Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-(4-Chlorophenyl)-7,7-dimethyl-7,8-dihydro-4*H*-1-benzopyran-2,5(3*H*,6*H*)-dione

Hao Shi

The College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China
Correspondence e-mail: shihao@zjut.edu.cn

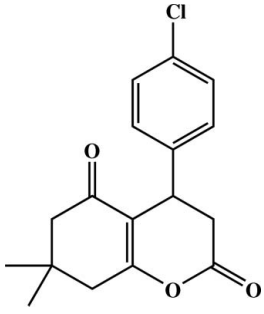
Received 15 November 2009; accepted 28 November 2009

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.062; wR factor = 0.186; data-to-parameter ratio = 14.5.

The title compound, $C_{17}H_{17}ClO_3$, has been synthesized by the reaction of *p*-chlorobenzaldehyde, isopropylidene malonate and 5,5-dimethylcyclohexane-1,3-dione with triethylbenzylammonium chloride in water as a green solvent. The six membered pyranone ring of the hexahydrocoumarin system has a screw-boat conformation while the dimethylcyclohexenone system has a distorted envelope conformation. The dihedral angle between the least-squares planes of the coumarin ring system and the benzene ring is 85.64 (9)°.

Related literature

For applications of coumarin derivatives, see: Wang *et al.* (1999); Yang (2001). For related structures, see: Itoh & Kanemasa (2003); Itoh *et al.* (2005). For ring puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

$C_{17}H_{17}ClO_3$
M_r = 304.76
Monoclinic, $P2_1/n$
a = 11.9005 (12) Å
b = 5.7971 (8) Å
c = 22.608 (2) Å
β = 93.972 (1)°
V = 1555.9 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.25 mm^{-1}
T = 298 K
0.48 × 0.39 × 0.34 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.889, T_{max} = 0.919
7519 measured reflections
2789 independent reflections
1585 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.186
S = 1.05
2789 reflections
192 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The research was supported by the Open Foundation of Key Disciplines within the Zhejiang Provincial Key Disciplines.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2260).

References

Bruker (1999). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Itoh, K., Hasegawa, M., Tanaka, J. & Kanemasa, S. (2005). *Org. Lett.* **7**, 979–981.
Itoh, K. & Kanemasa, S. (2003). *Tetrahedron Lett.* **44**, 1799–1802.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wang, X. F., Qu, Y. & Gu, F. (1999). *Speciality Petrochemicals*, **1**, 49–52.
Yang, J. S. (2001). *West China J. Pharm. Sci.* **16**, 285–288.

supporting information

Acta Cryst. (2010). E**66**, o56 [doi:10.1107/S1600536809051320]

4-(4-Chlorophenyl)-7,7-dimethyl-7,8-dihydro-4*H*-1-benzopyran-2,5(3*H*,6*H*)-dione

Hao Shi

S1. Comment

Coumarin is an important chemical having unique characteristics. It is widely used in hand soaps, detergents, lotions and laser dyes (Wang *et al.*, 1999). Coumarin and some of its derivatives have been tested in pharmacology for treatment of HIV (Yang, 2001). To obtain coumarin in a more environment friendly way, water was used as a green solvent in the synthesis of the title compound (Fig.1 and *Experimental*).

In the molecule of the title compound (Fig. 2), the two six membered rings of the hexahydrocoumarin system are not planar, having screw-boat and envelope conformations respectively: the pyranone ring *A* (O1/C1···C4/C9) adopts the screw-boat conformation with puckering parameters (Cremer & Pople, 1975) Q= 0.430 (5) Å, θ= 61.8 (5)° and φ = 134.7 (6)°; the ring *B* (C4···C9) exists in a distorted envelope conformation [Q = 0.408 (4) Å, θ= 127.0 (6)° and φ= 343.4 (7)°)] with C7 displaced by 0.558 (5) Å from the plane of the other ring atoms. Ring *C* (C12···C17) is a benzene ring, which makes a dihedral angle of 85.64 (9)° with the least-squares plane of the coumarin ring. The analogue of the title compound including Br in place of Cl has been reported and an enantiomerically pure crystal characterized by X-ray diffraction (Itoh & Kanemasa, 2003; Itoh *et al.*, 2005).

