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3-(4-Bromophenyl)cyclopent-2-en-1-one

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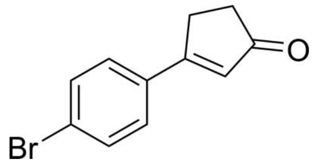
Key indicators: single-crystal X-ray study; *T* = 100 K; mean σ(C–C) = 0.003 Å; *R* factor = 0.025; *wR* factor = 0.057; data-to-parameter ratio = 19.6.

In the title compound, $C_{11}H_9BrO$, the cyclopentenone ring is almost planar with an r.m.s. deviation of 0.0097 Å. The largest inter-ring torsion angles [2.4 (3), 1.3 (3) and 3.53 (2)°] reveal only a very small twist between the rings, and suggest that the two rings are conjugated. The molecule is slightly bowed, as shown by the small dihedral angle between the rings [5.3 (1)°]. The crystal packing pattern consists of parallel sheets that stack parallel to the *ac* plane. Each sheet consists of molecules that pack side-to-side with the same relative orientation of phenyl and cyclopentenone rings along the *a*- and *c*-axis directions. Slipped side-to-side, face-to-face and edge-to-face interactions exist between pairs of sheets with edge-to-edge and edge-to-face O$\cdots$H—C(sp^2) weak hydrogen-bond contacts. A relatively short edge-to-face contact (2.77 Å) also exists between pairs of sheets.

Related literature

For structures of related 3-Ph substituted cyclopent-2-ene-1-ones, see: Zhao *et al.* (2008); Marjani *et al.* (2007, 2008); Jedrzejas *et al.* (1996). For leading references on the synthesis and uses of substituted cyclopentenones, see: Gibson *et al.* (2004); Gibson & Mainolfi (2005); Liu *et al.* (2013); Barluenga *et al.* (2012); Varea *et al.* (2012). For materials chemistry applications, see: Peloquin *et al.* (2012); Li *et al.* (2008). For the synthesis of the title compound, see: Heck (1965). For weak hydrogen bonds, see: Arunan *et al.* (2011).



Experimental

Crystal data

$C_{11}H_9BrO$
M_r = 237.09
Monoclinic, $P2_1/c$
a = 10.0219 (12) Å
b = 9.7818 (11) Å
c = 9.9945 (12) Å
β = 107.4375 (14)°
V = 934.76 (19) Å^3
Z = 4
Mo *Kα* radiation
μ = 4.35 mm^{-1}
T = 100 K
0.30 × 0.13 × 0.07 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan *SADABS* (Bruker, 2013)
T_{min} = 0.53, T_{max} = 0.75
9994 measured reflections
2316 independent reflections
1917 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.057
S = 1.02
2316 reflections
118 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C2—H2$\cdots$O1^{i}	0.95	2.58	3.465 (2)	154
C7—H7$\cdots$O1^{i}	0.95	2.58	3.484 (3)	158
C10—H10$\cdots$O1^{ii}	0.95	2.52	3.377 (2)	150

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

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *SHELXP* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2008).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: MW2122).

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Acta Cryst. (2014). E**70**, o692–o693 Shurdha *et al.* • $C_{11}H_9BrO$ **o693**

supplementary materials

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3-(4-Bromophenyl)cyclopent-2-en-1-one

Endrit Shurdha, Kelsey Dees, Hannah A. Miller, Scott T. Iacono and Gary J. Balaich

1. Comment

Substituted cyclopentenones are found most frequently as intermediates for or parts of complex bioactive molecules and are synthesized by a variety of metal- and non-metal-mediated methodologies (Liu *et al.* (2013), Barluenga *et al.* (2012), Varea *et al.* (2012), Gibson *et al.* (2005), Gibson *et al.* (2004)). We are interested in the use of substituted cyclopentenones as intermediates in the synthesis of fulvenes or fulvene-based polymers with optoelectronic properties suitable for possible molecular electronics applications (Peloquin *et al.* (2012)). The title compound was targeted due to the importance of the Br substituent in Sonagashira or Suzuki coupling methods which will be used to extend the π conjugation of the cyclopentenone and resulting fulvene molecular frameworks. In the course of purifying the title compound, crystals were obtained and, as its structure had not been published, its structure was determined.

