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Crystal structure of 3-hydroxy-2-(4-hydroxy-3-methoxyphenylmethyl)-5,5-dimethylcyclohex-2-enone

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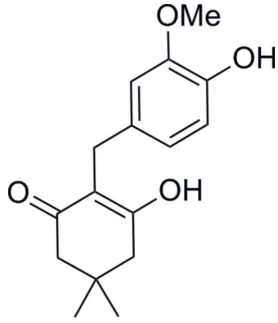
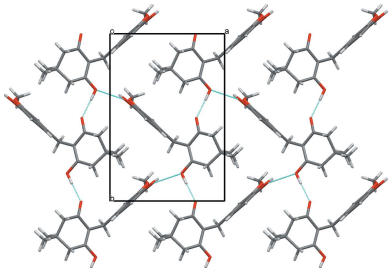
In the title compound, $C_{16}H_{20}O_4$, a new starting compound for the synthesis of various heterocycles, the partially saturated six-membered ring adopts a sofa conformation. An intramolecular O—H···O hydrogen bond is observed in the guaiacol residue. In the crystal, molecules are assembled into a sheet structure parallel to the *ab* plane *via* O—H···O hydrogen bonds. The hydrogen-bond pattern is described by an $R_4^4(28)$ graph-set motif. The sheets are further linked by C—H···O hydrogen bonds into a three-dimensional network.

1. Chemical context

Cyclic 2-arylmethyl-1,3-diketones attract interest as valuable intermediates for organic chemistry. A few of the latest examples of these cyclohexanedione derivatives have been used as starting compounds for the synthesis of various heterocycles [*e.g.* tetrahydrobenzofuranones (Yoshida *et al.*, 2010) or tetrahydro-1*H*-xanthen-1-ones (Sudheendran *et al.*, 2012)], as well as carbocycles, *e.g.* analogues of Wieland–Miesher and Hajos–Parrish ketones (Xu *et al.*, 2013).



1a



2. Structural commentary

Fig. 1 shows the molecular structure of the title compound, which exhibits an intramolecular O—H···O hydrogen bond (Table 1). In crystalline state, the molecules assume the enol tautomeric form, **1a**. In the dimedone fragment, the bond distances reflect the effect of conjugation in the flat fragment O1═C3—C4═C5—O2. The double bonds, O1═C3 and C4═C5, are elongated [1.246 (2) and 1.357 (3) Å, respectively], while the single bond C3—C4 is shortened

[1.447 (3) Å] as compared with standard double and single bonds (Allen *et al.*, 1987). The general shape of the molecule is characterized by the torsion angles C3—C4—C7—C8 = −62.8 (2)° and C4—C7—C8—C9 = 152.2 (2)°, thus exhibiting an extended conformation. The partially saturated C1–C6 ring adopts a sofa conformation. The distance of atom C1 from the mean plane formed by atoms C2–C6 is 0.612 (3) Å. The dihedral angle between the mean plane of the C1–C6 ring and the C8–C13 benzene ring is 75.69 (6)°.

3. Supramolecular features

In the crystal, the molecules are assembled into a sheet structure parallel to the *ab* plane *via* O—H···O hydrogen bonds (Table 1). The hydrogen-bonding pattern in the sheet is described by an $R_4^4(28)$ graph-set motif (Fig. 2). Furthermore, weak C—H···O hydrogen bonds join the sheets into a three-dimensional network (Table 1).

