Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*E*)-(2,4-Dichlorophenyl)[2-hydroxy-6-(methoxyimino)cyclohex-1-enyl]-methanone

Guang-Dong Huang,[a] Jian-Wei Zou,[b]* Wen-Na Zhao[b] and Shu-Min Zhao[b]

[a]Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China, and [b]Ningbo Institute of Technology, Zhejiang University, Ningbo, Zhejiang 315100, People's Republic of China
Correspondence e-mail: jwzou@nit.net.cn

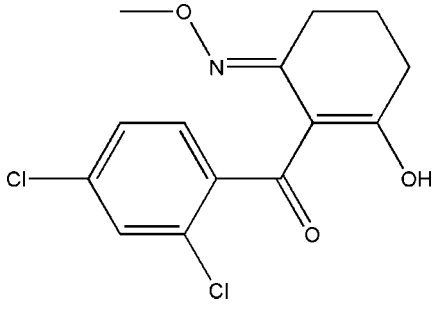
Received 5 December 2008; accepted 15 January 2009

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.049; wR factor = 0.144; data-to-parameter ratio = 13.9.

The title compound, $C_{14}H_{13}Cl_2NO_3$, was obtained as the product of an attempted synthesis of herbicidally active compounds containing oxime ether and cyclohexenone groups. In the crystal structure, the molecule adopts an endocyclic enol tautomeric form and the cyclohexene ring adopts a distorted envelope form. The oxime ether group has an *E* configuration, with the methoxy group *anti* to the *ortho*-chloro substitutent. Intramolecular O—H···O and intermolecular C—H···O hydrogen bonds are found in the crystal structure.

Related literature

For the structure of 5-chloro-2-methylthio-3*H*-indole-3-one 3-oxime *O*-methyl ether, see: Beddoes *et al.* (1992). For theoretical studies on the tautomerism of benzoylcyclohexane-1,3-dione and its derivatives, see: Huang *et al.* (2002). For the potential herbicidal property of the title compound and related compounds, see: Knudsen (1988). For the chemistry of 2-acylcycloalkane-1,3-diones, see: Rubinov *et al.* (1999).



Experimental

Crystal data

$C_{14}H_{13}Cl_2NO_3$
M_r = 314.15
Triclinic, $P\overline{1}$
a = 8.4096 (17) Å
b = 8.9944 (18) Å
c = 11.740 (2) Å
α = 68.38 (3)°
β = 74.50 (3)°
γ = 62.32 (3)°
V = 726.0 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.45 mm^{-1}
T = 298 (2) K
0.68 × 0.34 × 0.23 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.748, T_{max} = 0.903
6630 measured reflections
3247 independent reflections
2162 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.144
S = 1.08
3247 reflections
233 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.35 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
O2—H10···O1	0.91 (3)	1.64 (3)	2.485 (2)	152 (3)
C4—H1···O1^{i}	0.99 (2)	2.51 (2)	3.347 (3)	143 (2)
C2—H3···O2^{ii}	0.91 (4)	2.57 (3)	3.438 (3)	160 (3)

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

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

The authors are grateful to the Natural Science Foundation of Zhejiang Province (No. Y406042) and the Natural Science Foundation of Ningbo City (No. 2008A610068) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2144).

References

Beddoes, R. L., Kearney, T., Jackson, A. & Joule, J. A. (1992). *Acta Cryst.* C**48**, 1444–1446.
Bruker (2003). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Huang, M.-L., Zou, J.-W., Yang, D.-Y., Ning, B.-Z., Shang, Z.-C. & Yu, Q.-S. (2002). *J. Mol. Struct. (THEOCHEM)*, **589–590**, 321–328.
Knudsen, C. G. (1988). US Patent 4 775 411.
Rubinov, D. B., Rubinova, I. L. & Akhrem, A. A. (1999). *Chem. Rev.* **99**, 1047–1065.
Sheldrick, G. M. (2001). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2009). E**65**, o355 [doi:10.1107/S1600536809001883]

(*E*)-(2,4-Dichlorophenyl)[2-hydroxy-6-(methoxyimino)cyclohex-1-enyl]methanone

Guang-Dong Huang, Jian-Wei Zou, Wen-Na Zhao and Shu-Min Zhao

S1. Comment

2-Acylcycloalkanone derivatives, either natural or synthetic products, have been widely studied because of their versatile biological activity (Rubinov *et al.* 1999). The title compound, which was reported previously as a potential herbicide (Knudsen, 1988), was synthesized using 3-chloro-2-(2,4-dichlorobenzoyl)cyclohex-2-enone and methoxyamine hydrochloride as reactants and triethylamine as a catalyst. Herin we report its crystal structure with an attempt to understand better the structure-activity relationship of this class of compounds.

