Ethyl 6-(4-chlorophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2H-pyran-5-carboxylate

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The title compound, $C_{16}H_{17}ClO_4$, is a derivative of 3,4-dihydro-2H-pyran-4-one in which the root moiety forms a dihedral angle of 49.36 (5)° with the pendent chlorobenzene ring. The crystal structure features weak methyl-C—H···O(ring carbonyl) contacts, leading to an $R_2^2(12)$ ring motif, and benzene-C—H···O(ester) interactions, leading to a supramolecular chain along the b axis, to form a three-dimensional network.

3D view

Chemical scheme

Structure description

4H-Pyran-4-ones and their various derivatives are known for their significant biological and pharmacological activities, and are structurally similar to biologically active 1,4-dihydropyridines (1,4-DHPs) (Zonouz et al., 2014). They act as calcium antagonists (Súarez et al., 2002) and serve as potent apoptosis inducers (Zhang et al., 2005). As a continuation of structural investigations of a series of 4H-pyran-4-one derivatives, we report herein on the crystal structure determination and the geometry optimization of the title compound, (I).

A perspective view of (I) with the atomic numbering scheme is illustrated in Fig. 1. The 3,4-dihydro-2H-pyran-4-one moiety (C7–C11/O1/O2) forms a dihedral angle of 49.36 (5)° with the benzene ring. The bond distances and angles are essentially equivalent compared to those in the previously reported structure ethyl 2,2-dimethyl-4-oxo-6-phenyl-3,4-dihydro-2H-pyran-5-carboxylate (II) (Sharmila et al., 2016). However, the benzene group has rotated about the C6—C7 bond as evident from the change in torsion angles namely, C1—C6—C7—C11 and C5—C6—C7—C11 of −133.37 (15) and 50.56 (19)°, respectively, cf. 138.6 (2) and −43.3 (3)° in (II). Also, a fragment overlay
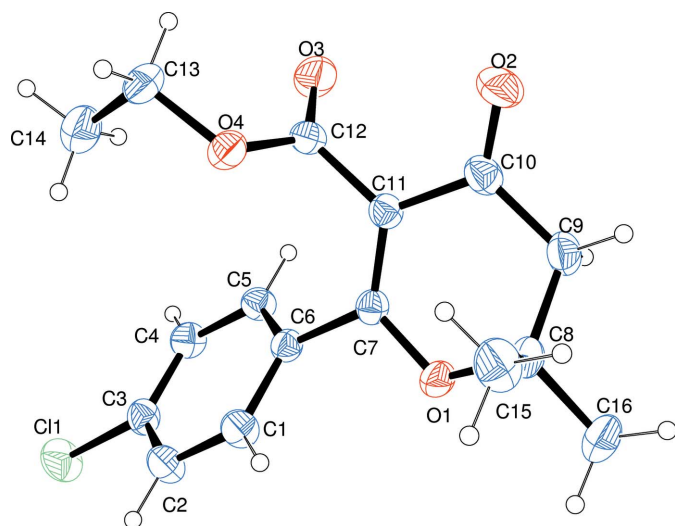
Figure 1
The molecular structure of (I), with displacement ellipsoids for the non-H atoms drawn at the 30% probability level.

(Gans & Shalloway, 2001) analysis of (I) with (II) gives an r.m.s. deviation of 2.91 Å (Fig. 2). These observations indicate that the structural changes could be attributed to the substitution of the heavier Cl atom at C3 and the involvement of C2 in making a hydrogen bond with O4 *via* H2 (Table 1). Another superposition analysis of (I) but, with 4-(4-fluorophenyl)-6-methylamino-5-nitro-2-phenyl-4*H*-pyran-3- carbonitrile (III) (Vishnupriya *et al.*, 2013) gives an r.m.s. deviation of 1.57 Å, which confirms the effect of relatively heavier Cl substitution at C3 resulting in the small conformational changes in the molecule.