4. Database survey

A search of the Cambridge Structural Database (Version 5.39, last update February 2018; Groom *et al.*, 2016) gave 76 structures of 3-hydroxy-5,5-dimethylcyclohex-2-enone derivatives. The closest structures are 2-(naphthalen-1-ylmethyl)- and 2-(3-chlorophenyl)methyl-substituted dimedones (NIHTEE and NIHTII, respectively; Ramachary & Kishor, 2007).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···O4^{i}	0.97	2.49	3.417 (3)	161
C14—H14*C*···O1^{ii}	0.96	2.49	3.247 (3)	136
O2—H2···O1^{iii}	0.88 (3)	1.74 (3)	2.586 (2)	161 (3)
O4—H4···O3	0.94 (4)	2.10 (4)	2.638 (2)	115 (3)
O4—H4···O2^{iv}	0.94 (4)	2.11 (4)	2.919 (2)	142 (3)

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

5. Antiradical activity against free radicals

Compound **1** demonstrates notable antiradical activity against free radicals. Free radical tests were realized according to the procedures described previously (Mierina *et al.*, 2017). 1,1-Diphenyl-2-picrylhydrazyl test: inhibition, when molar ratio of the compound and free radical is 1:1, was 93.3±2.5%; IC_{50} was 23.0±0.6 µM (starting concentration of free radical was 100 µM). Galvinoxyl test: inhibition was 82.3±1.0% and IC_{50} – 20.3±2.0 µM.

6. Synthesis and crystallization

3-Hydroxy-2-(4-hydroxy-3-methoxyphenylmethyl)-5,5-dimethylcyclohex-2-enone (**1a**) was synthesized according to the reaction scheme in Fig. 3. Formic acid (3.6 ml) was added to a solution of dimedone **2** (500 mg, 3.6 mmol) and vanillin **3** (543 mg, 3.6 mmol) in triethylamine (5.5 ml) while cooling in an ice-bath. The reaction mixture was then heated at 413 K for 5 h, followed by cooling to room temperature, pouring into ice (700–800 ml) and filtering the formed solid. The solid material

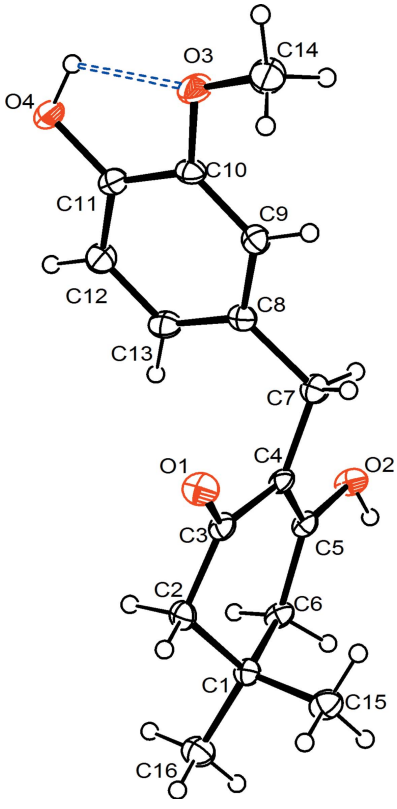


Figure 1
The molecular structure of the title compound, with the atom-numbering scheme and 50% probability displacement ellipsoids. The intramolecular hydrogen bond is shown as a double-dashed line.

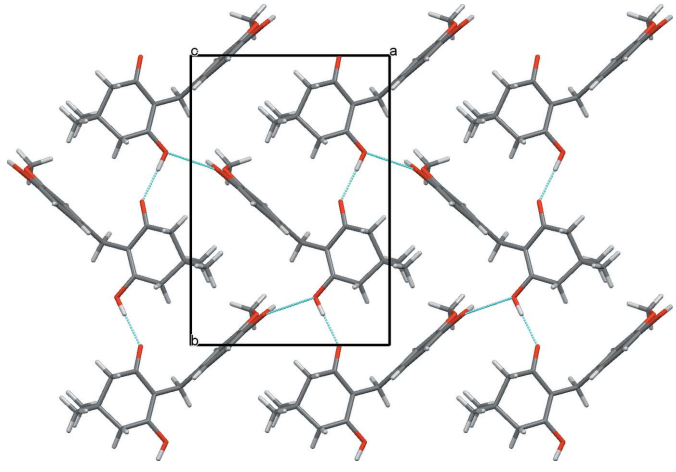


Figure 2
A packing diagram of the title compound, viewed along the *c* axis. O—H···O hydrogen bonds are shown as dashed lines. For clarity weak C—H···O bonds are not depicted.

was purified by crystallization from chloroform leading to the target compound **1a** (615 mg, 62%) with m.p. 466–468 K. Single crystals were obtained from a methanol solution. IR (KBr) ν, cm^{-1}: 3470, 2935, 2645, 1580, 1515, 1375, 1250, 1230, 1200, 1040.

