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4-Methoxyquinolinium-2-carboxylate dihydrate

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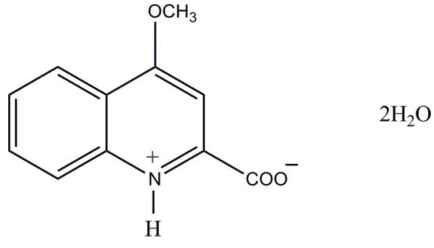
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.051; wR factor = 0.140; data-to-parameter ratio = 20.5.

The title hydrated quinoline derivative, $C_{11}H_9NO_3\cdot 2H_2O$, crystallizes as a zwitterion in which the quinoline N atom is protonated. The quinoline ring is essentially planar, with a maximum deviation of 0.017 (2) Å. An intramolecular N—H···O hydrogen bond between the protonated N atom and the O atom of the carboxylate group in the zwitterion forms an $S(5)$ ring motif. In the crystal, the zwitterions are connected into inversion dimers *via* pairs of N—H···O and C—H···O hydrogen bonds with $R_2^2(4)$ and $R_2^1(6)$ motifs. The water molecules are connected *via* O—H···O hydrogen bonds, forming supramolecular chains along the c axis. Furthermore, the chains and the dimers are connected *via* O—H···O hydrogen bonds, forming ladder-like supramolecular ribbons along the c axis.

Related literature

For background to and the biological activity of quinoline derivatives, see: Morimoto *et al.* (1991); Michael (1997); Markees *et al.* (1970); Campbell *et al.* (1988); Zhou *et al.* (1989); Elman *et al.* (1985); Loh *et al.* (2010*a*,*b*); Sasaki *et al.* (1998); Reux *et al.* (2009). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{11}H_9NO_3\cdot 2H_2O$
M_r = 239.22
Monoclinic, $P2_1/c$
a = 5.7674 (11) Å
b = 21.196 (4) Å
c = 10.0993 (15) Å
β = 115.978 (8)°
V = 1109.9 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 K
0.23 × 0.13 × 0.09 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.974, T_{max} = 0.990
8743 measured reflections
3176 independent reflections
2123 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.140
S = 1.01
3176 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.94	1.84	2.7608 (18)	164
O1W—H2···O2W	0.86	1.89	2.7478 (19)	176
O1W—H3···O2^{ii}	0.91	1.86	2.7685 (16)	177
O2W—H4···O2^{iii}	0.88	1.88	2.7498 (18)	171
O2W—H5···O1W^{iv}	0.87	1.91	2.7860 (19)	176
C6—H6A···O1W^{v}	0.93	2.59	3.418 (2)	149
C8—H8A···O1^{i}	0.93	2.53	3.229 (2)	132
C11—H11A···O1W^{vi}	0.96	2.58	3.317 (2)	134
C11—H11B···O2^{iii}	0.96	2.53	3.272 (2)	134

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

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: IS2654).

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supporting information

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4-Methoxyquinolinium-2-carboxylate dihydrate

Madhukar Hemamalini and Hoong-Kun Fun

S1. Comment

Quinolines and their derivatives are very important compounds because of their wide occurrence in natural products (Morimoto *et al.*, 1991; Michael, 1997) and biologically active compounds (Markees *et al.*, 1970; Campbell *et al.*, 1988). Quinoline-2-carboxylic acid (quinaldic acid) and tryptophan metabolite (Zhou *et al.*, 1989) are well-known chelating ligands (Elman *et al.*, 1985). Recently, hydrogen-bonding patterns involving quinoline and its derivatives with organic acid have been investigated (Loh *et al.*, 2010*a,b*). Syntheses of the quinoline derivatives have been discussed (Sasaki *et al.*, 1998; Reux *et al.*, 2009).

The title molecule, (Fig. 1), crystallizes as a zwitterion in which the quinoline N atom is protonated. The asymmetric unit consists of one 4-methoxyquinolinium-2-carboxylate molecule and two water molecules. The quinoline ring (N1/C1–C9) is essentially planar, with a maximum deviation of 0.017 (2) Å for atom C4.