S2. Experimental

A mixture of 4-chlorobenzaldehyde (100 mmol), 5,5-dimethyl-1,3-cyclohexanedione (100 mmol), isopropylidene malonate (100 mmol), triethylbenzylammonium chloride (TEBA) (15 mmol) and 400 mL of water was transferred into a flask connected with refluxing equipment (Fig. 1). After stirring at 345 K (72°C) for 5 h, the reaction mixture was cooled to room temperature, the precipitated product was filtered and recrystallized with ethanol to give the title compound. Crystals suitable for X-ray structure analysis were obtained by slow evaporation from a solution of isopropyl alcohol at room temperature.

S3. Refinement

All H atoms were placed in geometrical positions and constrained to ride on their parent atoms with C—H distances in the range 0.93–0.98 Å. They were treated as riding atoms, with U_{iso}(H) = 1.5U_{eq}(carrier C) for methyl groups and U_{iso}(H) = 1.2U_{eq}(carrier C) for other H atoms.

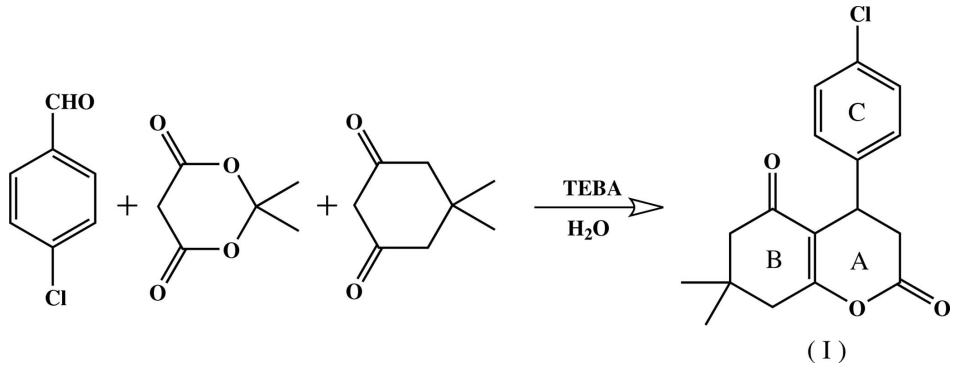


Figure 1

The preparation of the title compound.