The pyran ring of (I) is puckered (puckering parameters: Q = 0.4539 (16) Å, $q2$ = 0.378 (15) Å, $q3$ = −0.2512 (15) Å, θ =
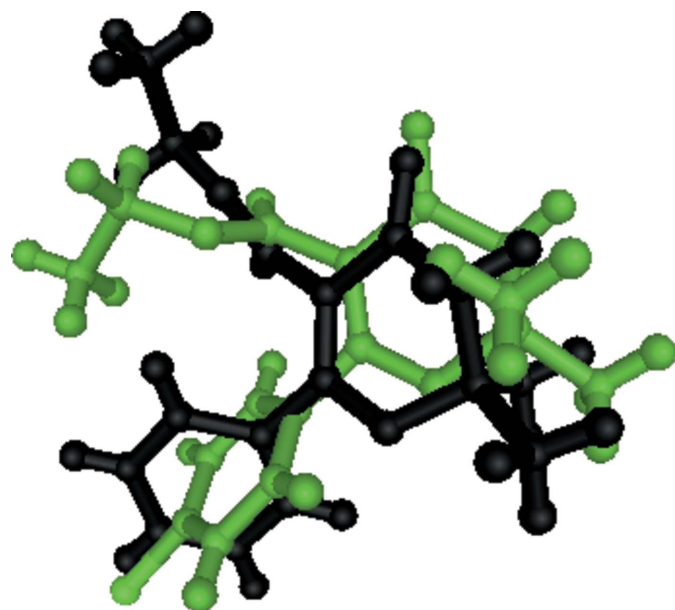
Table 1
Hydrogen-bond geometry (Å, °).

Cg is the centroid of the C1–C6 ring.

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
C2—H2···O4^i	0.93	2.66	3.3694 (18)	134
C15—H15B···O2^{ii}	0.96	2.66	3.553 (2)	156
C13—H13B···Cg^{iii}	0.97	2.96	3.6463 (17)	129

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

123.61 (19)° and φ = 91.6 (2)°, with atom C8 showing the maximum deviation of 0.2946 (16) Å from the plane defined by O1/C7/C11–C8.

Theoretical calculations of the molecular structure were performed using MOPAC2016′s PM7 geometry optimization algorithm (Stewart, 2016). This shows satisfactory agreement with the results of the X-ray crystal structure analysis. The HOMO and LUMO energy levels were found to be −9.829 and −1.127 eV, respectively. The total energy and dipole moment values of (I) are −3643.34886 eV and 5.235 Debye, respectively. In the geometry optimized structure of (I), a decrease in bond distances seems to be observed for the bonds O1—C8 (1.46 Å) and C6—C7 (1.47 Å) when compared to those in the crystal, *i.e.* 1.4732 (16) and 1.4832 (16) Å. The O1—C7—C6 bond angle decreased from 110.78 (11) to 110.2°, and the O1—C8—C9 bond angle increased from 108.65 (11) to 110.5°. The relative conformation about the bond joining the 3,4-dihydro-2*H*-pyran-4-one moiety with the chlorobenzene group of (I) is defined by the torsion angles C1—C6—C7—O1 and C5—C6—C7—O1 of 47.68 (17) and −128.38 (13)° in the crystal, *i.e.* show (+) *syn*-clinal and (−) *anti*-clinal conformations, respectively, and compare with 49.9 and −130.8° in the optimized structure. A superimposed fit of (I) with its energy-minimized molecule gives an r.m.s. deviation of 0.152 Å (Fig. 3).
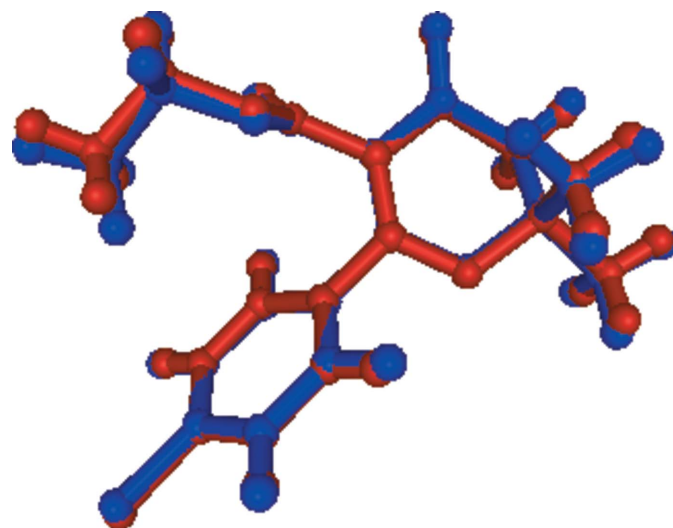

Figure 2
A superimposed fit of (I) (green) and related structure (II) (black).

Figure 3
A superimposed fit of (I) (red) and its energy-minimized counterpart (blue).