In the crystal structure (Fig. 2), the 4-methoxyquinolinium-2- carboxylate molecules are connected via N—H···O and C—H···O hydrogen bonds to form $R_2^2(4)$ and $R^1_2(6)$ (Bernstein *et al.*, 1995) motifs. There is an intramolecular N—H···O hydrogen bond observed between the protonated nitrogen atom of the cationic part of the quinolinium and the oxygen atom of anionic part of the carboxylate group in the zwitterion forming an *S*(5) ring motif. The water molecules are connected *via* O—H···O hydrogen bonds to form one-dimensional supramolecular chains along the *c*-axis. Furthermore, the chains formed by water molecules and the 4-methoxyquinolinium-2-carboxylate molecules are connected *via* O—H···O (Table 1) hydrogen bonds to form ladder-like supramolecular ribbons along the *c*-axis.

S2. Experimental

A methanol solution (20 ml) of 4-methoxyquinoline-2-carboxylic acid (50. 8 mg, Aldrich) was warmed over a heating magnetic stirrer for 5 minutes. The resulting solution was allowed to cool slowly at room temperature. Crystals of the title compound appeared from the mother liquor after a few days.

S3. Refinement

All the H atoms were positioned geometrically (N—H = 0.9437 Å; C—H = 0.93 or 0.96 Å and O—H = 0.8586–0.9083 Å) and were refined using a riding model, with U_{iso}(H) = 1.2 or 1.5U_{eq}(C,O).

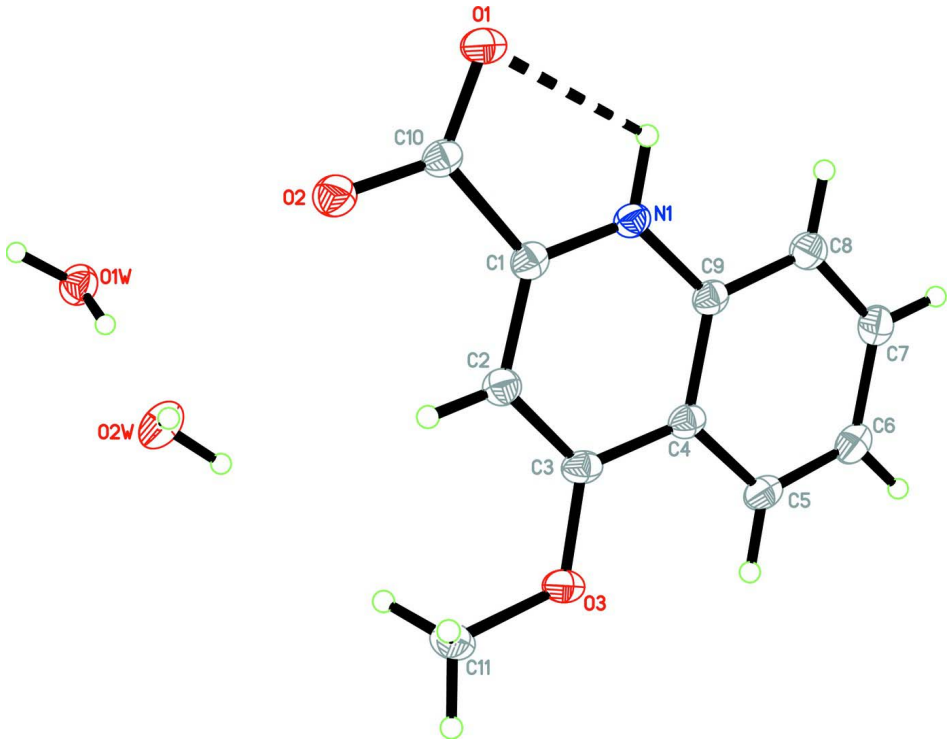

Figure 1

The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular hydrogen bonds shown by dotted lines.