The title compound (Fig. 1) consists of a planar Ph ring and an almost planar cyclopentenone ring with r.m.s deviations from the least squares planes of 0.0062 Å (Ph) and 0.0097 Å (cyclopentenone). Conjugation of both rings is evident from the small torsion angles about the C3—C6 bond (C2C3C6C7 = 2.4 (3)°, C4C3C6C11 = 1.3 (3)° and C4C3C6C7 = 3.53 (2)°). The dihedral angle between the phenyl and cyclopentenone rings is 5.3 (1)° resulting in the molecule being slightly bowed along its long axis.

The crystal packing pattern consists of parallel sheets of cyclopentenone molecules (sheets A—D, Fig. 2) that stack parallel to the *ac* plane. Each sheet consists of molecules that pack side-to-side with the same relative orientation of Ph and cyclopentenone groups along the a- and c-axis directions. Slipped side-to-side, face-to-face and edge-to-face interactions exist between pairs of sheets AB, CD, BC, and AD. The shortest intermolecular contacts are weak O···H—C(sp^2) hydrogen bonds (Table 1) with molecules in edge-to-edge and edge-to-face orientations. Although the D—H···A angles (Table 1) deviate substantially from the 180° expected for strong hydrogen bonds, they are large enough to be classified as weak hydrogen bonds (Arunan *et al.* (2011). Furthermore, the H···A distances are shorter than the sum of the H and O van der Waals radii (2.72 Å) (Arunan *et al.* (2011)). The shortest intermolecular contact besides the noted weak hydrogen bonds is the edge-to-face C11–H8 distance (2.77 Å).

2. Experimental

The synthesis of the title compound was carried out using a modification to the original literature procedure (Heck (1965)). The diketone, 1-(4-bromophenyl)-1,4-pentanedione (10.0 g, 39.2 mmol) was combined with 0.5 M NaOH (1 L) and the reaction mixture vigorously stirred and heated at 90 °C for 4 hours. Aliquots were periodically removed to monitor the progress of the reaction by MS-TOF. The reaction mixture was allowed to cool and subsequently neutralized with 1M H_2SO_4. The resulting precipitate was collected by vacuum filtration, washed with water (100 mL), and vacuum dried to give a light brown crude product. Purification was best achieved by column chromatography (dry loaded from CH_2Cl_2) using an EtOAc/hexane mobile phase. A mobile phase of 10% EtOAc/hexane was used to initially remove the colored impurities. This process was followed by 20% EtOAc/hexane to obtain 3-(4-bromophenyl)cyclopent-2-en-1-one as a yellow solid (Yield 5.85 g, 63%). ^{1}H NMR (CDCl$_3$) d 2.55, 2.98 (m, 4H, CH$_2$); 6.52 (t, 1H, CHCO, ^{4}J = 2 Hz); 7.48, 7.55 (m, 4H, BrPhH). ^{13}C NMR (CDCl$_3$) d 28.5, 35.2 (CH$_2$); 125.6, 127.8, 128.1, 132.1, 132.9 (CH and C); 172.3 (CBr); 208.8 (CO). MS-TOF [M+H]$^+$calcd. For $C_{11}H_9BrO$ 236.9915; found 236.9927.

3. Refinement

All hydrogen atoms were placed in calculated positions using a riding model (aryl C—H = 0.95 Å, methylene C—H = 0.99 Å; $U_{iso}(H) = 1.2\ U_{eq}(C)$).