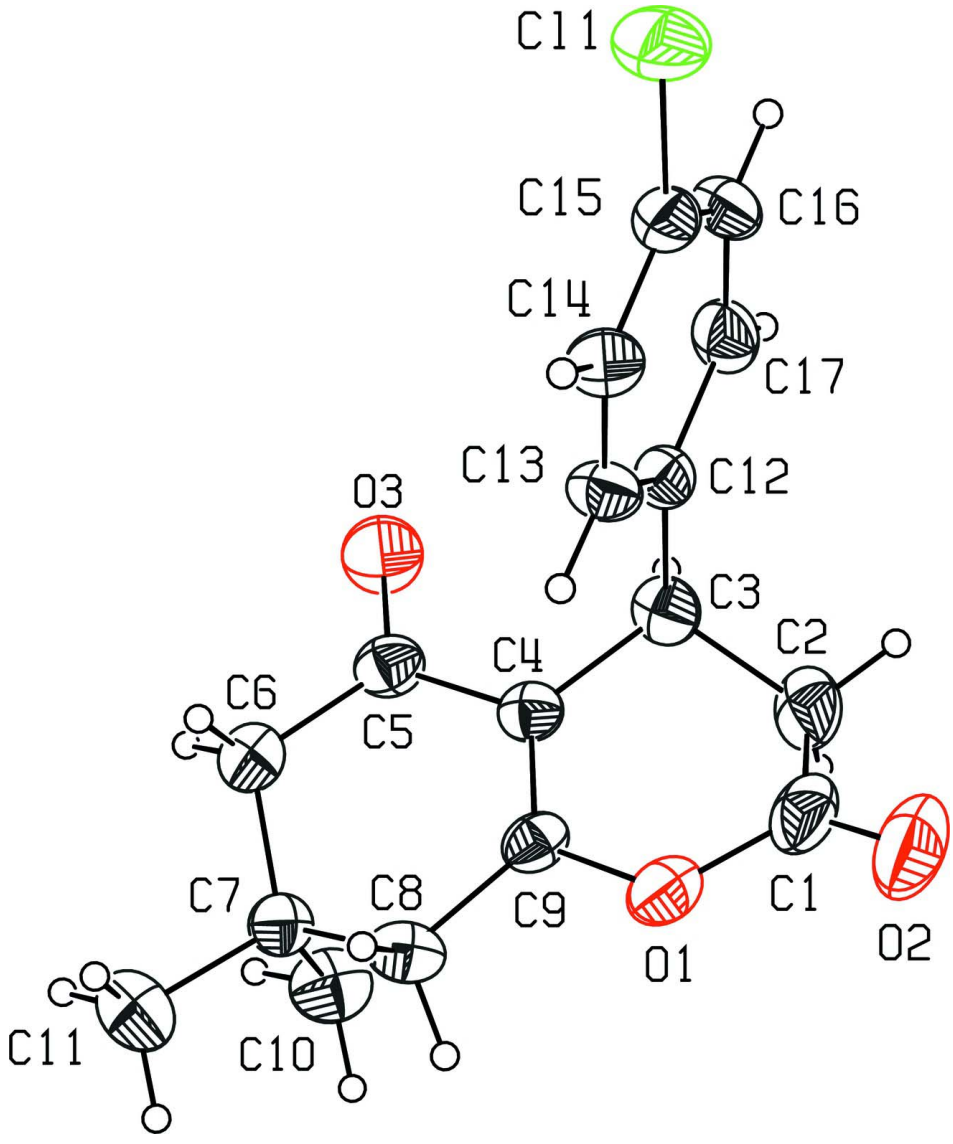


Figure 2

Structure of the title compound, showing 30% probability displacement ellipsoids with atomic numbering scheme.

4-(4-Chlorophenyl)-7,7-dimethyl-7,8-dihydro-4*H*-1-benzopyran- 2,5(3*H*,6*H*)-dione

Crystal data

$C_{17}H_{17}ClO_3$
M_r = 304.76
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 11.9005 (12) Å
b = 5.7971 (8) Å
c = 22.608 (2) Å
β = 93.972 (1)°
V = 1555.9 (3) Å^3
Z = 4
$F(000)$ = 640
D_x = 1.301 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1909 reflections
θ = 2.7–23.0°
μ = 0.25 mm^{-1}
T = 298 K
Prism, colorless
0.48 × 0.39 × 0.34 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.889, T_{max} = 0.919
7519 measured reflections
2789 independent reflections
1585 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25.2°, θ_{min} = 1.8°
h = −12→14
k = −6→6
l = −27→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.186
S = 1.05
2789 reflections
192 parameters
0 restraints
0 constraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 1.4872P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	−0.43477 (9)	0.5886 (3)	0.12137 (6)	0.1069 (6)
O1	0.1778 (2)	0.6708 (5)	0.18437 (12)	0.0681 (8)
O2	0.1132 (3)	0.5408 (7)	0.26641 (15)	0.1127 (13)
O3	0.0220 (3)	1.3042 (5)	0.07706 (14)	0.0936 (10)
C1	0.1180 (4)	0.7039 (10)	0.2336 (2)	0.0765 (13)
C2	0.0708 (4)	0.9367 (9)	0.24091 (17)	0.0810 (14)
H2A	0.1305	1.0395	0.2559	0.097*
H2B	0.0149	0.9303	0.2701	0.097*
C3	0.0160 (3)	1.0357 (7)	0.18295 (16)	0.0598 (10)
H3	0.0049	1.2017	0.1883	0.072*

