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Crystal structure of the enol form of mesotrione: a benzoylcyclohexanedione herbicide

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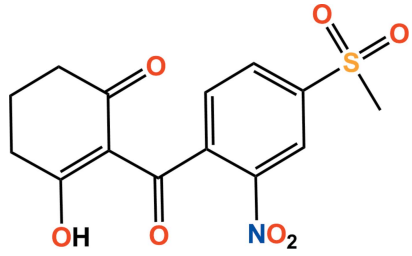
The title compound [systematic name: 3-hydroxy-2-(4-methylsulfonyl-2-nitrobenzoyl)cyclohex-2-enone], $C_{14}H_{13}NO_7S$, is the enol form of a benzoylcyclohexanedione herbicide. As a result of this tautomerization, there is intramolecular O—H···O hydrogen bond enclosing an $S(6)$ ring motif. The cyclohexene ring has an envelope conformation, with the central CH_2 C atom as the flap. Its mean plane is inclined to the benzene ring by 87.46 (8)°. In the crystal, molecules are linked by a series of C—H···O hydrogen bonds, forming a three-dimensional framework.

Keywords: crystal structure; tautomerization; enol form; intramolecular O—H···O hydrogen bond..

CCDC reference: 1410192

1. Related literature

For information on the herbicidal properties of the title compound, see: Mitchell *et al.* (2001). For related crystal structures, see: Eftekhari-Sis *et al.* (2012); Liu & Tang (2012).



2. Experimental

2.1. Crystal data

$C_{14}H_{13}NO_7S$
M_r = 339.31
Monoclinic, $P2_1/c$
a = 10.4208 (2) Å
b = 11.2525 (3) Å
c = 12.3550 (3) Å
β = 95.370 (1)°
V = 1442.39 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 173 K
0.43 × 0.30 × 0.20 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.895, T_{max} = 0.949
12093 measured reflections
2828 independent reflections
2572 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.097
S = 1.04
2828 reflections
213 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6*O*···O5	0.91 (3)	1.71 (3)	2.524 (2)	148 (2)
C1—H1*B*···O4^{i}	0.98	2.58	3.393 (2)	140
C1—H1*B*···O7^{ii}	0.98	2.58	3.265 (2)	127
C11—H11*A*···O3^{iii}	0.99	2.40	3.135 (2)	131

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXTL* (Sheldrick 2008).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5166).

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supporting information

Acta Cryst. (2015). E**71**, o548–o549 [https://doi.org/10.1107/S2056989015012803]

Crystal structure of the enol form of mesotrione: a benzoylcyclohexanedione herbicide

Gihaeng Kang, Jineun Kim, Hyunjin Park and Tae Ho Kim

S1. Comment

Mesotrione, [keto form systematic name: 2-(4-mesyl-2-nitrobenzoyl)cyclohexane-1,3-dione], is a benzoylcyclohexanedione herbicide and it has been developed for the selective pre- and post-emergence control of a wide range of broad-leaved and grass weeds in maize (Mitchell *et al.*, 2001). However, until now its crystal structure has not been reported.

The title compound crystallized in the enol form (Fig. 1 and Table 1), with an intramolecular O6—H6O···O5 hydrogen bond embedded in an *S*(6) ring. The cyclohexene ring has an envelope conformation with the central CH_2 C-atom, C12, as the flap. Its mean plane is inclined to the benzene ring by 87.46 (8) °.

All bond lengths and bond angles are normal and comparable to those observed in the crystal structures of similar compounds (Eftekhari-Sis *et al.*, 2012; Liu *et al.*, 2012).

In the crystal, molecules are linked by a series of C—H···O hydrogen bonds forming a three-dimensional framework (Fig. 2 and Table 1).

S2. Experimental

The title compound was purchased from the Dr. Ehrenstorfer GmbH Company. Slow evaporation of a solution in CH_3CN gave single crystals suitable for X-ray analysis.

S3. Refinement

The O-bound H atom was located in a difference Fourier map and freely refined [O—H = 0.91 (3) Å]. The C-bound H atoms were positioned geometrically and refined using a riding model: C-H = 0.95 - 0.99 \%A with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and

1.2U_{eq}(C) for other H atoms.