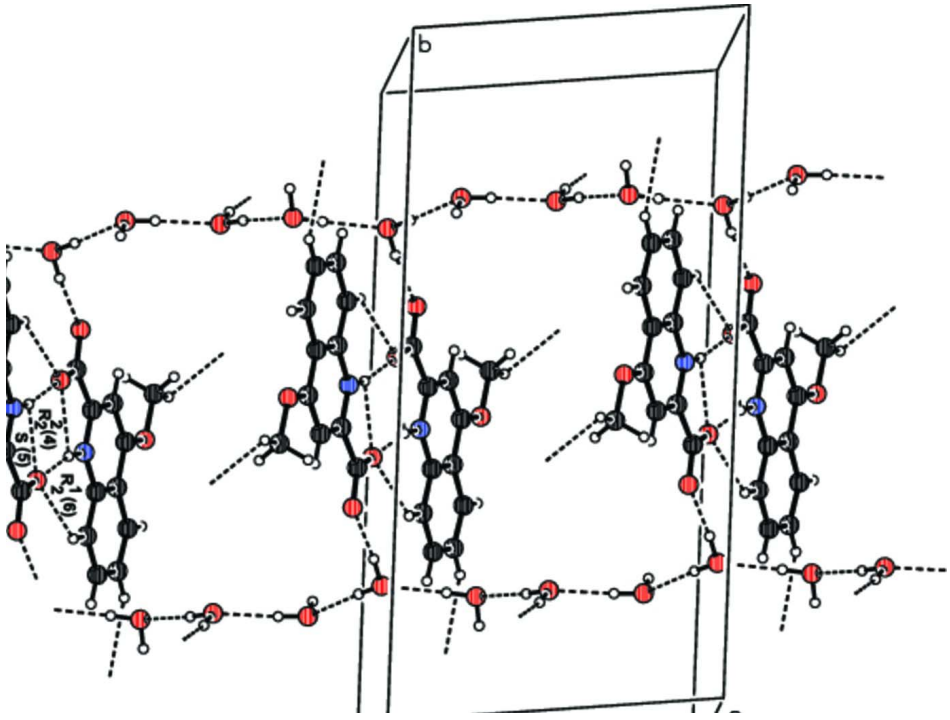

Figure 2

The crystal packing of the title compound, showing a hydrogen-bonded (dashed lines) ladder-like network.