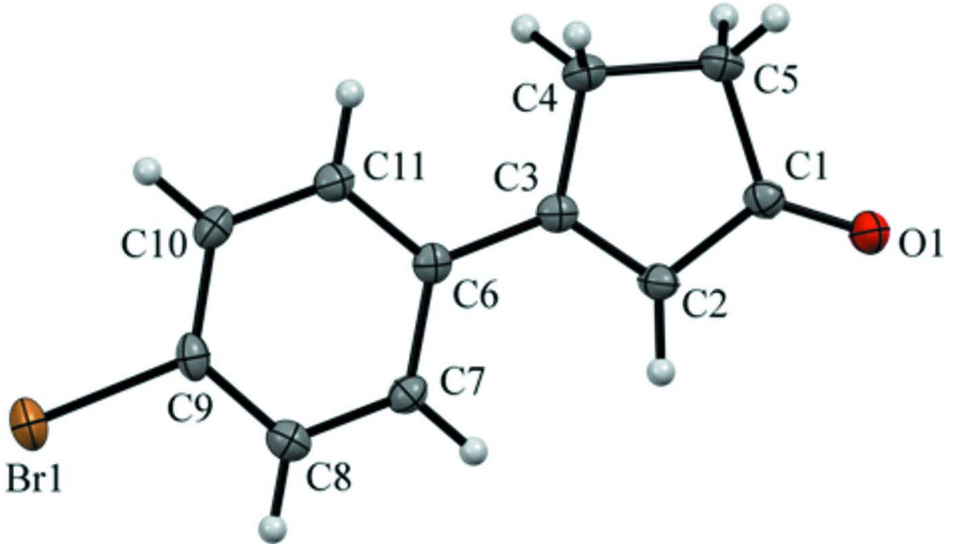

Figure 1

Molecular structure of 3-(4-bromophenyl)cyclopent-2-en-1-one. Ellipsoids are shown at the 50% probability level.

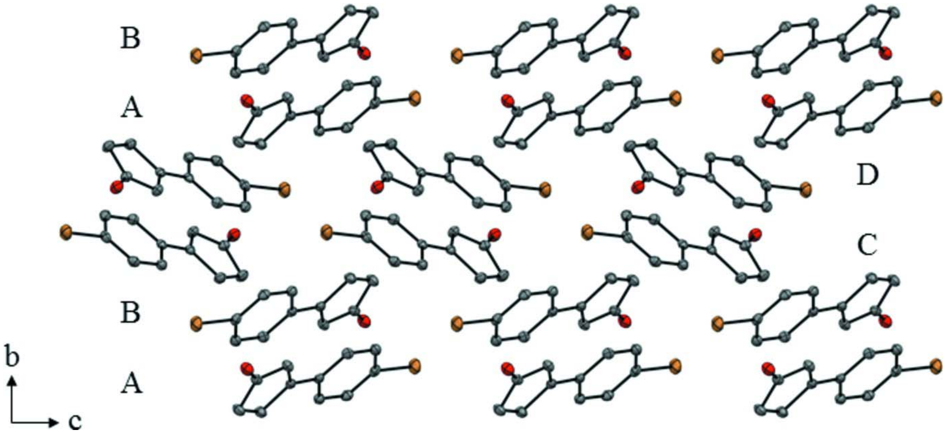

Figure 2

Crystal packing view of 3-(4-bromophenyl)cyclopent-2-en-1-one. View is down the a axis, and shows sheets A-D which stack parallel to the ac plane. Ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

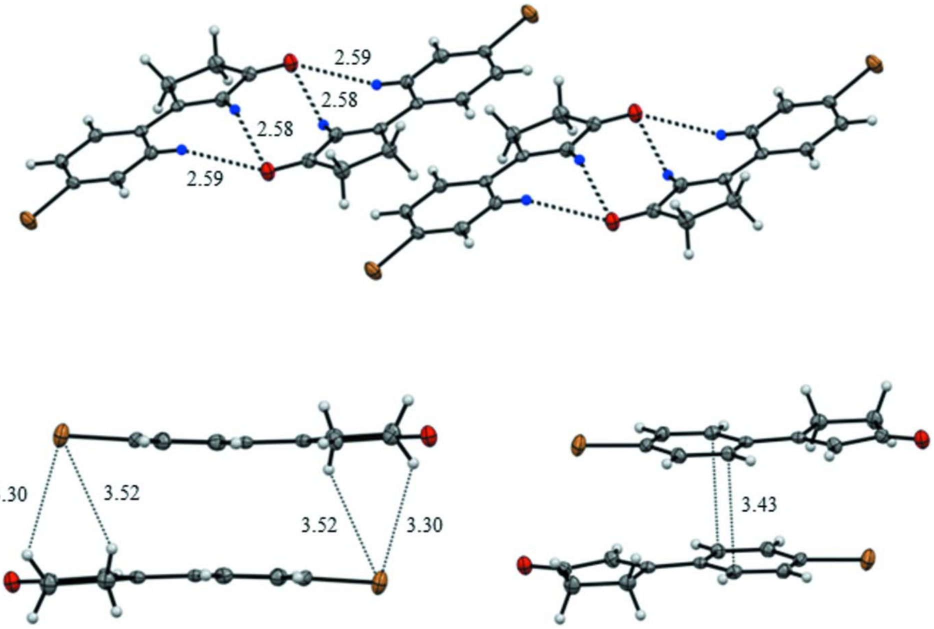

Figure 3

Molecular packing motifs depicting side-to-side and face-to-face intermolecular contacts. The bottom left diagram depicts the bowed molecular axis. The bottom right diagram indicates the C6–Ph ring centroid distance (3.43 Å), which is within error of the C7–C11 distances (3.42 Å, dashed lines). Ellipsoids are shown at the 50% probability level. Distances shown are in Å.