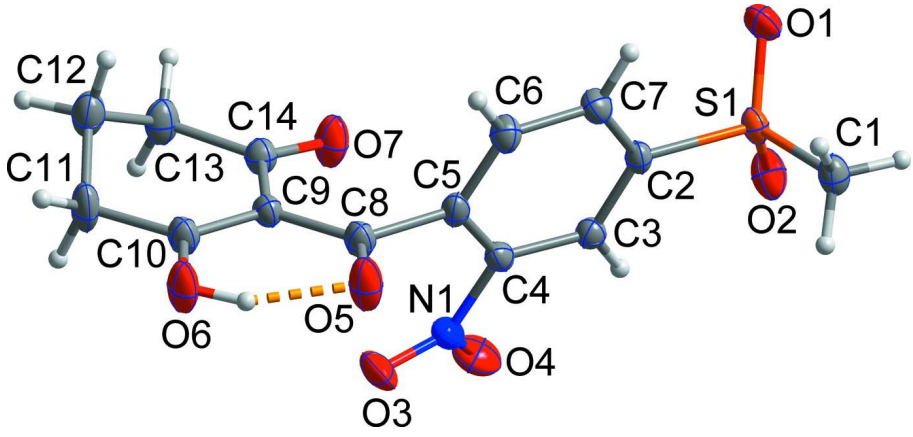

Figure 1

The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular O—H···O hydrogen bond is shown as a dashed line (see Table 1 for details).

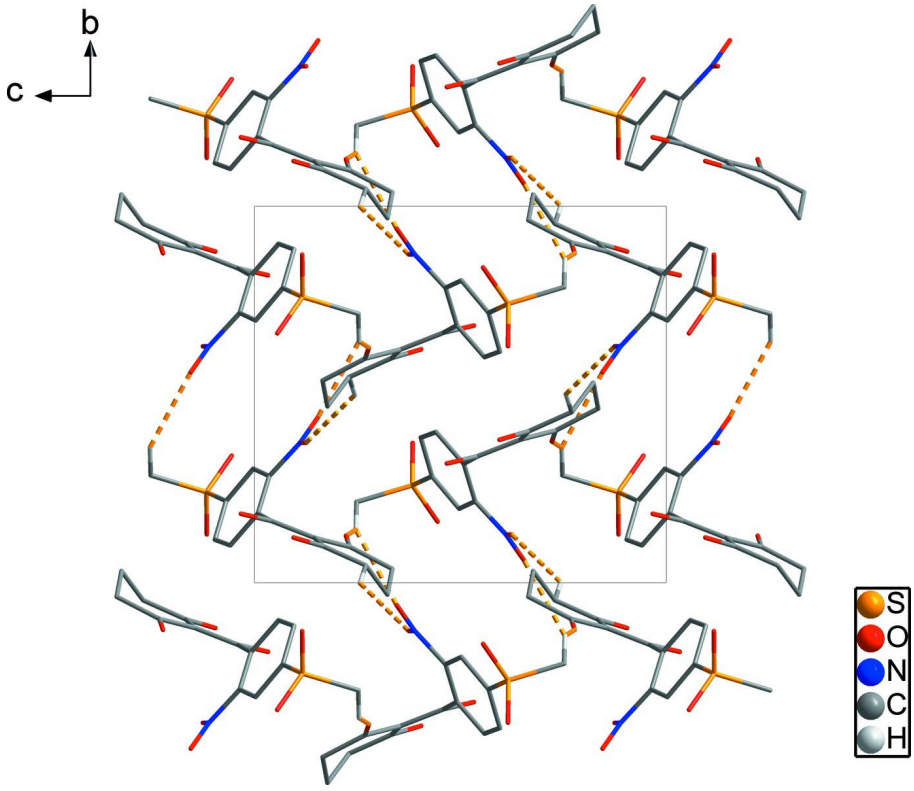

Figure 2

Crystal packing of the title compound viewed along the *a* axis. The intermolecular C—H···O hydrogen bonds are shown as dashed lines (see Table 1 for details).