One of the methyl carbons, C15, is involved in hydrogen bond with O2 of a symmetry-related molecule *via* H15*B* to form a $R_2^2(12)$ ring motif. The phenyl carbon C2 is involved in an interaction with O4 of a symmetry-related molecule *via* H2 to form a chain along the *b* axis (Table 1 and Fig. 4). These combine to give a three-dimensional architecture. Further, a weak C—H⋯π interaction between C13 and the centroid (*Cg*) of the C1–C6 ring *via* H13*B*, provides additional stabilization to the crystal (Table 1).

Synthesis and crystallization

To a solution of ethyl 3-(4-chlorophenyl)-3-oxopropanoate (226 mg, 1.0 mmol), $CaCl_2$ (11 mg, 0.1 mmol), triethylamine (278 µ*L*, 2.0 mmol) and 3-methylbut-2-enoyl chloride (112 µ*L*, 1.0 mmol), dichloromethane (4 ml) was added at ambient temperature. After completion of the addition, the reaction mixture was subjected to stirring at room temperature for 3 h. The progress of the reaction was monitored by thin-layer chromatography. The organic layer was separated, filtered and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/hexane = 2:8 *v*/*v* as eluent). The product was a colourless solid (yield 90%, 277 mg) and was crystallized in hexane/EtOAc (6:4 *v*/*v* (m.p. 354–356 K).

Refinement

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{17}ClO_4$
M_r	308.74
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	10.4412 (3), 7.6959 (2), 20.2651 (5)
β (°)	102.311 (2)
V (Å^3)	1590.94 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.25
Crystal size (mm)	$0.25 \times 0.17 \times 0.12$
Data collection	
Diffractometer	Bruker Smart CCD Area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.746, 0.845
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15125, 3995, 2978
R_{int}	0.018
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.670
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.108, 1.03
No. of reflections	3995
No. of parameters	193
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.28, −0.26

Computer programs: *SMART* and *SAINT* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *QMOL* (Gans & Shalloway, 2001), *Mercury* (Macrae *et al.*, 2008), *ORTEPIII* (Burnett & Johnson, 1996), *WinGX* publication routines (Farrugia, 2012) and *PLATON* (Spek, 2009).

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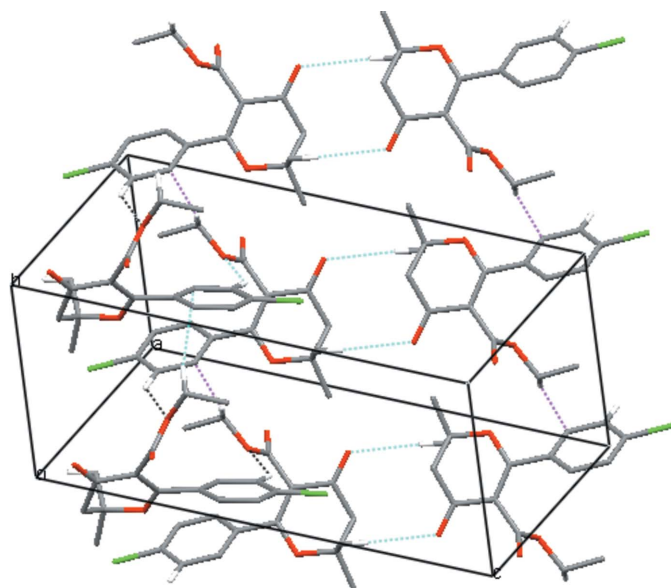Zonouz, A. M., Moghani, D. & Okhravi, S. (2014). *Curr. Chem. Lett.* **3**, 71–74.

Figure 4
Molecular packing of (I), showing the C—H⋯O interactions as dashed lines. Other H-atoms are omitted for clarity.

full crystallographic data

Ethyl 6-(4-chlorophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-pyran-5-carboxylate

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Ethyl 2,2-dimethyl-4-oxo-6-phenyl-2,3-dihydro-4H-pyran-5-carboxylate

Crystal data

$C_{16}H_{17}ClO_4$	$D_x = 1.289$ Mg m^{-3}
$M_r = 308.74$	Melting point: 356 K
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.4412$ (3) Å	Cell parameters from 3995 reflections
$b = 7.6959$ (2) Å	$\theta = 2.0–28.4°$
$c = 20.2651$ (5) Å	$\mu = 0.25$ mm^{-1}
$\beta = 102.311$ (2)°	$T = 296$ K
$V = 1590.94$ (7) Å^3	Block, colourless
$Z = 4$	$0.25 \times 0.17 \times 0.12$ mm
$F(000) = 648$	

