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4-(3-Bromopropyloxy)-1-hydroxy-9,10-anthraquinone

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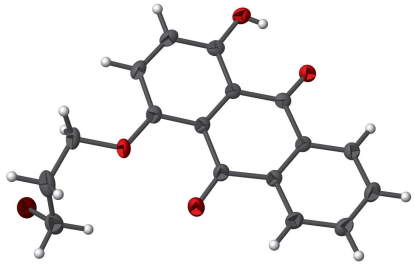
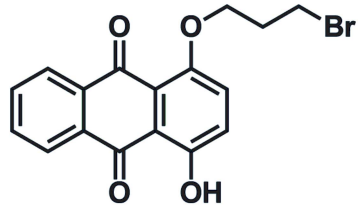
In the molecule of the title compound, $C_{17}H_{13}BrO_4$, the anthraquinone ring system is slightly bent, with a dihedral angle of 169.99 (7)° between the planes of the two benzene rings. The side chain (O—C—C—C—Br) has a *gauche–gauche* conformation, as indicated by the O—C—C—C and C—C—C—Br torsion angles of −66.9 (2) and −65.8 (2)°, respectively. In addition, there is an intramolecular O—H···O hydrogen bond enclosing an *S*(6) ring motif. The hydrogen-bond donor is bifurcated; in the crystal, a pair of O—H···O hydrogen bonds connects two molecules, forming an inversion dimer with an $R_2^2(12)$ ring motif.

3D view



Chemical scheme



Structure description

A large number of anthraquinone derivatives have been manufactured as dyes and pigments. We have recently investigated alkoxy-substituted anthraquinone molecules (Kitamura *et al.* 2015*a*,*b*; Ohta *et al.* 2012*a*,*b*). As a continuation of our efforts to synthesize new anthraquinone derivatives, we report here the crystal structure of the title compound.

The molecular structure of the title compound is shown in Fig. 1. The anthraquinone ring is slightly bent with a dihedral angle of 169.99 (7)° between the two terminal benzene rings due to repulsion between two O atoms in *peri* positions on the anthracene ring. The side chain (O–C–C–C–Br) has a *gauche-gauche* conformation, as indicated by the O2—C15—C16—C17 and C15—C16—C17—Br1 torsion angles of −66.9 (2) and −65.8 (2)°, respectively. In addition, there is an intramolecular O1–H1···O4 hydrogen bond enclosing an *S*(6) ring motif (Table 1).

The crystal packing of the title compound is shown in Figs. 2 and 3. The sole hydrogen-bond donor is bifurcated, as a pair of O1—H1···O4^{i} [symmetry code: (i) $-x-\frac{1}{2}, -y+\frac{5}{2}, -z+1$] hydrogen bonds connect two molecules, forming an inversion dimer that

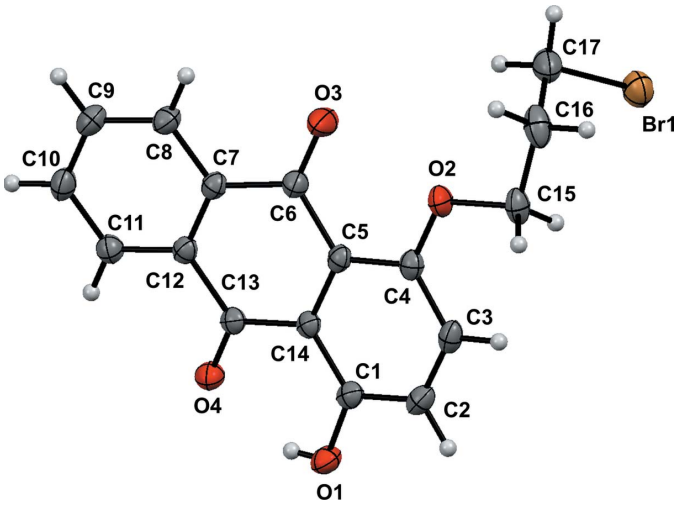


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme, with 50% probability displacement ellipsoids.

generates a $R_2^2(12)$ ring motif (Table 1 and Fig. 2). The molecules adopt a herringbone-like arrangement without π–π stacking (Fig. 3).