C4	0.0969 (3)	1.0017 (6)	0.13547 (15)	0.0505 (9)
C5	0.0888 (3)	1.1459 (7)	0.08223 (17)	0.0602 (10)
C6	0.1584 (3)	1.0799 (8)	0.03203 (18)	0.0751 (12)
H6A	0.1720	1.2168	0.0089	0.090*
H6B	0.1156	0.9727	0.0064	0.090*
C7	0.2710 (3)	0.9703 (7)	0.05132 (16)	0.0580 (10)
C8	0.2544 (3)	0.7783 (7)	0.09489 (18)	0.0631 (10)
H8A	0.2291	0.6416	0.0731	0.076*
H8B	0.3265	0.7424	0.1155	0.076*
C9	0.1725 (3)	0.8325 (6)	0.13923 (16)	0.0518 (9)
C10	0.3488 (4)	1.1568 (8)	0.0813 (2)	0.0812 (13)
H10A	0.3137	1.2211	0.1145	0.122*
H10B	0.3616	1.2767	0.0532	0.122*
H10C	0.4195	1.0883	0.0947	0.122*
C11	0.3302 (4)	0.8824 (9)	−0.0017 (2)	0.0955 (15)
H11A	0.4020	0.8187	0.0115	0.143*
H11B	0.3409	1.0077	−0.0285	0.143*
H11C	0.2849	0.7653	−0.0217	0.143*
C12	−0.0981 (3)	0.9254 (6)	0.16736 (15)	0.0524 (9)
C13	−0.1075 (3)	0.7218 (7)	0.13616 (17)	0.0585 (10)
H13	−0.0428	0.6531	0.1235	0.070*
C14	−0.2100 (3)	0.6170 (7)	0.12320 (17)	0.0636 (10)
H14	−0.2141	0.4778	0.1027	0.076*
C15	−0.3048 (3)	0.7190 (8)	0.14062 (17)	0.0638 (11)
C16	−0.3001 (3)	0.9189 (9)	0.17169 (18)	0.0719 (12)
H16	−0.3658	0.9854	0.1838	0.086*
C17	−0.1966 (3)	1.0245 (7)	0.18543 (17)	0.0666 (11)
H17	−0.1932	1.1618	0.2068	0.080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0534 (6)	0.1496 (13)	0.1172 (11)	−0.0213 (7)	0.0011 (6)	0.0253 (9)
O1	0.0610 (16)	0.0693 (18)	0.0721 (18)	−0.0014 (13)	−0.0099 (14)	0.0155 (15)
O2	0.128 (3)	0.132 (3)	0.075 (2)	−0.020 (2)	−0.0128 (19)	0.040 (2)
O3	0.110 (2)	0.074 (2)	0.097 (2)	0.0438 (19)	0.0137 (19)	0.0108 (18)
C1	0.072 (3)	0.101 (4)	0.054 (3)	−0.020 (3)	−0.017 (2)	0.008 (3)
C2	0.081 (3)	0.110 (4)	0.050 (2)	−0.024 (3)	−0.004 (2)	−0.018 (3)
C3	0.064 (2)	0.057 (2)	0.059 (2)	−0.0037 (19)	0.0033 (18)	−0.0186 (19)
C4	0.0476 (18)	0.048 (2)	0.055 (2)	−0.0025 (16)	−0.0024 (15)	−0.0082 (18)
C5	0.060 (2)	0.053 (2)	0.067 (3)	0.0078 (19)	−0.0015 (19)	−0.001 (2)
C6	0.073 (3)	0.091 (3)	0.061 (2)	0.014 (2)	0.002 (2)	0.007 (2)
C7	0.055 (2)	0.062 (2)	0.057 (2)	0.0042 (18)	0.0022 (17)	−0.002 (2)
C8	0.051 (2)	0.055 (2)	0.084 (3)	0.0043 (18)	0.0070 (19)	0.001 (2)
C9	0.0462 (19)	0.051 (2)	0.057 (2)	−0.0052 (17)	−0.0076 (16)	0.0054 (19)
C10	0.073 (3)	0.069 (3)	0.101 (3)	−0.013 (2)	0.002 (2)	0.005 (3)
C11	0.092 (3)	0.110 (4)	0.087 (3)	0.014 (3)	0.025 (3)	−0.007 (3)
C12	0.056 (2)	0.054 (2)	0.047 (2)	0.0089 (17)	0.0058 (16)	−0.0044 (18)