Data collection

Bruker Smart CCD Area-detector diffractometer	15125 measured reflections
Radiation source: fine-focus sealed tube	3995 independent reflections
Graphite monochromator	2978 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{int} = 0.018$
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	$\theta_{max} = 28.4°$, $\theta_{min} = 2.0°$
	$h = -13 \rightarrow 13$
	$k = -10 \rightarrow 10$
$T_{min} = 0.746$, $T_{max} = 0.845$	$l = -24 \rightarrow 27$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.037$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.108$	
$S = 1.03$	H-atom parameters constrained
3995 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.3683P]$ where $P = (F_o^2 + 2F_c^2)/3$
193 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.28$ e Å^{-3}
	$\Delta\rho_{min} = -0.26$ 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 ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.43713 (4)	0.28175 (7)	0.02231 (2)	0.06956 (16)
O1	0.76719 (10)	0.25784 (13)	0.33513 (5)	0.0475 (2)
O2	1.03226 (13)	0.63993 (19)	0.40015 (6)	0.0736 (4)
O3	0.96413 (11)	0.71077 (17)	0.24439 (7)	0.0670 (3)
O4	0.76146 (10)	0.76716 (13)	0.25811 (5)	0.0494 (3)
C1	0.56401 (14)	0.3304 (2)	0.22085 (7)	0.0476 (3)
H1	0.5298	0.3190	0.2594	0.057*
C2	0.48338 (14)	0.3058 (2)	0.15815 (7)	0.0515 (4)
H2	0.3950	0.2802	0.1541	0.062*
C3	0.53638 (14)	0.3198 (2)	0.10154 (7)	0.0451 (3)
C4	0.66627 (14)	0.3583 (2)	0.10654 (7)	0.0464 (3)
H4	0.7003	0.3669	0.0678	0.056*
C5	0.74647 (13)	0.38433 (18)	0.16963 (7)	0.0420 (3)
H5	0.8347	0.4102	0.1733	0.050*
C6	0.69542 (12)	0.37183 (17)	0.22726 (6)	0.0368 (3)
C7	0.78238 (12)	0.39149 (17)	0.29499 (6)	0.0374 (3)
C8	0.83024 (15)	0.2695 (2)	0.40731 (7)	0.0498 (4)
C9	0.96580 (15)	0.3470 (2)	0.41366 (7)	0.0524 (4)
H9A	1.0057	0.3629	0.4611	0.063*
H9B	1.0200	0.2667	0.3948	0.063*
C10	0.96159 (14)	0.5182 (2)	0.37801 (7)	0.0486 (3)
C11	0.86698 (12)	0.52417 (18)	0.31346 (6)	0.0391 (3)
C12	0.87223 (13)	0.67511 (18)	0.26829 (7)	0.0415 (3)
C13	0.75166 (17)	0.9164 (2)	0.21306 (9)	0.0601 (4)
H13A	0.8384	0.9637	0.2147	0.072*
H13B	0.6989	1.0060	0.2279	0.072*
C14	0.6913 (2)	0.8648 (3)	0.14272 (10)	0.0745 (5)
H14A	0.7470	0.7826	0.1269	0.112*
H14B	0.6805	0.9657	0.1142	0.112*
H14C	0.6072	0.8128	0.1416	0.112*
C15	0.74350 (17)	0.3815 (3)	0.44129 (8)	0.0685 (5)
H15A	0.7383	0.4966	0.4226	0.103*
H15B	0.7800	0.3869	0.4889	0.103*
H15C	0.6573	0.3319	0.4339	0.103*
C16	0.8362 (2)	0.0834 (3)	0.43209 (10)	0.0813 (6)
H16A	0.7490	0.0372	0.4255	0.122*
H16B	0.8768	0.0801	0.4793	0.122*
H16C	0.8866	0.0149	0.4072	0.122*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0693 (3)	0.0924 (4)	0.0396 (2)	−0.0122 (2)	−0.00473 (17)	−0.0057 (2)
O1	0.0577 (6)	0.0468 (6)	0.0350 (5)	−0.0092 (5)	0.0030 (4)	0.0070 (4)
O2	0.0762 (8)	0.0824 (9)	0.0531 (7)	−0.0320 (7)	−0.0067 (6)	−0.0001 (6)
O3	0.0486 (6)	0.0729 (8)	0.0846 (9)	−0.0020 (6)	0.0258 (6)	0.0254 (7)
O4	0.0498 (6)	0.0426 (5)	0.0581 (6)	0.0033 (4)	0.0169 (5)	0.0065 (5)
C1	0.0446 (7)	0.0631 (9)	0.0370 (7)	−0.0032 (6)	0.0127 (5)	0.0018 (6)
C2	0.0396 (7)	0.0701 (10)	0.0439 (7)	−0.0049 (7)	0.0067 (6)	0.0000 (7)
C3	0.0495 (7)	0.0482 (8)	0.0343 (6)	−0.0006 (6)	0.0015 (5)	−0.0007 (6)
C4	0.0531 (8)	0.0531 (8)	0.0347 (6)	−0.0021 (6)	0.0137 (6)	−0.0010 (6)
C5	0.0416 (7)	0.0468 (8)	0.0391 (7)	−0.0037 (6)	0.0120 (5)	−0.0007 (6)
C6	0.0403 (6)	0.0359 (6)	0.0338 (6)	−0.0003 (5)	0.0067 (5)	0.0016 (5)
C7	0.0396 (6)	0.0408 (7)	0.0326 (6)	0.0016 (5)	0.0095 (5)	0.0020 (5)
C8	0.0545 (8)	0.0584 (9)	0.0336 (7)	−0.0035 (7)	0.0025 (6)	0.0105 (6)
C9	0.0478 (8)	0.0663 (10)	0.0393 (7)	0.0017 (7)	0.0009 (6)	0.0076 (7)
C10	0.0435 (7)	0.0632 (9)	0.0377 (7)	−0.0068 (7)	0.0057 (6)	−0.0012 (6)
C11	0.0382 (6)	0.0442 (7)	0.0347 (6)	−0.0014 (5)	0.0075 (5)	0.0008 (5)
C12	0.0397 (7)	0.0428 (7)	0.0416 (7)	−0.0057 (6)	0.0079 (5)	−0.0018 (6)
C13	0.0657 (10)	0.0389 (8)	0.0749 (11)	0.0025 (7)	0.0134 (8)	0.0102 (8)
C14	0.0836 (13)	0.0675 (12)	0.0673 (11)	0.0038 (10)	0.0047 (10)	0.0165 (9)
C15	0.0616 (10)	0.1026 (15)	0.0442 (8)	0.0000 (10)	0.0179 (7)	0.0050 (9)
C16	0.0993 (15)	0.0726 (13)	0.0627 (11)	−0.0121 (11)	−0.0035 (10)	0.0308 (10)