4-Methoxyquinolinium-2-carboxylate dihydrate

Crystal data

$C_{11}H_9NO_3 \cdot 2H_2O$
$M_r = 239.22$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 5.7674$ (11) Å
$b = 21.196$ (4) Å
$c = 10.0993$ (15) Å
$\beta = 115.978$ (8)°
$V = 1109.9$ (3) Å^3
$Z = 4$
$F(000) = 504$
$D_x = 1.432$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1896 reflections
$\theta = 3.0$–$29.6°$
$\mu = 0.11$ mm^{-1}
$T = 100$ K
Block, colourless
0.23 × 0.13 × 0.09 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.974$, $T_{max} = 0.990$
8743 measured reflections
3176 independent reflections
2123 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 30.0°$, $\theta_{min} = 3.0°$
$h = -7 \rightarrow 8$
$k = -29 \rightarrow 29$
$l = -10 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.140$
$S = 1.01$
3176 reflections
155 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0701P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ 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}
O1	−0.5092 (2)	0.92971 (5)	0.52984 (13)	0.0215 (3)
O2	−0.2912 (2)	0.83869 (5)	0.60229 (13)	0.0215 (3)
O3	0.6369 (2)	0.91915 (5)	0.88880 (13)	0.0209 (3)
N1	−0.0747 (2)	0.99667 (6)	0.64651 (14)	0.0164 (3)
H1	−0.2351	1.0154	0.5860	0.020*
C1	−0.0569 (3)	0.93435 (7)	0.66638 (17)	0.0167 (3)
C2	0.1785 (3)	0.90548 (7)	0.74844 (17)	0.0179 (3)
H2A	0.1879	0.8620	0.7624	0.022*
C3	0.4006 (3)	0.94219 (7)	0.80976 (17)	0.0172 (3)
C4	0.3838 (3)	1.00878 (7)	0.78808 (17)	0.0165 (3)
C5	0.6021 (3)	1.04912 (7)	0.84392 (18)	0.0196 (3)
H5A	0.7657	1.0325	0.8995	0.024*
C6	0.5718 (3)	1.11260 (8)	0.81587 (18)	0.0215 (4)
H6A	0.7157	1.1388	0.8513	0.026*
C7	0.3247 (3)	1.13855 (7)	0.73390 (18)	0.0213 (3)
H7A	0.3077	1.1818	0.7171	0.026*
C8	0.1083 (3)	1.10119 (7)	0.67844 (17)	0.0192 (3)
H8A	−0.0542	1.1187	0.6248	0.023*
C9	0.1385 (3)	1.03559 (7)	0.70470 (17)	0.0163 (3)
C10	−0.3094 (3)	0.89756 (7)	0.59208 (17)	0.0165 (3)
C11	0.6630 (3)	0.85142 (7)	0.91289 (19)	0.0229 (4)
H11A	0.8409	0.8411	0.9726	0.034*
H11B	0.6036	0.8302	0.8198	0.034*
H11C	0.5617	0.8382	0.9622	0.034*
O1W	0.0737 (2)	0.75591 (5)	0.16811 (14)	0.0248 (3)
H2	0.1349	0.7589	0.2622	0.037*
H3	−0.0434	0.7242	0.1451	0.037*
O2W	0.2854 (2)	0.76156 (6)	0.47021 (14)	0.0283 (3)
H4	0.4092	0.7895	0.5074	0.042*
H5	0.2167	0.7580	0.5317	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0150 (5)	0.0235 (5)	0.0221 (7)	0.0015 (4)	0.0045 (4)	0.0012 (4)
O2	0.0189 (5)	0.0199 (5)	0.0235 (6)	−0.0012 (4)	0.0073 (5)	0.0017 (4)
O3	0.0162 (5)	0.0211 (5)	0.0204 (6)	0.0024 (4)	0.0034 (4)	0.0024 (4)
N1	0.0153 (6)	0.0185 (6)	0.0135 (7)	0.0000 (5)	0.0046 (5)	−0.0006 (5)
C1	0.0171 (7)	0.0205 (7)	0.0137 (8)	−0.0010 (6)	0.0077 (6)	−0.0016 (6)
C2	0.0172 (7)	0.0189 (7)	0.0168 (8)	0.0004 (6)	0.0066 (6)	−0.0002 (6)
C3	0.0152 (7)	0.0244 (7)	0.0118 (8)	0.0026 (6)	0.0056 (6)	0.0004 (6)
C4	0.0154 (7)	0.0216 (7)	0.0126 (7)	0.0001 (6)	0.0061 (5)	−0.0011 (6)
C5	0.0160 (7)	0.0253 (7)	0.0153 (8)	−0.0016 (6)	0.0050 (6)	−0.0024 (6)
C6	0.0201 (7)	0.0245 (7)	0.0196 (9)	−0.0049 (6)	0.0083 (6)	−0.0049 (6)
C7	0.0236 (8)	0.0191 (7)	0.0207 (9)	−0.0016 (6)	0.0094 (6)	−0.0019 (6)

C8	0.0199 (7)	0.0209 (7)	0.0168 (8)	0.0010 (6)	0.0080 (6)	0.0000 (6)
C9	0.0167 (7)	0.0199 (7)	0.0122 (7)	−0.0005 (6)	0.0064 (6)	−0.0011 (6)
C10	0.0159 (7)	0.0201 (7)	0.0134 (8)	−0.0008 (5)	0.0061 (6)	−0.0004 (6)
C11	0.0214 (8)	0.0216 (7)	0.0228 (9)	0.0042 (6)	0.0070 (6)	0.0047 (6)
O1W	0.0256 (6)	0.0228 (5)	0.0244 (7)	−0.0035 (5)	0.0093 (5)	0.0004 (5)
O2W	0.0256 (6)	0.0335 (6)	0.0255 (7)	−0.0098 (5)	0.0110 (5)	−0.0068 (5)

Geometric parameters (Å, º)