Synthesis and crystallization

A mixture of 1,4-dihydroxy-9,10-anthraquinone (243 mg, 1.01 mmol), 1,3-dibromopropane (1.02 g, 5.07 mmol), and potassium carbonate (142 mg, 1.02 mmol) in DMF (5 ml) was stirred at 80 °C for 3 h. After cooling to room temperature, water (50 ml) was added to the mixture, then the resulting solid was extracted with dichloromethane. The organic extract was washed with 1 *M* NaOH and brine successively, and dried over Na_2SO_4. After filtration and evaporation, chromatography on silica gel with eluents of dichloromethane–hexane (2:1 to 3:1) afforded the title compound as an orange solid in 50% yield. Suitable single crystals for X-ray diffraction were obtained by slow evaporation from a dichloromethane solution. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41–2.47 (*m*, 2H), 3.86 (*t*, *J* = 6.2 Hz, 2H), 4.28 (*t*, *J* = 5.6 Hz, 2H), 7.32 (*d*, *J* = 9.5 Hz, 1H), 7.42 (*d*, *J* = 9.5 Hz, 1H), 7.75–7.83 (*m*, 2H), 8.26–8.30 (*m*, 2H), 13.03 (*s*, 1H).

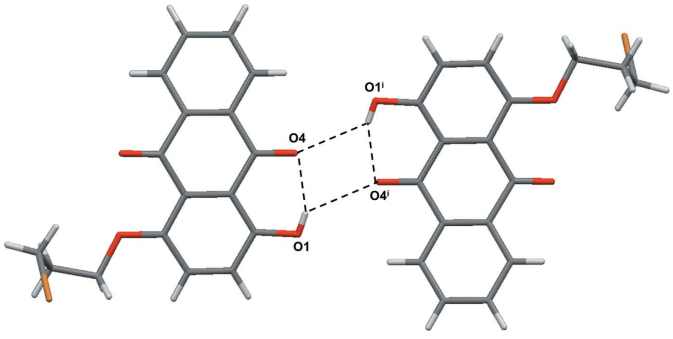


Figure 2
A pair of molecules connected by hydrogen bonds (dashed lines).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4	0.67 (3)	1.96 (3)	2.569 (2)	152 (3)
O1—H1···O4^{i}	0.67 (3)	2.52 (3)	3.018 (2)	133 (3)

Symmetry code: (i) $-x-\frac{1}{2}, -y+\frac{5}{2}, -z+1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{13}BrO_4$
M_r	361.17
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	200
a, *b*, *c* (Å)	29.889 (2), 4.8479 (3), 20.0427 (16)
β (°)	104.337 (2)
V (Å^3)	2813.7 (3)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	2.94
Crystal size (mm)	0.53 × 0.23 × 0.13
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Numerical (*NUMABS*; Higashi, 1999)
T_{min}, T_{max}	0.634, 0.825
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12835, 3215, 2628
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.03, 0.080, 1.10
No. of reflections	3215
No. of parameters	203
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.69

Computer programs: *PROCESS-AUTO* (Rigaku, 1998), *SIR2004* (Burla *et al.*, 2005), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *WinGX* (Farrugia, 2012).

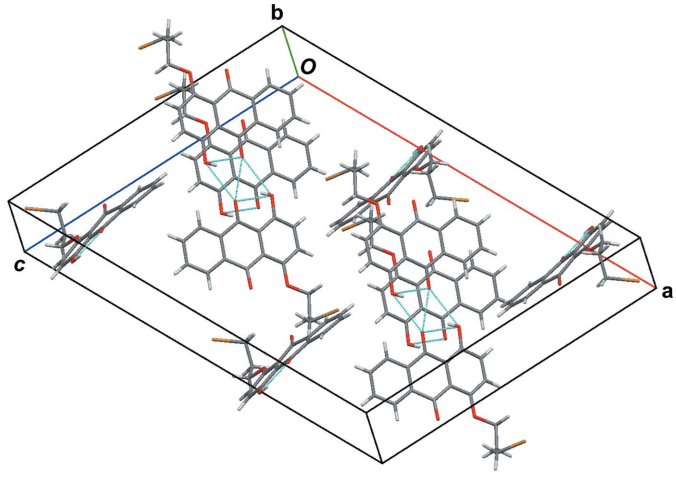


Figure 3
The crystal packing of the title compound. Hydrogen bonds are shown as blue lines.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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Crystal data