The title compound consists of 2,4-dichlorobenzoyl and cyclohexenone oxime *O*-methyl ether moieties. It has several possible tautomers in solution due to the existence of a 1,3-dione structure (Huang *et al.* 2002). The title molecule adopts an endocyclic enol tautomeric form in the crystal structure, *i.e.* the carbonyl group of the cyclohexenone unit is enolized. The cyclohexene ring adopts a distorted envelope form. The oxime ether is in an *E* configuration, with the methoxy group being *anti* to the substitutent group at the C-11 position (Fig. 1). The bond length of C6=N1 is 1.284 (3) Å and the C=N—O angle is 110.89 (17)°, which is close to the value in 5-chloro-2-methylthio-3*H*-indole-3-one 3-oxime *O*-methyl ether, (111.3 (5)°) (Beddoes *et al.*, 1992), showing that the C6=N1 bond is conjugated with the C8=C11 and C9=O1 bonds.

There is a strong intramolecular hydrogen bond, O2—H10···O1 (Table 1) and, as a result, a *pseudo*-six-membered ring (C8—O2—H10···O1—C9—C11) is formed in the structure (Fig. 1). The torsional angle of O1—C9—C8—C11 is 11.9 (3)°. In addition, two weak intermolecular C—H···O hydrogen bonding contacts, which form columns along the *b* axis, are found in the packing structure (Table 1 and Fig. 2).

S2. Experimental

A mixture of 2-(2,4-dichlorobenzoyl)cyclohexen-1,3-dione (0.57 g, 2 mmol), methoxyamine hydrochloride (0.18 g, 2.2 mmol) and anhydrous sodium acetate (0.2 g, 2.4 mmol) was stirred in methanol (30 ml) at room temperature for 16 h. The mixture was diluted with 100 ml of water and extracted with 30 ml e thyl acetate three times. The combined organic layer was dried with anhydrous magnesium sulfate and purified by column chromatography (ethyl acetate:petroleum ether = 1:12) to afford the title compound (70% yield). A crystal suitable for X-ray analysis was obtained by recrystallization of the product with acetone/pentane (1:10) at room temperature over a period of 3 d.

S3. Refinement

All H atoms were located in difference Fourier maps and refined independently with isotropic displacement parameters.

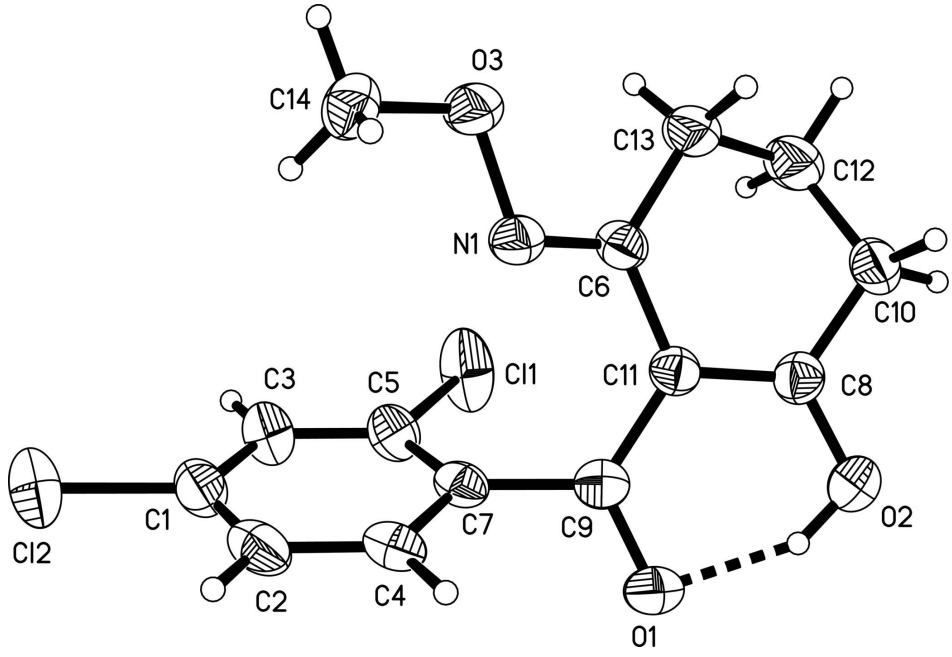


Figure 1

Perspective view of the title complex with atom numbering scheme. Thermal ellipsoids are shown at 30% probability level.