O1—C10	1.2461 (18)	C5—H5A	0.9300
O2—C10	1.2528 (18)	C6—C7	1.409 (2)
O3—C3	1.3337 (18)	C6—H6A	0.9300
O3—C11	1.4530 (18)	C7—C8	1.373 (2)
N1—C1	1.3332 (19)	C7—H7A	0.9300
N1—C9	1.3800 (19)	C8—C9	1.412 (2)
N1—H1	0.9437	C8—H8A	0.9300
C1—C2	1.385 (2)	C11—H11A	0.9600
C1—C10	1.528 (2)	C11—H11B	0.9600
C2—C3	1.391 (2)	C11—H11C	0.9600
C2—H2A	0.9300	O1W—H2	0.8586
C3—C4	1.425 (2)	O1W—H3	0.9083
C4—C9	1.411 (2)	O2W—H4	0.8759
C4—C5	1.419 (2)	O2W—H5	0.8743
C5—C6	1.370 (2)		
C3—O3—C11	117.76 (12)	C7—C6—H6A	119.7
C1—N1—C9	122.17 (13)	C8—C7—C6	121.28 (14)
C1—N1—H1	120.2	C8—C7—H7A	119.4
C9—N1—H1	117.5	C6—C7—H7A	119.4
N1—C1—C2	121.24 (14)	C7—C8—C9	118.44 (14)
N1—C1—C10	115.95 (13)	C7—C8—H8A	120.8
C2—C1—C10	122.80 (13)	C9—C8—H8A	120.8
C1—C2—C3	119.30 (14)	N1—C9—C4	119.14 (13)
C1—C2—H2A	120.3	N1—C9—C8	119.69 (13)
C3—C2—H2A	120.3	C4—C9—C8	121.16 (14)
O3—C3—C2	124.18 (14)	O1—C10—O2	127.72 (14)
O3—C3—C4	115.95 (13)	O1—C10—C1	116.14 (13)
C2—C3—C4	119.86 (13)	O2—C10—C1	116.14 (13)
C9—C4—C5	118.55 (14)	O3—C11—H11A	109.5
C9—C4—C3	118.28 (13)	O3—C11—H11B	109.5
C5—C4—C3	123.16 (14)	H11A—C11—H11B	109.5
C6—C5—C4	119.94 (14)	O3—C11—H11C	109.5
C6—C5—H5A	120.0	H11A—C11—H11C	109.5
C4—C5—H5A	120.0	H11B—C11—H11C	109.5
C5—C6—C7	120.61 (15)	H2—O1W—H3	103.8
C5—C6—H6A	119.7	H4—O2W—H5	106.9
C9—N1—C1—C2	0.7 (2)	C5—C6—C7—C8	−0.8 (3)

C9—N1—C1—C10	−178.65 (13)	C6—C7—C8—C9	−0.3 (2)
N1—C1—C2—C3	−0.8 (2)	C1—N1—C9—C4	0.0 (2)
C10—C1—C2—C3	178.50 (15)	C1—N1—C9—C8	179.18 (15)
C11—O3—C3—C2	−0.4 (2)	C5—C4—C9—N1	178.33 (14)
C11—O3—C3—C4	−179.67 (14)	C3—C4—C9—N1	−0.5 (2)
C1—C2—C3—O3	−179.06 (15)	C5—C4—C9—C8	−0.9 (2)
C1—C2—C3—C4	0.2 (2)	C3—C4—C9—C8	−179.68 (15)
O3—C3—C4—C9	179.73 (14)	C7—C8—C9—N1	−178.06 (15)
C2—C3—C4—C9	0.4 (2)	C7—C8—C9—C4	1.1 (2)
O3—C3—C4—C5	1.0 (2)	N1—C1—C10—O1	−5.3 (2)
C2—C3—C4—C5	−178.38 (15)	C2—C1—C10—O1	175.42 (15)
C9—C4—C5—C6	−0.3 (2)	N1—C1—C10—O2	175.44 (14)
C3—C4—C5—C6	178.51 (16)	C2—C1—C10—O2	−3.9 (2)
C4—C5—C6—C7	1.1 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.94	2.31	2.6638 (18)	102
N1—H1···O1^{i}	0.94	1.84	2.7608 (18)	164
O1*W*—H2···O2*W*	0.86	1.89	2.7478 (19)	176
O1*W*—H3···O2^{ii}	0.91	1.86	2.7685 (16)	177
O2*W*—H4···O2^{iii}	0.88	1.88	2.7498 (18)	171
O2*W*—H5···O1*W*^{iv}	0.87	1.91	2.7860 (19)	176
C6—H6*A*···O1*W*^{v}	0.93	2.59	3.418 (2)	149
C8—H8*A*···O1^{i}	0.93	2.53	3.229 (2)	132
C11—H11*A*···O1*W*^{vi}	0.96	2.58	3.317 (2)	134
C11—H11*B*···O2^{iii}	0.96	2.53	3.272 (2)	134

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