$C_{17}H_{13}BrO_4$
M_r = 361.17
Monoclinic, $C2/c$
Hall symbol: -C 2yc
a = 29.889 (2) Å
b = 4.8479 (3) Å
c = 20.0427 (16) Å
β = 104.337 (2)°
V = 2813.7 (3) Å^3
Z = 8
$F(000)$ = 1456
D_x = 1.705 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 10102 reflections
θ = 3.1–27.5°
μ = 2.94 mm^{-1}
T = 200 K
Prism, orange
0.53 × 0.23 × 0.13 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed x-ray tube
Graphite monochromator
Detector resolution: 10 pixels mm^{-1}
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
T_{min} = 0.634, T_{max} = 0.825
12835 measured reflections
3215 independent reflections
2628 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 27.5°, θ_{min} = 3.1°
h = −38→38
k = −5→6
l = −26→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.03
$wR(F^2)$ = 0.080
S = 1.10
3215 reflections
203 parameters
0 restraints
0 constraints
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 2.572P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. All the H atoms except for the OH group were positioned geometrically and refined using a riding model. The H atom of the OH group was located in a difference Fourier map and freely refined [O1—H1 = 0.67 (3) Å].

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.18216 (7)	0.7307 (4)	0.48851 (10)	0.0231 (4)
C2	−0.16048 (7)	0.5298 (4)	0.45775 (10)	0.0271 (4)
H2	−0.1698	0.5048	0.4093	0.033*
C3	−0.12604 (7)	0.3680 (4)	0.49621 (11)	0.0264 (4)
H3	−0.1118	0.233	0.4739	0.032*
C4	−0.11142 (7)	0.3985 (4)	0.56807 (10)	0.0235 (4)
C5	−0.13341 (7)	0.5936 (4)	0.60097 (10)	0.0211 (4)
C6	−0.11938 (7)	0.6333 (4)	0.67703 (10)	0.0251 (4)
C7	−0.14927 (7)	0.8127 (4)	0.70852 (10)	0.0218 (4)
C8	−0.14180 (8)	0.8172 (4)	0.78014 (10)	0.0267 (4)
H8	−0.1183	0.7057	0.808	0.032*
C9	−0.16879 (8)	0.9849 (4)	0.81046 (10)	0.0290 (5)
H9	−0.1643	0.9839	0.8591	0.035*
C10	−0.20230 (8)	1.1541 (5)	0.77035 (11)	0.0299 (5)
H10	−0.2203	1.2703	0.7917	0.036*
C11	−0.20967 (7)	1.1542 (4)	0.69926 (11)	0.0255 (4)
H11	−0.2323	1.2722	0.6718	0.031*
C12	−0.18360 (7)	0.9795 (4)	0.66838 (10)	0.0215 (4)
C13	−0.19313 (6)	0.9690 (4)	0.59259 (9)	0.0211 (4)
C14	−0.16913 (7)	0.7614 (4)	0.56037 (10)	0.0204 (4)
C15	−0.05195 (7)	0.0603 (4)	0.57274 (12)	0.0294 (5)
H15A	−0.0392	0.1641	0.5392	0.035*
H15B	−0.0726	−0.0857	0.5478	0.035*
C16	−0.01362 (8)	−0.0647 (5)	0.62740 (13)	0.0371 (5)
H16A	0.0012	−0.2119	0.6062	0.045*
H16B	−0.0271	−0.152	0.6626	0.045*
C17	0.02288 (8)	0.1368 (6)	0.66265 (12)	0.0375 (5)
H17A	0.0447	0.044	0.7014	0.045*
H17B	0.0082	0.2912	0.6817	0.045*
O1	−0.21479 (6)	0.8858 (4)	0.44614 (8)	0.0289 (3)
O2	−0.07696 (5)	0.2429 (3)	0.60734 (8)	0.0290 (3)
O3	−0.08479 (6)	0.5313 (4)	0.71384 (8)	0.0456 (5)
O4	−0.22127 (5)	1.1299 (3)	0.55713 (7)	0.0279 (3)
Br1	0.05677 (2)	0.28203 (5)	0.59770 (2)	0.03874 (10)
H1	−0.2231 (10)	0.970 (6)	0.4668 (16)	0.046 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0230 (10)	0.0262 (10)	0.0209 (9)	−0.0059 (9)	0.0069 (8)	0.0016 (8)
C2	0.0336 (11)	0.0290 (10)	0.0202 (9)	−0.0061 (10)	0.0096 (8)	−0.0035 (8)
C3	0.0299 (11)	0.0256 (10)	0.0276 (10)	−0.0046 (9)	0.0145 (8)	−0.0075 (8)
C4	0.0233 (10)	0.0239 (9)	0.0258 (10)	−0.0019 (9)	0.0106 (8)	−0.0001 (8)
C5	0.0217 (9)	0.0229 (9)	0.0208 (9)	−0.0028 (9)	0.0093 (7)	0.0000 (8)
C6	0.0263 (10)	0.0276 (10)	0.0224 (10)	0.0029 (9)	0.0079 (8)	−0.0001 (8)