3-(4-Bromophenyl)cyclopent-2-en-1-one

Crystal data

$C_{11}H_9BrO$
$M_r = 237.09$
Monoclinic, $P2_1/c$
$a = 10.0219$ (12) Å
$b = 9.7818$ (11) Å
$c = 9.9945$ (12) Å
$\beta = 107.4375$ (14)°
$V = 934.76$ (19) Å^3
$Z = 4$
$F(000) = 472$
$D_x = 1.685$ Mg m^{-3}
Melting point: 127.0 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3089 reflections
$\theta = 3.0$–28.6°
$\mu = 4.35$ mm^{-1}
$T = 100$ K
Rectangular prism, colourless
0.30 × 0.13 × 0.07 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
ω scans
Absorption correction: multi-scan *SADABS* (Bruker, 2013)
$T_{\min} = 0.53$, $T_{\max} = 0.75$
9994 measured reflections
2316 independent reflections
1917 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.031$
$\theta_{\max} = 28.3°$, $\theta_{\min} = 2.1°$
$h = -13 \rightarrow 13$
$k = -12 \rightarrow 13$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.057$
$S = 1.02$
2316 reflections
118 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
$w = 1/[\sigma^2(F_o^2) + (0.0233P)^2 + 0.4987P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.46$ 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 (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Br1	−0.30717 (2)	0.07926 (2)	0.08100 (2)	0.02888 (8)
O1	0.59890 (14)	0.08928 (13)	0.72449 (14)	0.0228 (3)
C1	0.4771 (2)	0.12867 (19)	0.68736 (19)	0.0181 (4)
C2	0.3642 (2)	0.07755 (19)	0.56825 (19)	0.0181 (4)
H2	0.3743	0.0067	0.507	0.022*
C3	0.2442 (2)	0.14462 (17)	0.55725 (18)	0.0154 (4)
C4	0.2622 (2)	0.24952 (19)	0.67199 (19)	0.0204 (4)
H4A	0.2025	0.2274	0.732	0.024*
H4B	0.2377	0.342	0.6319	0.024*
C5	0.4180 (2)	0.2416 (2)	0.7563 (2)	0.0229 (4)
H5A	0.4655	0.3295	0.7519	0.027*
H5B	0.4294	0.2194	0.8558	0.027*
C6	0.10968 (19)	0.12424 (18)	0.44782 (18)	0.0152 (4)
C7	0.0981 (2)	0.03111 (18)	0.33801 (19)	0.0177 (4)
H7	0.1767	−0.0228	0.3368	0.021*
C8	−0.0265 (2)	0.01702 (19)	0.23155 (19)	0.0198 (4)
H8	−0.0338	−0.0465	0.1578	0.024*
C9	−0.1403 (2)	0.09624 (19)	0.23345 (19)	0.0187 (4)
C10	−0.1341 (2)	0.18783 (19)	0.34090 (19)	0.0191 (4)
H10	−0.2135	0.2406	0.3416	0.023*
C11	−0.0086 (2)	0.20035 (18)	0.44772 (19)	0.0181 (4)
H11	−0.0029	0.2622	0.5225	0.022*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02309 (12)	0.03472 (13)	0.02207 (11)	0.00371 (9)	−0.00349 (8)	−0.00033 (8)
O1	0.0171 (7)	0.0241 (7)	0.0251 (7)	0.0006 (5)	0.0031 (6)	−0.0043 (6)
C1	0.0187 (10)	0.0163 (8)	0.0192 (9)	−0.0016 (7)	0.0054 (8)	−0.0006 (7)
C2	0.0183 (10)	0.0187 (9)	0.0179 (9)	−0.0011 (7)	0.0063 (8)	−0.0043 (7)