The enol form, **1a**, was observed exclusively in a DMSO solution. ^{1}H NMR for compound **1a** (300 MHz, DMSO-d_6) δ, ppm: 10.71–10.08 (1H, *brs*, OH), 8.68–8.37 (1H, *brs*, OH), 6.68 (1H, *s*, H^{Ar}), 6.59 (1H, *d*, J = 7.7 Hz, H^{Ar}), 6.50 (1H, *d*, J = 7.7 Hz, H^{Ar}), 3.68 (3H, *s*, OMe), 3.41 (2H, *brs*, CH_2Ar, overlapping with H_2O signal), 2.34–2.13 (4H, *brs*, 2CH_2), 0.98 (6H, *s*, 2Me). ^{13}C NMR for compound **1a** (75 MHz, DMSO-d_6) δ, ppm: 147.1, 144.1, 132.7, 120.2, 115.0, 113.3, 112.5, 55.5, 31.7, 28.0, 26.5. Mixture of keto–enol tautomers (**1a** and **1b**) was observed in a chloroform solution. The ratio of enol **1a** and ketone **1b** was 1.35:1 (at room temperature). ^{1}H NMR for compound **1a** (300 MHz, $CDCl_3$) δ, ppm: 6.84–6.63 (3H, *m*, H^{Ar}), (2H, *brs*, 2OH), 3.82 (3H, *s*, OMe), 3.61 (2H, *s*, CH_2Ar), 2.33–2.29 (4H, *brs*, 2CH_2), 1.07 (6H, *s*, 2Me). ^{1}H NMR for compound **1b** (300 MHz, $CDCl_3$) δ, ppm: 6.84–6.63 (3H, *m*, H^{Ar}), 5.62–5.68 (1H, *brs*, OH), 3.86 (3H, *s*, OMe), 3.56 (1H, *t*, J = 5.4 Hz, $CHCH_2$), 3.11 (2H, *d*, J = 5.4 Hz, $CHCH_2$), 2.65 (2H, *d*, J = 13.4 Hz, H^a from CH_2), 2.44 (2H, *d*, J = 13.4 Hz, H^b from CH_2), 1.16 (3H, *s*, Me), 0.82 (3H, s, Me).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms bonded to O atoms were refined freely. Other H atoms were included in the refinement at geometrically calculated positions with C—H = 0.93–0.97 Å and treated as riding with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C-methyl).