C7	0.0232 (10)	0.0226 (9)	0.0210 (9)	−0.0018 (8)	0.0080 (7)	0.0000 (7)
C8	0.0311 (11)	0.0290 (10)	0.0200 (9)	0.0009 (9)	0.0065 (8)	0.0007 (8)
C9	0.0361 (12)	0.0311 (11)	0.0211 (10)	−0.0005 (10)	0.0096 (8)	−0.0020 (8)
C10	0.0320 (12)	0.0325 (11)	0.0287 (11)	0.0000 (10)	0.0140 (9)	−0.0065 (9)
C11	0.0245 (10)	0.0261 (10)	0.0265 (10)	0.0015 (9)	0.0075 (8)	−0.0004 (8)
C12	0.0209 (9)	0.0237 (9)	0.0212 (9)	−0.0046 (8)	0.0075 (7)	−0.0019 (7)
C13	0.0199 (9)	0.0226 (9)	0.0216 (9)	−0.0034 (8)	0.0066 (7)	0.0017 (8)
C14	0.0193 (9)	0.0226 (9)	0.0207 (9)	−0.0040 (8)	0.0076 (7)	0.0010 (7)
C15	0.0287 (11)	0.0244 (10)	0.0395 (12)	0.0017 (9)	0.0168 (9)	−0.0062 (9)
C16	0.0382 (13)	0.0282 (11)	0.0522 (15)	0.0085 (11)	0.0248 (11)	0.0073 (10)
C17	0.0317 (12)	0.0496 (14)	0.0338 (12)	0.0079 (12)	0.0132 (9)	0.0061 (11)
O1	0.0346 (9)	0.0318 (8)	0.0200 (7)	0.0025 (8)	0.0059 (6)	0.0018 (7)
O2	0.0273 (8)	0.0313 (8)	0.0298 (8)	0.0099 (7)	0.0098 (6)	−0.0027 (6)
O3	0.0430 (10)	0.0651 (12)	0.0256 (8)	0.0297 (9)	0.0026 (7)	−0.0026 (8)
O4	0.0293 (8)	0.0304 (7)	0.0238 (7)	0.0054 (7)	0.0064 (6)	0.0034 (6)
Br1	0.03190 (15)	0.04575 (16)	0.04142 (15)	−0.00323 (11)	0.01446 (10)	−0.00340 (10)

Geometric parameters (Å, º)

C1—O1	1.352 (3)	C10—C11	1.387 (3)
C1—C2	1.395 (3)	C10—H10	0.95
C1—C14	1.404 (3)	C11—C12	1.395 (3)
C2—C3	1.370 (3)	C11—H11	0.95
C2—H2	0.95	C12—C13	1.475 (3)
C3—C4	1.406 (3)	C13—O4	1.235 (2)
C3—H3	0.95	C13—C14	1.475 (3)
C4—O2	1.359 (3)	C15—O2	1.443 (2)
C4—C5	1.406 (3)	C15—C16	1.503 (3)
C5—C14	1.426 (3)	C15—H15A	0.99
C5—C6	1.490 (3)	C15—H15B	0.99
C6—O3	1.216 (3)	C16—C17	1.504 (4)
C6—C7	1.494 (3)	C16—H16A	0.99
C7—C12	1.395 (3)	C16—H16B	0.99
C7—C8	1.397 (3)	C17—Br1	1.967 (2)
C8—C9	1.387 (3)	C17—H17A	0.99
C8—H8	0.95	C17—H17B	0.99
C9—C10	1.387 (3)	O1—H1	0.67 (3)
C9—H9	0.95		

O1—C1—C2	116.91 (18)	C10—C11—H11	120.3
O1—C1—C14	124.01 (19)	C12—C11—H11	120.3
C2—C1—C14	119.08 (19)	C11—C12—C7	120.53 (18)
C3—C2—C1	121.18 (19)	C11—C12—C13	119.41 (18)
C3—C2—H2	119.4	C7—C12—C13	120.06 (18)
C1—C2—H2	119.4	O4—C13—C14	120.99 (17)
C2—C3—C4	121.08 (19)	O4—C13—C12	120.08 (18)
C2—C3—H3	119.5	C14—C13—C12	118.92 (17)
C4—C3—H3	119.5	C1—C14—C5	120.23 (18)