Geometric parameters (Å, º)

Cl1—C3	1.7401 (13)	C8—C9	1.516 (2)
O1—C7	1.3415 (16)	C8—C15	1.518 (2)
O1—C8	1.4732 (16)	C9—C10	1.498 (2)
O2—C10	1.2177 (19)	C9—H9A	0.9700
O3—C12	1.1954 (17)	C9—H9B	0.9700
O4—C12	1.3343 (17)	C10—C11	1.4622 (18)
O4—C13	1.4571 (18)	C11—C12	1.4871 (19)
C1—C2	1.3795 (19)	C13—C14	1.484 (3)
C1—C6	1.3876 (19)	C13—H13A	0.9700
C1—H1	0.9300	C13—H13B	0.9700
C2—C3	1.380 (2)	C14—H14A	0.9600
C2—H2	0.9300	C14—H14B	0.9600
C3—C4	1.371 (2)	C14—H14C	0.9600
C4—C5	1.3854 (18)	C15—H15A	0.9600
C4—H4	0.9300	C15—H15B	0.9600
C5—C6	1.3866 (18)	C15—H15C	0.9600
C5—H5	0.9300	C16—H16A	0.9600
C6—C7	1.4832 (16)	C16—H16B	0.9600
C7—C11	1.3498 (18)	C16—H16C	0.9600
C8—C16	1.515 (2)		