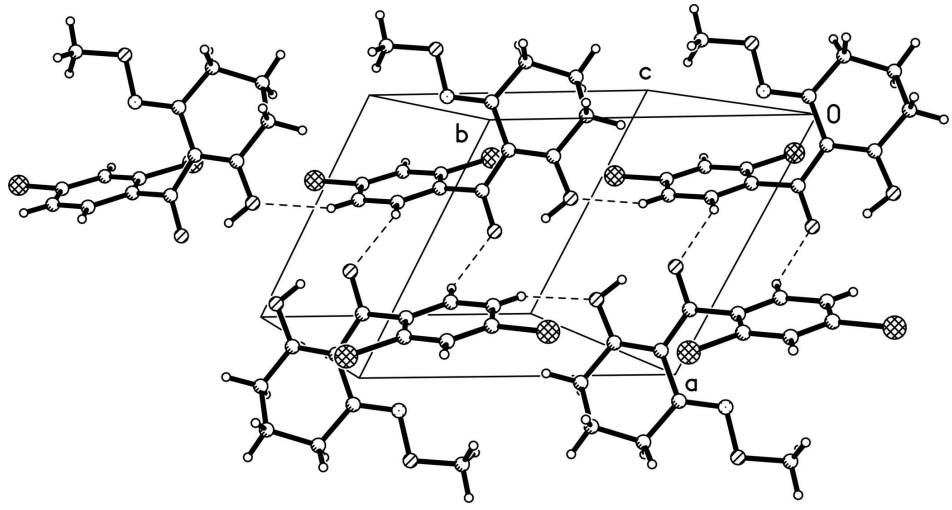


Figure 2

One-dimensional supramolecular structure showing intermolecular C—H···O hydrogen bonding contacts.

(*E*)-(2,4-Dichlorophenyl)[2-hydroxy-6-(methoxyimino)cyclohex-1- enyl]methanone

Crystal data

$C_{14}H_{13}Cl_2NO_3$
M_r = 314.15
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.4096 (17) Å
b = 8.9944 (18) Å
c = 11.740 (2) Å
α = 68.38 (3)°
β = 74.50 (3)°
γ = 62.32 (3)°
V = 726.0 (3) Å^3
Z = 2

$F(000) = 324$
$D_x = 1.437$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3247 reflections
$\theta = 3.2–27.5°$
$\mu = 0.45$ mm^{-1}
$T = 298$ K
Block, green
0.68 × 0.34 × 0.23 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.40 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.748$, $T_{max} = 0.903$
6630 measured reflections
3247 independent reflections
2162 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.2°$
$h = -10 \rightarrow 9$
$k = -11 \rightarrow 10$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.144$
$S = 1.08$
3247 reflections
233 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0701P)^2 + 0.0941P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ 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.

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.20742 (14)	0.71882 (10)	0.43507 (6)	0.0984 (3)
Cl2	0.28869 (13)	1.27753 (12)	0.43224 (9)	0.1098 (3)
O1	0.4465 (2)	0.7560 (2)	0.09971 (15)	0.0676 (4)
O2	0.3124 (2)	0.5952 (2)	0.05046 (15)	0.0658 (4)
H10	0.389 (4)	0.641 (4)	0.050 (3)	0.099 (10)*
O3	−0.25125 (19)	1.1694 (2)	0.24393 (17)	0.0686 (5)
N1	−0.0704 (2)	1.0779 (2)	0.19908 (16)	0.0551 (4)
C1	0.2934 (3)	1.1452 (3)	0.3538 (3)	0.0689 (6)
C2	0.3365 (3)	1.1861 (3)	0.2287 (3)	0.0677 (7)
H3	0.361 (4)	1.281 (4)	0.184 (3)	0.087 (9)*