3-Hydroxy-2-(4-methylsulfonyl-2-nitrobenzoyl)cyclohex-2-enone

Crystal data

$C_{14}H_{13}NO_7S$
M_r = 339.31

Monoclinic, $P2_1/c$
a = 10.4208 (2) Å

b = 11.2525 (3) Å
c = 12.3550 (3) Å
β = 95.370 (1)°
V = 1442.39 (6) Å^3
Z = 4
F(000) = 704
D_x = 1.563 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7168 reflections
θ = 2.5–27.5°
μ = 0.26 mm^{-1}
T = 173 K
Block, colourless
0.43 × 0.30 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.895, T_{max} = 0.949
12093 measured reflections

2828 independent reflections
2572 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 26.0°, θ_{min} = 2.0°
h = −12→12
k = −13→13
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.097
S = 1.04
2828 reflections
213 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.7458P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
S1	0.31056 (3)	0.24106 (4)	1.11672 (3)	0.02141 (13)
O1	0.24559 (11)	0.12877 (11)	1.11593 (11)	0.0333 (3)
O2	0.24978 (11)	0.33729 (12)	1.05544 (10)	0.0341 (3)
O3	0.78663 (13)	0.37212 (12)	0.87472 (13)	0.0461 (4)
O4	0.59220 (13)	0.44028 (12)	0.84539 (11)	0.0406 (3)
O5	0.92622 (11)	0.18323 (14)	1.03272 (11)	0.0420 (4)
O6	1.08825 (11)	0.11994 (14)	0.90444 (11)	0.0387 (3)
H6O	1.057 (3)	0.151 (2)	0.965 (2)	0.062 (8)*
O7	0.64741 (11)	0.12478 (13)	0.77772 (11)	0.0367 (3)
N1	0.67227 (14)	0.37175 (13)	0.88940 (12)	0.0280 (3)
C1	0.34825 (16)	0.28528 (17)	1.25212 (13)	0.0279 (4)
H1A	0.2685	0.2995	1.2863	0.042*
H1B	0.3993	0.3585	1.2540	0.042*
H1C	0.3981	0.2225	1.2918	0.042*

C2	0.46359 (14)	0.21719 (14)	1.06875 (12)	0.0195 (3)
C3	0.51015 (14)	0.30302 (14)	1.00287 (12)	0.0206 (3)
H3	0.4624	0.3733	0.9847	0.025*
C4	0.62836 (15)	0.28346 (14)	0.96419 (12)	0.0213 (3)
C5	0.70348 (14)	0.18398 (15)	0.99181 (13)	0.0224 (3)
C6	0.65419 (15)	0.09958 (15)	1.05868 (13)	0.0247 (3)
H6	0.7035	0.0309	1.0792	0.030*
C7	0.53315 (15)	0.11459 (14)	1.09596 (13)	0.0234 (3)
H7	0.4986	0.0552	1.1396	0.028*
C8	0.83866 (15)	0.16470 (15)	0.95976 (14)	0.0258 (4)
C9	0.86333 (14)	0.11938 (14)	0.85403 (13)	0.0221 (3)
C10	0.98924 (15)	0.09727 (16)	0.83365 (14)	0.0268 (4)
C11	1.02509 (16)	0.0464 (2)	0.72964 (16)	0.0378 (5)
H11A	1.1048	−0.0012	0.7437	0.045*
H11B	1.0428	0.1117	0.6795	0.045*
C12	0.91933 (17)	−0.03099 (19)	0.67708 (16)	0.0368 (4)
H12A	0.9099	−0.1027	0.7220	0.044*
H12B	0.9416	−0.0569	0.6046	0.044*
C13	0.79406 (16)	0.03715 (17)	0.66546 (14)	0.0312 (4)
H13A	0.7239	−0.0180	0.6393	0.037*
H13B	0.7995	0.0992	0.6093	0.037*
C14	0.75890 (15)	0.09568 (15)	0.76871 (13)	0.0238 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0139 (2)	0.0295 (2)	0.0211 (2)	0.00081 (14)	0.00345 (15)	0.00020 (15)
O1	0.0245 (6)	0.0388 (7)	0.0376 (7)	−0.0102 (5)	0.0082 (5)	−0.0049 (6)
O2	0.0242 (6)	0.0461 (8)	0.0324 (7)	0.0129 (5)	0.0046 (5)	0.0085 (6)
O3	0.0384 (8)	0.0357 (8)	0.0693 (10)	−0.0057 (6)	0.0325 (7)	0.0051 (7)
O4	0.0450 (8)	0.0374 (8)	0.0395 (8)	−0.0054 (6)	0.0042 (6)	0.0145 (6)
O5	0.0205 (6)	0.0733 (10)	0.0320 (7)	−0.0026 (6)	0.0022 (5)	−0.0197 (7)
O6	0.0158 (6)	0.0656 (10)	0.0350 (7)	−0.0005 (6)	0.0033 (5)	−0.0182 (7)
O7	0.0193 (6)	0.0557 (9)	0.0344 (7)	0.0087 (5)	−0.0007 (5)	−0.0121 (6)
N1	0.0321 (8)	0.0249 (7)	0.0286 (8)	−0.0075 (6)	0.0116 (6)	−0.0025 (6)
C1	0.0227 (8)	0.0394 (10)	0.0222 (8)	0.0006 (7)	0.0043 (6)	−0.0043 (7)
C2	0.0155 (7)	0.0250 (8)	0.0185 (7)	−0.0002 (6)	0.0035 (6)	−0.0027 (6)
C3	0.0196 (7)	0.0219 (8)	0.0203 (7)	0.0000 (6)	0.0022 (6)	−0.0026 (6)
C4	0.0220 (8)	0.0236 (8)	0.0190 (7)	−0.0050 (6)	0.0054 (6)	−0.0028 (6)
C5	0.0183 (7)	0.0282 (9)	0.0212 (8)	−0.0014 (6)	0.0039 (6)	−0.0074 (6)
C6	0.0219 (7)	0.0267 (8)	0.0259 (8)	0.0047 (6)	0.0040 (6)	0.0005 (7)
C7	0.0226 (8)	0.0252 (8)	0.0228 (8)	0.0001 (6)	0.0046 (6)	0.0027 (6)
C8	0.0183 (7)	0.0318 (9)	0.0276 (8)	−0.0019 (6)	0.0042 (6)	−0.0052 (7)
C9	0.0181 (7)	0.0249 (8)	0.0240 (8)	−0.0010 (6)	0.0051 (6)	−0.0029 (6)
C10	0.0185 (7)	0.0340 (9)	0.0283 (8)	−0.0013 (7)	0.0044 (6)	−0.0047 (7)
C11	0.0218 (8)	0.0590 (13)	0.0341 (10)	0.0007 (8)	0.0103 (7)	−0.0155 (9)
C12	0.0304 (9)	0.0471 (11)	0.0338 (10)	0.0009 (8)	0.0082 (8)	−0.0131 (8)
C13	0.0269 (8)	0.0437 (10)	0.0227 (8)	0.0024 (7)	0.0006 (6)	−0.0060 (7)