C7—O1—C8	118.01 (11)	H9A—C9—H9B	107.9
C12—O4—C13	117.26 (11)	O2—C10—C11	123.09 (14)
C2—C1—C6	120.99 (12)	O2—C10—C9	123.08 (13)
C2—C1—H1	119.5	C11—C10—C9	113.82 (13)
C6—C1—H1	119.5	C7—C11—C10	120.09 (12)
C1—C2—C3	118.74 (13)	C7—C11—C12	121.88 (11)
C1—C2—H2	120.6	C10—C11—C12	117.96 (12)
C3—C2—H2	120.6	O3—C12—O4	124.04 (13)
C4—C3—C2	121.41 (13)	O3—C12—C11	124.53 (13)
C4—C3—Cl1	119.33 (11)	O4—C12—C11	111.43 (11)
C2—C3—Cl1	119.24 (11)	O4—C13—C14	110.47 (14)
C3—C4—C5	119.57 (12)	O4—C13—H13A	109.6
C3—C4—H4	120.2	C14—C13—H13A	109.6
C5—C4—H4	120.2	O4—C13—H13B	109.6
C4—C5—C6	120.13 (12)	C14—C13—H13B	109.6
C4—C5—H5	119.9	H13A—C13—H13B	108.1
C6—C5—H5	119.9	C13—C14—H14A	109.5
C5—C6—C1	119.15 (12)	C13—C14—H14B	109.5
C5—C6—C7	120.20 (11)	H14A—C14—H14B	109.5
C1—C6—C7	120.54 (11)	C13—C14—H14C	109.5
O1—C7—C11	124.54 (11)	H14A—C14—H14C	109.5
O1—C7—C6	110.78 (11)	H14B—C14—H14C	109.5
C11—C7—C6	124.68 (11)	C8—C15—H15A	109.5
O1—C8—C16	104.45 (13)	C8—C15—H15B	109.5
O1—C8—C9	108.65 (11)	H15A—C15—H15B	109.5
C16—C8—C9	111.84 (14)	C8—C15—H15C	109.5
O1—C8—C15	107.56 (12)	H15A—C15—H15C	109.5
C16—C8—C15	111.90 (15)	H15B—C15—H15C	109.5
C9—C8—C15	112.02 (14)	C8—C16—H16A	109.5
C10—C9—C8	111.96 (12)	C8—C16—H16B	109.5
C10—C9—H9A	109.2	H16A—C16—H16B	109.5
C8—C9—H9A	109.2	C8—C16—H16C	109.5
C10—C9—H9B	109.2	H16A—C16—H16C	109.5
C8—C9—H9B	109.2	H16B—C16—H16C	109.5
C6—C1—C2—C3	1.2 (2)	C16—C8—C9—C10	169.65 (14)
C1—C2—C3—C4	−0.4 (2)	C15—C8—C9—C10	−63.80 (16)
C1—C2—C3—Cl1	177.82 (13)	C8—C9—C10—O2	141.88 (16)
C2—C3—C4—C5	−0.2 (2)	C8—C9—C10—C11	−39.47 (18)
Cl1—C3—C4—C5	−178.35 (12)	O1—C7—C11—C10	7.7 (2)
C3—C4—C5—C6	−0.2 (2)	C6—C7—C11—C10	−171.07 (12)
C4—C5—C6—C1	1.0 (2)	O1—C7—C11—C12	−175.43 (12)
C4—C5—C6—C7	177.14 (13)	C6—C7—C11—C12	5.8 (2)
C2—C1—C6—C5	−1.6 (2)	O2—C10—C11—C7	−173.28 (15)
C2—C1—C6—C7	−177.69 (14)	C9—C10—C11—C7	8.07 (19)
C8—O1—C7—C11	10.50 (19)	O2—C10—C11—C12	9.8 (2)
C8—O1—C7—C6	−170.55 (11)	C9—C10—C11—C12	−168.88 (13)
C5—C6—C7—O1	−128.38 (13)	C13—O4—C12—O3	2.3 (2)

C1—C6—C7—O1	47.68 (17)	C13—O4—C12—C11	−178.24 (12)
C5—C6—C7—C11	50.56 (19)	C7—C11—C12—O3	−115.07 (17)
C1—C6—C7—C11	−133.37 (15)	C10—C11—C12—O3	61.8 (2)
C7—O1—C8—C16	−160.72 (14)	C7—C11—C12—O4	65.43 (17)
C7—O1—C8—C9	−41.22 (17)	C10—C11—C12—O4	−117.67 (13)
C7—O1—C8—C15	80.23 (16)	C12—O4—C13—C14	91.59 (17)
O1—C8—C9—C10	54.88 (17)		

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O4[i]	0.93	2.66	3.3694 (18)	134
C15—H15*B*···O2[ii]	0.96	2.66	3.553 (2)	156
C13—H13*B*···Cg[iii]	0.97	2.96	3.6463 (17)	129

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