C3	0.2551 (4)	1.0015 (3)	0.4191 (3)	0.0702 (7)
H6	0.231 (4)	0.968 (4)	0.507 (3)	0.089 (9)*
C4	0.3381 (3)	1.0831 (3)	0.1661 (2)	0.0583 (5)
H1	0.370 (3)	1.110 (3)	0.076 (2)	0.064 (7)*
C5	0.2563 (3)	0.9004 (3)	0.3541 (2)	0.0604 (5)
C6	−0.0470 (3)	0.9302 (3)	0.19137 (19)	0.0511 (5)
C7	0.2943 (2)	0.9405 (3)	0.22713 (19)	0.0510 (5)
C8	0.1559 (3)	0.6921 (3)	0.09904 (19)	0.0539 (5)
C9	0.2954 (3)	0.8347 (3)	0.15450 (19)	0.0518 (5)
C10	0.0020 (3)	0.6524 (4)	0.1021 (3)	0.0688 (7)
H8	−0.056 (4)	0.718 (4)	0.021 (3)	0.113 (11)*
H11	0.041 (4)	0.528 (4)	0.105 (3)	0.108 (10)*
C11	0.1366 (3)	0.8193 (3)	0.14735 (18)	0.0485 (5)
C12	−0.1359 (4)	0.6906 (4)	0.2117 (3)	0.0826 (8)
H7	−0.244 (4)	0.675 (4)	0.210 (3)	0.100 (9)*
H14	−0.080 (5)	0.606 (5)	0.301 (4)	0.139 (13)*
C13	−0.1984 (3)	0.8748 (4)	0.2142 (3)	0.0746 (7)
H2	−0.259 (4)	0.888 (4)	0.289 (3)	0.086 (9)*
H15	−0.275 (5)	0.953 (5)	0.131 (4)	0.143 (14)*
C14	−0.2681 (4)	1.3347 (3)	0.2447 (3)	0.0700 (7)
H4	−0.178 (4)	1.311 (4)	0.295 (3)	0.101 (10)*
H5	−0.386 (4)	1.389 (4)	0.281 (3)	0.085 (8)*
H9	−0.252 (4)	1.405 (4)	0.157 (3)	0.096 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.1770 (9)	0.0882 (5)	0.0587 (4)	−0.0887 (6)	−0.0179 (4)	−0.0028 (3)
Cl2	0.1302 (7)	0.1061 (6)	0.1376 (8)	−0.0655 (6)	−0.0103 (6)	−0.0629 (6)
O1	0.0478 (9)	0.0763 (11)	0.0799 (11)	−0.0253 (8)	0.0041 (8)	−0.0315 (9)
O2	0.0621 (10)	0.0652 (10)	0.0717 (10)	−0.0211 (9)	−0.0022 (8)	−0.0318 (9)
O3	0.0475 (8)	0.0587 (9)	0.1003 (12)	−0.0155 (7)	−0.0036 (8)	−0.0352 (9)
N1	0.0437 (9)	0.0536 (10)	0.0654 (11)	−0.0154 (8)	−0.0069 (8)	−0.0198 (9)
C1	0.0621 (14)	0.0655 (14)	0.0918 (19)	−0.0265 (12)	−0.0169 (13)	−0.0299 (14)
C2	0.0538 (13)	0.0547 (13)	0.098 (2)	−0.0278 (11)	−0.0148 (12)	−0.0138 (13)
C3	0.0854 (18)	0.0705 (16)	0.0681 (16)	−0.0395 (14)	−0.0169 (13)	−0.0183 (13)
C4	0.0441 (11)	0.0593 (13)	0.0698 (14)	−0.0252 (10)	−0.0098 (10)	−0.0090 (11)
C5	0.0694 (14)	0.0562 (12)	0.0603 (13)	−0.0317 (11)	−0.0142 (10)	−0.0090 (10)
C6	0.0455 (11)	0.0521 (11)	0.0573 (11)	−0.0198 (9)	−0.0103 (9)	−0.0146 (9)
C7	0.0388 (10)	0.0511 (11)	0.0605 (12)	−0.0163 (9)	−0.0125 (9)	−0.0113 (10)
C8	0.0528 (12)	0.0514 (12)	0.0548 (11)	−0.0165 (10)	−0.0091 (9)	−0.0167 (10)
C9	0.0475 (11)	0.0495 (11)	0.0516 (11)	−0.0183 (9)	−0.0069 (9)	−0.0085 (9)
C10	0.0619 (14)	0.0684 (15)	0.0903 (18)	−0.0237 (12)	−0.0170 (13)	−0.0361 (15)
C11	0.0457 (11)	0.0484 (11)	0.0490 (10)	−0.0169 (9)	−0.0096 (8)	−0.0117 (9)
C12	0.0660 (16)	0.0835 (19)	0.121 (3)	−0.0422 (15)	0.0002 (16)	−0.0455 (19)
C13	0.0544 (14)	0.0774 (17)	0.108 (2)	−0.0333 (13)	0.0044 (15)	−0.0450 (17)
C14	0.0738 (17)	0.0558 (14)	0.0770 (17)	−0.0174 (13)	−0.0090 (15)	−0.0272 (14)