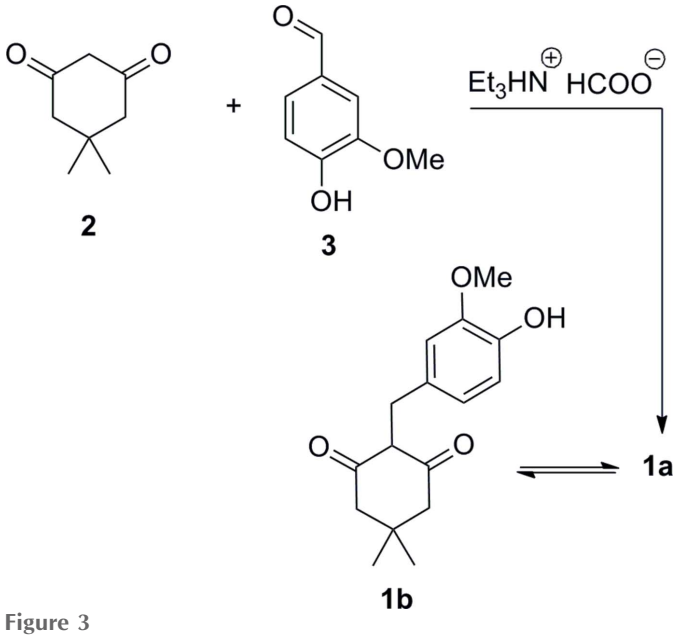


Figure 3
Reaction scheme for the title compound (**1a**) and its tautomer (**1 b**).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{20}O_4$
M_r	276.32
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	190
a, b, c (Å)	9.3504 (3), 13.6265 (4), 22.8790 (9)
V (Å^3)	2915.09 (17)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.32 × 0.17 × 0.12
Data collection	
Diffractometer	Bruker KappaCCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6082, 3295, 2149
R_{int}	0.057
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.131, 1.04
No. of reflections	3295
No. of parameters	192
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.21, −0.19

Computer programs: *COLLECT* (Bruker, 2001), *SCALEPACK* (Otwinowski & Minor, 1997), *DENZO* (Otwinowski & Minor, 1997), *SIR2004* (Burla *et al.*, 2005), *SHELXL2017* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bruker (2001). *COLLECT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Mierina, I., Jure, M., Zeberga, S., Makareviciene, V., Zicane, D., Tetere, Z. & Ravina, I. (2017). *Eur. J. Lipid Sci. Technol.* **119**, 1700172.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Ramachary, D. B. & Kishor, M. (2007). *J. Org. Chem.* **72**, 5056–5068.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Sudheendran, K., Malakar, C. C., Conrad, J. & Beifuss, U. (2012). *J. Org. Chem.* **77**, 10194–10210.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Xu, C., Zhang, L., Zhou, P., Luo, S. & Cheng, J.-P. (2013). *Synthesis*, **45**, 1939–1945.
Yoshida, M., Higuchi, M. & Shishido, K. (2010). *Tetrahedron*, **66**, 2675–2682.

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Computing details

Data collection: *COLLECT* (Bruker, 2001); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

3-Hydroxy-2-(4-hydroxy-3-methoxyphenylmethyl)-5,5-dimethylcyclohex-2-enone

Crystal data

$C_{16}H_{20}O_4$
$M_r = 276.32$
Orthorhombic, *Pbca*
$a = 9.3504$ (3) Å
$b = 13.6265$ (4) Å
$c = 22.8790$ (9) Å
$V = 2915.09$ (17) Å^3
$Z = 8$
$F(000) = 1184$
$D_x = 1.259$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 32401 reflections
$\theta = 1.0$–$27.5°$
$\mu = 0.09$ mm^{-1}
$T = 190$ K
Block, colourless
0.32 × 0.17 × 0.12 mm