C3	0.0189 (9)	0.0134 (8)	0.0157 (8)	−0.0017 (7)	0.0077 (7)	0.0018 (6)
C4	0.0223 (10)	0.0172 (9)	0.0218 (9)	0.0016 (7)	0.0068 (8)	−0.0031 (7)
C5	0.0239 (10)	0.0203 (9)	0.0226 (9)	0.0004 (8)	0.0039 (8)	−0.0071 (8)
C6	0.0168 (9)	0.0135 (8)	0.0159 (8)	−0.0017 (7)	0.0061 (7)	0.0033 (6)
C7	0.0169 (10)	0.0175 (8)	0.0202 (9)	0.0012 (7)	0.0078 (8)	0.0007 (7)
C8	0.0219 (10)	0.0197 (9)	0.0180 (9)	−0.0028 (7)	0.0063 (8)	−0.0013 (7)
C9	0.0167 (10)	0.0215 (9)	0.0161 (9)	−0.0004 (7)	0.0021 (7)	0.0053 (7)
C10	0.0181 (10)	0.0178 (9)	0.0222 (9)	0.0041 (7)	0.0073 (8)	0.0028 (7)
C11	0.0211 (10)	0.0166 (8)	0.0177 (9)	0.0011 (7)	0.0076 (8)	0.0009 (7)

Geometric parameters (Å, º)

Br1—C9	1.9022 (19)	C5—H5B	0.99
O1—C1	1.226 (2)	C6—C11	1.399 (3)
C1—C2	1.463 (3)	C6—C7	1.404 (3)
C1—C5	1.514 (3)	C7—C8	1.383 (3)
C2—C3	1.346 (3)	C7—H7	0.95
C2—H2	0.95	C8—C9	1.384 (3)
C3—C6	1.473 (3)	C8—H8	0.95
C3—C4	1.509 (2)	C9—C10	1.386 (3)
C4—C5	1.538 (3)	C10—C11	1.391 (3)
C4—H4A	0.99	C10—H10	0.95
C4—H4B	0.99	C11—H11	0.95
C5—H5A	0.99		
O1—C1—C2	126.57 (17)	H5A—C5—H5B	108.8
O1—C1—C5	125.55 (17)	C11—C6—C7	118.25 (17)
C2—C1—C5	107.87 (16)	C11—C6—C3	120.99 (16)
C3—C2—C1	110.76 (16)	C7—C6—C3	120.72 (16)
C3—C2—H2	124.6	C8—C7—C6	120.64 (18)
C1—C2—H2	124.6	C8—C7—H7	119.7
C2—C3—C6	126.28 (17)	C6—C7—H7	119.7
C2—C3—C4	111.66 (16)	C7—C8—C9	119.44 (18)
C6—C3—C4	122.05 (16)	C7—C8—H8	120.3
C3—C4—C5	104.63 (15)	C9—C8—H8	120.3
C3—C4—H4A	110.8	C8—C9—C10	121.80 (18)
C5—C4—H4A	110.8	C8—C9—Br1	118.07 (14)
C3—C4—H4B	110.8	C10—C9—Br1	120.11 (14)
C5—C4—H4B	110.8	C9—C10—C11	118.16 (17)
H4A—C4—H4B	108.9	C9—C10—H10	120.9
C1—C5—C4	105.03 (15)	C11—C10—H10	120.9
C1—C5—H5A	110.7	C10—C11—C6	121.68 (17)
C4—C5—H5A	110.7	C10—C11—H11	119.2
C1—C5—H5B	110.7	C6—C11—H11	119.2
C4—C5—H5B	110.7		
O1—C1—C2—C3	−179.48 (18)	C4—C3—C6—C7	176.47 (16)
C5—C1—C2—C3	−0.5 (2)	C11—C6—C7—C8	1.1 (3)
C1—C2—C3—C6	177.94 (16)	C3—C6—C7—C8	−176.78 (16)
C1—C2—C3—C4	−1.0 (2)	C6—C7—C8—C9	0.3 (3)

C2—C3—C4—C5	2.0 (2)	C7—C8—C9—C10	−1.3 (3)
C6—C3—C4—C5	−176.98 (16)	C7—C8—C9—Br1	177.38 (14)
O1—C1—C5—C4	−179.30 (18)	C8—C9—C10—C11	0.9 (3)
C2—C1—C5—C4	1.7 (2)	Br1—C9—C10—C11	−177.78 (13)
C3—C4—C5—C1	−2.16 (19)	C9—C10—C11—C6	0.5 (3)
C2—C3—C6—C11	179.84 (18)	C7—C6—C11—C10	−1.5 (3)
C4—C3—C6—C11	−1.3 (3)	C3—C6—C11—C10	176.34 (16)
C2—C3—C6—C7	−2.4 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1^{i}	0.95	2.58	3.465 (2)	154
C7—H7···O1^{i}	0.95	2.58	3.484 (3)	158
C10—H10···O1^{ii}	0.95	2.52	3.377 (2)	150

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