C14	0.0212 (8)	0.0268 (8)	0.0234 (8)	0.0011 (6)	0.0026 (6)	−0.0005 (6)

Geometric parameters (Å, º)

S1—O1	1.4331 (13)	C5—C6	1.389 (2)
S1—O2	1.4343 (12)	C5—C8	1.514 (2)
S1—C1	1.7543 (17)	C6—C7	1.393 (2)
S1—C2	1.7730 (15)	C6—H6	0.9500
O3—N1	1.2222 (19)	C7—H7	0.9500
O4—N1	1.225 (2)	C8—C9	1.448 (2)
O5—C8	1.239 (2)	C9—C10	1.382 (2)
O6—C10	1.314 (2)	C9—C14	1.467 (2)
O6—H6O	0.91 (3)	C10—C11	1.486 (2)
O7—C14	1.222 (2)	C11—C12	1.504 (3)
N1—C4	1.459 (2)	C11—H11A	0.9900
C1—H1A	0.9800	C11—H11B	0.9900
C1—H1B	0.9800	C12—C13	1.509 (2)
C1—H1C	0.9800	C12—H12A	0.9900
C2—C3	1.380 (2)	C12—H12B	0.9900
C2—C7	1.388 (2)	C13—C14	1.511 (2)
C3—C4	1.380 (2)	C13—H13A	0.9900
C3—H3	0.9500	C13—H13B	0.9900
C4—C5	1.390 (2)		
O1—S1—O2	118.50 (8)	C2—C7—H7	120.4
O1—S1—C1	108.66 (8)	C6—C7—H7	120.4
O2—S1—C1	109.73 (8)	O5—C8—C9	122.34 (14)
O1—S1—C2	107.66 (7)	O5—C8—C5	115.18 (14)
O2—S1—C2	107.73 (7)	C9—C8—C5	122.32 (13)
C1—S1—C2	103.51 (7)	C10—C9—C8	118.67 (14)
C10—O6—H6O	107.8 (17)	C10—C9—C14	119.31 (14)
O3—N1—O4	124.40 (15)	C8—C9—C14	122.01 (14)
O3—N1—C4	117.66 (15)	O6—C10—C9	122.94 (15)
O4—N1—C4	117.94 (14)	O6—C10—C11	113.90 (14)
S1—C1—H1A	109.5	C9—C10—C11	123.15 (15)
S1—C1—H1B	109.5	C10—C11—C12	111.30 (14)
H1A—C1—H1B	109.5	C10—C11—H11A	109.4
S1—C1—H1C	109.5	C12—C11—H11A	109.4
H1A—C1—H1C	109.5	C10—C11—H11B	109.4
H1B—C1—H1C	109.5	C12—C11—H11B	109.4
C3—C2—C7	121.38 (14)	H11A—C11—H11B	108.0
C3—C2—S1	117.90 (12)	C11—C12—C13	109.84 (16)
C7—C2—S1	120.72 (12)	C11—C12—H12A	109.7
C2—C3—C4	117.84 (14)	C13—C12—H12A	109.7
C2—C3—H3	121.1	C11—C12—H12B	109.7
C4—C3—H3	121.1	C13—C12—H12B	109.7
C3—C4—C5	122.95 (14)	H12A—C12—H12B	108.2
C3—C4—N1	116.98 (14)	C12—C13—C14	114.66 (14)