Geometric parameters (Å, º)

Cl1—C5	1.735 (2)	C6—C11	1.473 (3)
Cl2—C1	1.735 (3)	C6—C13	1.500 (3)
O1—C9	1.262 (2)	C7—C9	1.490 (3)
O2—C8	1.310 (3)	C8—C11	1.383 (3)
O2—H10	0.91 (3)	C8—C10	1.483 (3)
O3—N1	1.413 (2)	C9—C11	1.432 (3)
O3—C14	1.429 (3)	C10—C12	1.509 (4)
N1—C6	1.284 (3)	C10—H8	1.03 (3)
C1—C2	1.366 (4)	C10—H11	1.00 (3)
C1—C3	1.373 (4)	C12—C13	1.497 (4)
C2—C4	1.373 (3)	C12—H7	0.99 (3)
C2—H3	0.90 (3)	C12—H14	1.12 (4)
C3—C5	1.381 (3)	C13—H2	0.91 (3)
C3—H6	0.96 (3)	C13—H15	1.13 (4)
C4—C7	1.384 (3)	C14—H4	0.99 (3)
C4—H1	0.99 (2)	C14—H5	0.94 (3)
C5—C7	1.382 (3)	C14—H9	1.00 (3)
C8—O2—H10	104.4 (19)	C11—C9—C7	122.91 (18)
N1—O3—C14	107.48 (18)	C8—C10—C12	110.6 (2)
C6—N1—O3	110.89 (17)	C8—C10—H8	112.0 (19)
C2—C1—C3	121.8 (2)	C12—C10—H8	111.5 (18)
C2—C1—Cl2	119.0 (2)	C8—C10—H11	112.8 (19)
C3—C1—Cl2	119.2 (2)	C12—C10—H11	108.9 (18)
C1—C2—C4	119.2 (2)	H8—C10—H11	101 (2)
C1—C2—H3	122.8 (18)	C8—C11—C9	118.71 (18)
C4—C2—H3	118.0 (18)	C8—C11—C6	118.12 (18)
C1—C3—C5	118.0 (2)	C9—C11—C6	123.15 (18)
C1—C3—H6	122.7 (17)	C13—C12—C10	111.8 (3)
C5—C3—H6	119.3 (17)	C13—C12—H7	107.1 (18)
C2—C4—C7	121.2 (2)	C10—C12—H7	111.0 (17)
C2—C4—H1	120.3 (14)	C13—C12—H14	105 (2)
C7—C4—H1	118.5 (14)	C10—C12—H14	112 (2)
C3—C5—C7	121.9 (2)	H7—C12—H14	109 (3)
C3—C5—Cl1	118.64 (19)	C12—C13—C6	113.5 (2)
C7—C5—Cl1	119.48 (17)	C12—C13—H2	110.8 (19)
N1—C6—C11	116.84 (18)	C6—C13—H2	106.2 (18)
N1—C6—C13	123.33 (19)	C12—C13—H15	102.1 (19)
C11—C6—C13	119.61 (19)	C6—C13—H15	106 (2)
C5—C7—C4	117.9 (2)	H2—C13—H15	118 (3)
C5—C7—C9	123.08 (19)	O3—C14—H4	107.5 (19)
C4—C7—C9	119.0 (2)	O3—C14—H5	105.9 (18)
O2—C8—C11	122.27 (19)	H4—C14—H5	111 (2)
O2—C8—C10	115.41 (19)	O3—C14—H9	108.2 (16)
C11—C8—C10	122.29 (19)	H4—C14—H9	114 (3)
O1—C9—C11	121.04 (19)	H5—C14—H9	110 (2)

O1—C9—C7	116.05 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H10···O1	0.91 (3)	1.64 (3)	2.485 (2)	152 (3)
C4—H1···O1^{i}	0.99 (2)	2.51 (2)	3.347 (3)	143 (2)
C2—H3···O2^{ii}	0.91 (4)	2.57 (3)	3.438 (3)	160 (3)

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