Data collection

Bruker KappaCCD diffractometer
CCD scans
6082 measured reflections
3295 independent reflections
2149 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.8°$
$h = -12 \rightarrow 12$
$k = -17 \rightarrow 17$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.131$
$S = 1.04$
3295 reflections
192 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 1.0327P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.75371 (16)	0.50507 (9)	0.63597 (7)	0.0331 (4)
O2	0.62541 (15)	0.83466 (10)	0.63025 (7)	0.0287 (4)
O3	0.16966 (16)	0.39470 (10)	0.68561 (7)	0.0367 (4)
O4	0.13650 (15)	0.39579 (10)	0.57111 (7)	0.0319 (4)
C1	0.9683 (2)	0.71070 (12)	0.58699 (9)	0.0224 (4)
C2	0.8992 (2)	0.60988 (13)	0.57748 (9)	0.0256 (5)
H2A	0.864618	0.605845	0.537577	0.031*
H2B	0.971321	0.559458	0.582589	0.031*
C3	0.7777 (2)	0.58996 (13)	0.61829 (9)	0.0230 (5)
C4	0.6838 (2)	0.66925 (13)	0.63552 (9)	0.0213 (4)
C5	0.7173 (2)	0.76168 (13)	0.61827 (9)	0.0216 (4)
C6	0.8495 (2)	0.78837 (13)	0.58489 (9)	0.0243 (5)
H6A	0.886941	0.849470	0.600375	0.029*
H6B	0.823687	0.799694	0.544389	0.029*
C7	0.5558 (2)	0.64569 (13)	0.67303 (10)	0.0277 (5)
H7A	0.508367	0.706600	0.683286	0.033*
H7B	0.589063	0.615710	0.709003	0.033*
C8	0.4470 (2)	0.57763 (13)	0.64472 (9)	0.0232 (5)
C9	0.3616 (2)	0.51732 (13)	0.68030 (9)	0.0258 (5)
H9	0.374309	0.517992	0.720617	0.031*
C10	0.2589 (2)	0.45705 (13)	0.65589 (9)	0.0252 (5)
C11	0.2391 (2)	0.45584 (13)	0.59560 (9)	0.0244 (5)
C12	0.3230 (2)	0.51344 (15)	0.56037 (10)	0.0300 (5)
H12	0.310764	0.512153	0.520037	0.036*
C13	0.4265 (2)	0.57391 (14)	0.58529 (10)	0.0287 (5)
H13	0.483160	0.612663	0.561127	0.034*
C14	0.1966 (3)	0.37943 (17)	0.74571 (11)	0.0469 (7)
H14A	0.293311	0.357396	0.750859	0.070*
H14B	0.131964	0.330679	0.760536	0.070*
H14C	0.182851	0.439830	0.766563	0.070*
C15	1.0448 (2)	0.71292 (14)	0.64588 (10)	0.0317 (5)
H15A	0.977325	0.700158	0.676564	0.048*
H15B	1.087200	0.776352	0.651680	0.048*
H15C	1.118201	0.663631	0.646450	0.048*
C16	1.0760 (2)	0.73067 (15)	0.53816 (10)	0.0345 (5)
H16A	1.115861	0.795077	0.543051	0.052*
H16B	1.028672	0.726735	0.500998	0.052*
H16C	1.151155	0.682745	0.539763	0.052*
H2	0.664 (3)	0.892 (2)	0.6238 (13)	0.079 (10)*

H4	0.085 (4)	0.368 (3)	0.6024 (16)	0.114 (14)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0372 (8)	0.0110 (6)	0.0510 (10)	−0.0009 (6)	0.0078 (8)	0.0033 (6)
O2	0.0240 (8)	0.0128 (7)	0.0493 (10)	0.0022 (6)	−0.0014 (7)	0.0001 (6)
O3	0.0393 (9)	0.0406 (9)	0.0304 (9)	−0.0196 (7)	0.0011 (7)	0.0042 (7)
O4	0.0283 (8)	0.0362 (8)	0.0312 (9)	−0.0096 (7)	−0.0035 (7)	−0.0033 (7)
C1	0.0241 (10)	0.0168 (9)	0.0262 (11)	−0.0004 (8)	0.0006 (9)	0.0004 (8)
C2	0.0287 (11)	0.0172 (9)	0.0308 (12)	0.0006 (8)	0.0033 (9)	−0.0035 (8)
C3	0.0253 (11)	0.0149 (9)	0.0288 (12)	−0.0019 (8)	−0.0012 (9)	−0.0016 (8)
C4	0.0199 (10)	0.0145 (9)	0.0297 (12)	−0.0023 (8)	−0.0019 (9)	−0.0035 (8)
C5	0.0207 (11)	0.0163 (9)	0.0278 (12)	0.0010 (8)	−0.0047 (8)	−0.0014 (8)
C6	0.0241 (10)	0.0151 (9)	0.0336 (12)	−0.0028 (8)	−0.0038 (9)	0.0029 (8)
C7	0.0306 (12)	0.0160 (9)	0.0366 (14)	−0.0026 (9)	0.0042 (10)	−0.0034 (8)
C8	0.0222 (10)	0.0164 (9)	0.0310 (12)	0.0031 (8)	0.0031 (9)	0.0003 (8)
C9	0.0283 (11)	0.0233 (10)	0.0260 (12)	0.0005 (9)	0.0014 (9)	0.0000 (8)
C10	0.0236 (10)	0.0198 (9)	0.0322 (12)	−0.0023 (9)	0.0060 (9)	0.0024 (8)
C11	0.0207 (10)	0.0197 (9)	0.0328 (12)	0.0011 (8)	−0.0013 (9)	−0.0003 (9)
C12	0.0330 (12)	0.0300 (11)	0.0271 (13)	−0.0028 (10)	−0.0005 (10)	0.0037 (9)
C13	0.0279 (11)	0.0222 (10)	0.0359 (13)	−0.0035 (9)	0.0038 (10)	0.0061 (9)
C14	0.0604 (17)	0.0503 (14)	0.0300 (14)	−0.0262 (13)	0.0077 (12)	0.0032 (11)
C15	0.0263 (11)	0.0273 (11)	0.0414 (14)	0.0024 (9)	−0.0045 (10)	−0.0003 (10)
C16	0.0333 (12)	0.0270 (11)	0.0432 (15)	−0.0024 (10)	0.0077 (10)	0.0000 (10)

