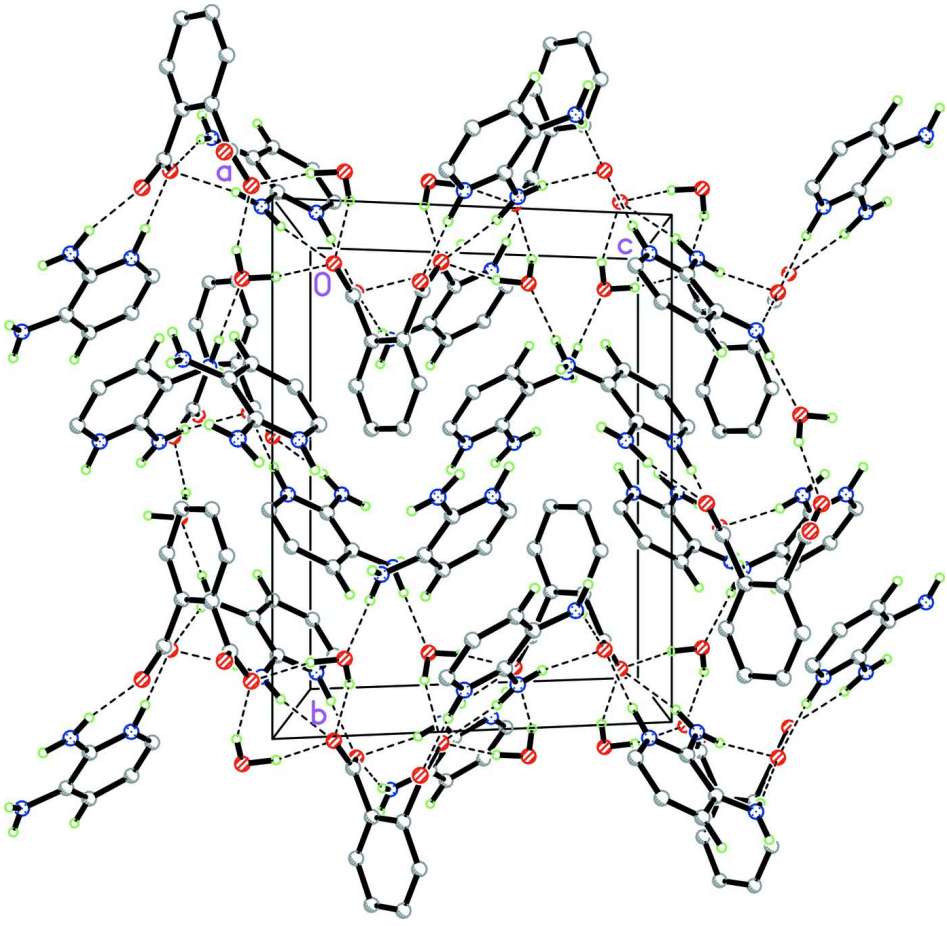

Figure 2

The crystal packing of the title compound showing hydrogen-bonded (dashed lines) networks. H atoms not involved in hydrogen bond interactions are omitted for clarity.

Bis(2,3-diaminopyridinium) benzene-1,2-dicarboxylate dihydrate

Crystal data

$2C_5H_8N_3^+·C_8H_4O_4^-·2H_2O$
$M_r = 420.43$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 15.795$ (5) Å
$b = 13.083$ (4) Å
$c = 11.012$ (4) Å
$\beta = 115.194$ (5)°
$V = 2059.2$ (11) Å^3
$Z = 4$
$F(000) = 888$
$D_x = 1.356$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3390 reflections
$\theta = 2.8$–29.8°
$\mu = 0.10$ mm^{-1}
$T = 100$ K
Plate, brown
0.42 × 0.36 × 0.03 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.958$, $T_{max} = 0.997$
10343 measured reflections
2955 independent reflections