O2—C4—C5	118.49 (17)	C1—C14—C13	118.69 (18)
O2—C4—C3	122.27 (18)	C5—C14—C13	121.07 (17)
C5—C4—C3	119.23 (19)	O2—C15—C16	106.80 (18)
C4—C5—C14	119.15 (17)	O2—C15—H15A	110.4
C4—C5—C6	121.38 (18)	C16—C15—H15A	110.4
C14—C5—C6	119.45 (17)	O2—C15—H15B	110.4
O3—C6—C5	123.34 (19)	C16—C15—H15B	110.4
O3—C6—C7	119.20 (18)	H15A—C15—H15B	108.6
C5—C6—C7	117.45 (17)	C15—C16—C17	114.46 (19)
C12—C7—C8	119.42 (19)	C15—C16—H16A	108.6
C12—C7—C6	121.69 (17)	C17—C16—H16A	108.6
C8—C7—C6	118.88 (18)	C15—C16—H16B	108.6
C9—C8—C7	119.80 (19)	C17—C16—H16B	108.6
C9—C8—H8	120.1	H16A—C16—H16B	107.6
C7—C8—H8	120.1	C16—C17—Br1	110.74 (16)
C10—C9—C8	120.50 (19)	C16—C17—H17A	109.5
C10—C9—H9	119.7	Br1—C17—H17A	109.5
C8—C9—H9	119.7	C16—C17—H17B	109.5
C9—C10—C11	120.3 (2)	Br1—C17—H17B	109.5
C9—C10—H10	119.9	H17A—C17—H17B	108.1
C11—C10—H10	119.9	C1—O1—H1	106 (3)
C10—C11—C12	119.43 (19)	C4—O2—C15	118.08 (16)

O1—C1—C2—C3	178.06 (19)	C6—C7—C12—C11	−177.15 (19)
C14—C1—C2—C3	−1.7 (3)	C8—C7—C12—C13	−177.60 (18)
C1—C2—C3—C4	0.1 (3)	C6—C7—C12—C13	3.9 (3)
C2—C3—C4—O2	−179.21 (19)	C11—C12—C13—O4	6.0 (3)
C2—C3—C4—C5	1.6 (3)	C7—C12—C13—O4	−175.04 (18)
O2—C4—C5—C14	179.03 (17)	C11—C12—C13—C14	−173.10 (18)
C3—C4—C5—C14	−1.8 (3)	C7—C12—C13—C14	5.9 (3)
O2—C4—C5—C6	0.6 (3)	O1—C1—C14—C5	−178.24 (18)
C3—C4—C5—C6	179.75 (19)	C2—C1—C14—C5	1.5 (3)
C4—C5—C6—O3	10.5 (3)	O1—C1—C14—C13	1.9 (3)
C14—C5—C6—O3	−168.0 (2)	C2—C1—C14—C13	−178.33 (18)
C4—C5—C6—C7	−170.74 (18)	C4—C5—C14—C1	0.2 (3)
C14—C5—C6—C7	10.8 (3)	C6—C5—C14—C1	178.72 (18)
O3—C6—C7—C12	166.6 (2)	C4—C5—C14—C13	−179.93 (17)
C5—C6—C7—C12	−12.2 (3)	C6—C5—C14—C13	−1.4 (3)
O3—C6—C7—C8	−11.9 (3)	O4—C13—C14—C1	−6.3 (3)
C5—C6—C7—C8	169.24 (19)	C12—C13—C14—C1	172.72 (17)
C12—C7—C8—C9	0.6 (3)	O4—C13—C14—C5	173.83 (18)
C6—C7—C8—C9	179.19 (19)	C12—C13—C14—C5	−7.1 (3)
C7—C8—C9—C10	−1.8 (3)	O2—C15—C16—C17	−66.9 (2)
C8—C9—C10—C11	1.0 (3)	C15—C16—C17—Br1	−65.8 (2)
C9—C10—C11—C12	1.0 (3)	C5—C4—O2—C15	−174.77 (17)
C10—C11—C12—C7	−2.2 (3)	C3—C4—O2—C15	6.1 (3)
C10—C11—C12—C13	176.79 (19)	C16—C15—O2—C4	174.93 (18)
C8—C7—C12—C11	1.4 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4	0.67 (3)	1.96 (3)	2.569 (2)	152 (3)
O1—H1···O4^{i}	0.67 (3)	2.52 (3)	3.018 (2)	133 (3)

Symmetry code: (i) −*x*−1/2, −*y*+5/2, −*z*+1.