Geometric parameters (Å, º)

O1—C3	1.246 (2)	C7—H7A	0.9700
O2—C5	1.342 (2)	C7—H7B	0.9700
O2—H2	0.88 (3)	C8—C13	1.374 (3)
O3—C10	1.371 (2)	C8—C9	1.406 (3)
O3—C14	1.413 (3)	C9—C10	1.381 (3)
O4—C11	1.380 (2)	C9—H9	0.9300
O4—H4	0.94 (4)	C10—C11	1.392 (3)
C1—C15	1.526 (3)	C11—C12	1.371 (3)
C1—C16	1.529 (3)	C12—C13	1.394 (3)
C1—C2	1.534 (3)	C12—H12	0.9300
C1—C6	1.534 (3)	C13—H13	0.9300
C2—C3	1.495 (3)	C14—H14A	0.9600
C2—H2A	0.9700	C14—H14B	0.9600
C2—H2B	0.9700	C14—H14C	0.9600
C3—C4	1.447 (3)	C15—H15A	0.9600
C4—C5	1.357 (3)	C15—H15B	0.9600
C4—C7	1.507 (3)	C15—H15C	0.9600
C5—C6	1.498 (3)	C16—H16A	0.9600
C6—H6A	0.9700	C16—H16B	0.9600
C6—H6B	0.9700	C16—H16C	0.9600