C5—C4—N1	120.06 (14)	C12—C13—H13A	108.6
C6—C5—C4	117.75 (14)	C14—C13—H13A	108.6
C6—C5—C8	117.56 (14)	C12—C13—H13B	108.6
C4—C5—C8	124.58 (15)	C14—C13—H13B	108.6
C5—C6—C7	120.71 (15)	H13A—C13—H13B	107.6
C5—C6—H6	119.6	O7—C14—C9	122.24 (15)
C7—C6—H6	119.6	O7—C14—C13	120.09 (14)
C2—C7—C6	119.30 (15)	C9—C14—C13	117.63 (14)
O1—S1—C2—C3	141.94 (12)	C6—C5—C8—O5	−73.6 (2)
O2—S1—C2—C3	13.08 (15)	C4—C5—C8—O5	102.5 (2)
C1—S1—C2—C3	−103.11 (13)	C6—C5—C8—C9	101.98 (19)
O1—S1—C2—C7	−37.36 (15)	C4—C5—C8—C9	−81.9 (2)
O2—S1—C2—C7	−166.22 (13)	O5—C8—C9—C10	−0.7 (3)
C1—S1—C2—C7	77.59 (15)	C5—C8—C9—C10	−175.97 (15)
C7—C2—C3—C4	0.3 (2)	O5—C8—C9—C14	178.90 (17)
S1—C2—C3—C4	−179.00 (11)	C5—C8—C9—C14	3.6 (3)
C2—C3—C4—C5	−2.4 (2)	C8—C9—C10—O6	−2.8 (3)
C2—C3—C4—N1	176.38 (13)	C14—C9—C10—O6	177.62 (16)
O3—N1—C4—C3	162.96 (15)	C8—C9—C10—C11	177.56 (17)
O4—N1—C4—C3	−17.2 (2)	C14—C9—C10—C11	−2.0 (3)
O3—N1—C4—C5	−18.3 (2)	O6—C10—C11—C12	151.87 (17)
O4—N1—C4—C5	161.57 (15)	C9—C10—C11—C12	−28.4 (3)
C3—C4—C5—C6	2.0 (2)	C10—C11—C12—C13	53.4 (2)
N1—C4—C5—C6	−176.65 (14)	C11—C12—C13—C14	−51.4 (2)
C3—C4—C5—C8	−174.05 (14)	C10—C9—C14—O7	−172.27 (17)
N1—C4—C5—C8	7.3 (2)	C8—C9—C14—O7	8.1 (3)
C4—C5—C6—C7	0.3 (2)	C10—C9—C14—C13	5.5 (2)
C8—C5—C6—C7	176.70 (14)	C8—C9—C14—C13	−174.07 (16)
C3—C2—C7—C6	2.0 (2)	C12—C13—C14—O7	−160.12 (17)
S1—C2—C7—C6	−178.77 (12)	C12—C13—C14—C9	22.0 (2)
C5—C6—C7—C2	−2.3 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*O*···O5	0.91 (3)	1.71 (3)	2.524 (2)	148 (2)
C1—H1*B*···O4^{i}	0.98	2.58	3.393 (2)	140
C1—H1*B*···O7^{ii}	0.98	2.58	3.265 (2)	127
C11—H11*A*···O3^{iii}	0.99	2.40	3.135 (2)	131

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