2148 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 29.9°$, $\theta_{min} = 2.1°$
$h = -22 \rightarrow 22$
$k = -18 \rightarrow 18$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.125$
$S = 1.04$
2955 reflections
184 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
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2 + 0.7423P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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}
N1	0.23077 (8)	0.94380 (9)	1.03746 (11)	0.0227 (3)
N2	0.30262 (8)	0.94315 (10)	0.89459 (13)	0.0256 (3)
N3	0.17815 (10)	0.78666 (11)	0.74285 (14)	0.0330 (3)
C1	0.23819 (9)	0.90400 (10)	0.93023 (13)	0.0192 (3)
C2	0.17516 (9)	0.82430 (9)	0.85688 (13)	0.0210 (3)
C3	0.11106 (9)	0.79131 (11)	0.90331 (14)	0.0249 (3)
C4	0.10585 (11)	0.83570 (13)	1.01540 (15)	0.0313 (3)
C5	0.16621 (11)	0.91224 (13)	1.08149 (15)	0.0310 (3)
O1	0.43751 (6)	0.07071 (7)	0.10193 (9)	0.0225 (2)
O2	0.32273 (6)	0.12167 (7)	0.15491 (9)	0.0225 (2)
C6	0.45346 (10)	0.41720 (10)	0.20469 (14)	0.0242 (3)
C7	0.40590 (9)	0.32537 (10)	0.16012 (13)	0.0201 (3)
C8	0.45249 (8)	0.23274 (9)	0.20552 (12)	0.0160 (2)
C9	0.40094 (8)	0.13405 (9)	0.15149 (12)	0.0168 (2)
O1W	0.45043 (8)	0.10881 (8)	0.86130 (12)	0.0315 (3)
H1	0.3388 (12)	0.3242 (12)	0.0959 (17)	0.028 (4)*
H2	0.0692 (11)	0.7346 (13)	0.8557 (17)	0.026 (4)*
H3	0.4209 (12)	0.4807 (14)	0.1749 (17)	0.032 (4)*
H4	0.1689 (13)	0.9496 (15)	1.160 (2)	0.043 (5)*
H5	0.3138 (13)	0.9165 (14)	0.8275 (19)	0.033 (5)*

H6	0.2697 (12)	1.0029 (15)	1.0806 (18)	0.036 (5)*
H7	0.3468 (13)	0.9879 (15)	0.9506 (19)	0.039 (5)*
H8	0.0557 (13)	0.8149 (14)	1.044 (2)	0.042 (5)*
H9	0.1404 (14)	0.7328 (17)	0.712 (2)	0.046 (5)*
H10	0.2265 (14)	0.7967 (14)	0.723 (2)	0.040 (5)*
H11	0.4555 (16)	0.1035 (17)	0.950 (3)	0.064 (7)*
H12	0.4828 (16)	0.0542 (18)	0.850 (2)	0.062 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0235 (6)	0.0244 (6)	0.0181 (5)	−0.0068 (5)	0.0070 (4)	−0.0020 (4)
N2	0.0237 (6)	0.0281 (6)	0.0260 (6)	−0.0104 (5)	0.0116 (5)	−0.0096 (5)
N3	0.0323 (7)	0.0332 (7)	0.0364 (7)	−0.0153 (6)	0.0174 (6)	−0.0188 (6)
C1	0.0186 (6)	0.0182 (6)	0.0175 (6)	−0.0001 (4)	0.0043 (5)	0.0016 (4)
C2	0.0195 (6)	0.0181 (6)	0.0197 (6)	−0.0001 (5)	0.0028 (5)	0.0004 (5)
C3	0.0232 (6)	0.0223 (6)	0.0224 (6)	−0.0060 (5)	0.0033 (5)	0.0024 (5)
C4	0.0312 (7)	0.0392 (8)	0.0237 (7)	−0.0138 (6)	0.0119 (6)	0.0001 (6)
C5	0.0348 (8)	0.0393 (8)	0.0223 (7)	−0.0128 (6)	0.0153 (6)	−0.0043 (6)
O1	0.0229 (5)	0.0220 (5)	0.0222 (5)	−0.0006 (4)	0.0093 (4)	−0.0059 (4)
O2	0.0205 (4)	0.0227 (5)	0.0253 (5)	−0.0041 (4)	0.0106 (4)	−0.0029 (4)
C6	0.0252 (7)	0.0173 (6)	0.0297 (7)	0.0038 (5)	0.0113 (6)	0.0033 (5)
C7	0.0191 (6)	0.0200 (6)	0.0196 (6)	0.0017 (5)	0.0068 (5)	0.0022 (4)
C8	0.0180 (6)	0.0171 (6)	0.0140 (5)	−0.0005 (4)	0.0078 (4)	−0.0002 (4)
C9	0.0178 (5)	0.0173 (6)	0.0124 (5)	0.0007 (4)	0.0036 (4)	0.0006 (4)
O1W	0.0361 (6)	0.0276 (6)	0.0363 (6)	0.0102 (4)	0.0208 (5)	0.0120 (4)

Geometric parameters (Å, º)