C7—C8	1.521 (3)		
C5—O2—H2	111 (2)	C13—C8—C9	118.18 (18)
C10—O3—C14	117.73 (17)	C13—C8—C7	122.47 (18)
C11—O4—H4	107 (2)	C9—C8—C7	119.33 (19)
C15—C1—C16	109.41 (17)	C10—C9—C8	120.5 (2)
C15—C1—C2	109.91 (16)	C10—C9—H9	119.7
C16—C1—C2	109.48 (16)	C8—C9—H9	119.7
C15—C1—C6	110.69 (16)	O3—C10—C9	126.20 (19)
C16—C1—C6	109.34 (16)	O3—C10—C11	113.78 (17)
C2—C1—C6	107.99 (16)	C9—C10—C11	120.02 (18)
C3—C2—C1	113.20 (15)	C12—C11—O4	119.9 (2)
C3—C2—H2A	108.9	C12—C11—C10	119.98 (19)
C1—C2—H2A	108.9	O4—C11—C10	120.14 (18)
C3—C2—H2B	108.9	C11—C12—C13	119.7 (2)
C1—C2—H2B	108.9	C11—C12—H12	120.2
H2A—C2—H2B	107.8	C13—C12—H12	120.2
O1—C3—C4	119.70 (18)	C8—C13—C12	121.57 (19)
O1—C3—C2	120.54 (17)	C8—C13—H13	119.2
C4—C3—C2	119.71 (16)	C12—C13—H13	119.2
C5—C4—C3	118.27 (18)	O3—C14—H14A	109.5
C5—C4—C7	123.16 (17)	O3—C14—H14B	109.5
C3—C4—C7	118.55 (16)	H14A—C14—H14B	109.5
O2—C5—C4	118.71 (17)	O3—C14—H14C	109.5
O2—C5—C6	116.90 (15)	H14A—C14—H14C	109.5
C4—C5—C6	124.37 (17)	H14B—C14—H14C	109.5
C5—C6—C1	114.44 (15)	C1—C15—H15A	109.5
C5—C6—H6A	108.7	C1—C15—H15B	109.5
C1—C6—H6A	108.7	H15A—C15—H15B	109.5
C5—C6—H6B	108.7	C1—C15—H15C	109.5
C1—C6—H6B	108.7	H15A—C15—H15C	109.5
H6A—C6—H6B	107.6	H15B—C15—H15C	109.5
C4—C7—C8	114.73 (17)	C1—C16—H16A	109.5
C4—C7—H7A	108.6	C1—C16—H16B	109.5
C8—C7—H7A	108.6	H16A—C16—H16B	109.5
C4—C7—H7B	108.6	C1—C16—H16C	109.5
C8—C7—H7B	108.6	H16A—C16—H16C	109.5
H7A—C7—H7B	107.6	H16B—C16—H16C	109.5
C15—C1—C2—C3	67.9 (2)	C3—C4—C7—C8	−62.8 (2)
C16—C1—C2—C3	−171.93 (17)	C4—C7—C8—C13	−29.1 (3)
C6—C1—C2—C3	−53.0 (2)	C4—C7—C8—C9	152.22 (17)
C1—C2—C3—O1	−146.67 (19)	C13—C8—C9—C10	−0.8 (3)
C1—C2—C3—C4	35.9 (3)	C7—C8—C9—C10	177.99 (17)
O1—C3—C4—C5	176.34 (19)	C14—O3—C10—C9	−9.4 (3)
C2—C3—C4—C5	−6.2 (3)	C14—O3—C10—C11	170.34 (19)
O1—C3—C4—C7	−2.0 (3)	C8—C9—C10—O3	179.63 (18)
C2—C3—C4—C7	175.47 (18)	C8—C9—C10—C11	−0.1 (3)

C3—C4—C5—O2	175.08 (17)	O3—C10—C11—C12	−178.86 (17)
C7—C4—C5—O2	−6.6 (3)	C9—C10—C11—C12	0.9 (3)
C3—C4—C5—C6	−3.2 (3)	O3—C10—C11—O4	0.3 (3)
C7—C4—C5—C6	175.11 (19)	C9—C10—C11—O4	−179.93 (16)
O2—C5—C6—C1	163.97 (17)	O4—C11—C12—C13	−179.95 (17)
C4—C5—C6—C1	−17.7 (3)	C10—C11—C12—C13	−0.8 (3)
C15—C1—C6—C5	−76.1 (2)	C9—C8—C13—C12	0.9 (3)
C16—C1—C6—C5	163.26 (17)	C7—C8—C13—C12	−177.81 (18)
C2—C1—C6—C5	44.2 (2)	C11—C12—C13—C8	−0.1 (3)
C5—C4—C7—C8	118.9 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···O4^{i}	0.97	2.49	3.417 (3)	161
C14—H14*C*···O1^{ii}	0.96	2.49	3.247 (3)	136
O2—H2···O1^{iii}	0.88 (3)	1.74 (3)	2.586 (2)	161 (3)
O4—H4···O3	0.94 (4)	2.10 (4)	2.638 (2)	115 (3)
O4—H4···O2^{iv}	0.94 (4)	2.11 (4)	2.919 (2)	142 (3)

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