N1—C1	1.3404 (17)	C4—H8	1.01 (2)
N1—C5	1.3663 (18)	C5—H4	0.98 (2)
N1—H6	0.98 (2)	O1—C9	1.2596 (15)
N2—C1	1.3388 (17)	O2—C9	1.2623 (15)
N2—H5	0.899 (19)	C6—C6^{i}	1.382 (3)
N2—H7	0.92 (2)	C6—C7	1.3910 (19)
N3—C2	1.3683 (19)	C6—H3	0.959 (18)
N3—H9	0.89 (2)	C7—C8	1.3954 (17)
N3—H10	0.89 (2)	C7—H1	0.993 (17)
C1—C2	1.4304 (18)	C8—C8^{i}	1.400 (2)
C2—C3	1.383 (2)	C8—C9	1.5072 (17)
C3—C4	1.398 (2)	O1W—H11	0.95 (3)
C3—H2	0.983 (17)	O1W—H12	0.91 (2)
C4—C5	1.360 (2)		
C1—N1—C5	123.61 (12)	C5—C4—H8	119.7 (11)
C1—N1—H6	117.6 (11)	C3—C4—H8	121.0 (11)
C5—N1—H6	118.5 (10)	C4—C5—N1	119.44 (14)
C1—N2—H5	122.2 (12)	C4—C5—H4	126.7 (11)

C1—N2—H7	120.2 (11)	N1—C5—H4	113.8 (11)
H5—N2—H7	116.0 (16)	C6^{i}—C6—C7	120.25 (8)
C2—N3—H9	111.0 (13)	C6^{i}—C6—H3	119.9 (10)
C2—N3—H10	122.9 (13)	C7—C6—H3	119.8 (10)
H9—N3—H10	121.6 (18)	C6—C7—C8	120.03 (12)
N2—C1—N1	118.16 (12)	C6—C7—H1	121.1 (10)
N2—C1—C2	123.13 (12)	C8—C7—H1	118.9 (10)
N1—C1—C2	118.67 (12)	C7—C8—C8^{i}	119.70 (7)
N3—C2—C3	122.93 (12)	C7—C8—C9	119.26 (11)
N3—C2—C1	119.54 (12)	C8^{i}—C8—C9	120.95 (6)
C3—C2—C1	117.49 (12)	O1—C9—O2	124.30 (11)
C2—C3—C4	121.61 (13)	O1—C9—C8	117.67 (11)
C2—C3—H2	118.0 (10)	O2—C9—C8	117.99 (11)
C4—C3—H2	120.4 (10)	H11—O1W—H12	105.6 (19)
C5—C4—C3	119.14 (13)		

C5—N1—C1—N2	178.22 (13)	C3—C4—C5—N1	−0.3 (2)
C5—N1—C1—C2	0.2 (2)	C1—N1—C5—C4	0.6 (2)
N2—C1—C2—N3	−1.5 (2)	C6^{i}—C6—C7—C8	−0.9 (2)
N1—C1—C2—N3	176.36 (12)	C6—C7—C8—C8^{i}	−0.9 (2)
N2—C1—C2—C3	−179.27 (13)	C6—C7—C8—C9	−177.35 (12)
N1—C1—C2—C3	−1.39 (18)	C7—C8—C9—O1	126.40 (13)
N3—C2—C3—C4	−175.91 (14)	C8^{i}—C8—C9—O1	−50.01 (19)
C1—C2—C3—C4	1.8 (2)	C7—C8—C9—O2	−51.38 (16)
C2—C3—C4—C5	−0.9 (2)	C8^{i}—C8—C9—O2	132.22 (15)

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (Å, º)

Cg1 and Cg2 are the centroids of the C6–C8/C6A–C8A and N1/C1–C5 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H5···O2^{ii}	0.90 (2)	2.03 (2)	2.9155 (19)	169.0 (18)
N1—H6···O2^{iii}	0.98 (2)	1.790 (19)	2.7565 (18)	170.3 (19)
N2—H7···O1^{iii}	0.92 (2)	1.99 (2)	2.8976 (19)	168.1 (19)
N3—H9···O1*W*^{iv}	0.89 (2)	2.09 (2)	2.978 (2)	179 (3)
N3—H10···O2^{ii}	0.89 (2)	2.23 (2)	3.078 (2)	158.8 (17)
O1*W*—H11···O1^{v}	0.95 (3)	1.86 (3)	2.7878 (18)	165 (3)
O1*W*—H12···O1^{vi}	0.92 (2)	1.99 (2)	2.8641 (18)	158.2 (19)
C3—H2···O1*W*^{vii}	0.984 (17)	2.516 (18)	3.369 (2)	145.0 (14)
C4—H8···*Cg*1^{iv}	1.01 (2)	2.76 (2)	3.629 (2)	144.3 (15)
C6—H3···*Cg*2^{viii}	0.959 (18)	2.568 (18)	3.497 (2)	163.4 (14)

Symmetry codes: (ii) $x, -y+1, z+1/2$; (iii) $x, y+1, z+1$; (iv) $-x+1/2, y+1/2, -z+3/2$; (v) $x, y, z+1$; (vi) $-x+1, -y, -z+1$; (vii) $x-1/2, y+1/2, z$; (viii) $-x+1/2, -y+3/2, -z+1$.