C13	0.0450 (19)	0.062 (2)	0.068 (2)	0.0058 (17)	0.0046 (17)	−0.014 (2)
C14	0.053 (2)	0.066 (3)	0.071 (3)	−0.0035 (19)	−0.0004 (18)	−0.002 (2)
C15	0.050 (2)	0.081 (3)	0.061 (2)	−0.002 (2)	0.0028 (18)	0.018 (2)
C16	0.053 (2)	0.094 (3)	0.071 (3)	0.020 (2)	0.022 (2)	0.018 (3)
C17	0.077 (3)	0.064 (3)	0.060 (2)	0.015 (2)	0.015 (2)	−0.004 (2)

Geometric parameters (Å, º)

Cl1—C15	1.749 (4)	C7—C10	1.549 (5)
O1—C1	1.374 (5)	C8—C9	1.480 (5)
O1—C9	1.384 (4)	C8—H8A	0.9700
O2—C1	1.206 (5)	C8—H8B	0.9700
O3—C5	1.214 (4)	C10—H10A	0.9600
C1—C2	1.475 (7)	C10—H10B	0.9600
C2—C3	1.534 (6)	C10—H10C	0.9600
C2—H2A	0.9700	C11—H11A	0.9600
C2—H2B	0.9700	C11—H11B	0.9600
C3—C4	1.503 (5)	C11—H11C	0.9600
C3—C12	1.520 (5)	C12—C13	1.376 (5)
C3—H3	0.9800	C12—C17	1.392 (5)
C4—C9	1.330 (5)	C13—C14	1.375 (5)
C4—C5	1.463 (5)	C13—H13	0.9300
C5—C6	1.501 (5)	C14—C15	1.357 (5)
C6—C7	1.519 (5)	C14—H14	0.9300
C6—H6A	0.9700	C15—C16	1.354 (6)
C6—H6B	0.9700	C16—C17	1.391 (6)
C7—C8	1.509 (5)	C16—H16	0.9300
C7—C11	1.520 (6)	C17—H17	0.9300
C1—O1—C9	120.2 (3)	C9—C8—H8B	108.7
O2—C1—O1	116.0 (5)	C7—C8—H8B	108.7
O2—C1—C2	127.8 (5)	H8A—C8—H8B	107.6
O1—C1—C2	116.2 (4)	C4—C9—O1	122.9 (3)
C1—C2—C3	112.9 (3)	C4—C9—C8	126.0 (3)
C1—C2—H2A	109.0	O1—C9—C8	110.9 (3)
C3—C2—H2A	109.0	C7—C10—H10A	109.5
C1—C2—H2B	109.0	C7—C10—H10B	109.5
C3—C2—H2B	109.0	H10A—C10—H10B	109.5
H2A—C2—H2B	107.8	C7—C10—H10C	109.5
C4—C3—C12	112.6 (3)	H10A—C10—H10C	109.5
C4—C3—C2	107.8 (3)	H10B—C10—H10C	109.5
C12—C3—C2	111.1 (3)	C7—C11—H11A	109.5
C4—C3—H3	108.4	C7—C11—H11B	109.5
C12—C3—H3	108.4	H11A—C11—H11B	109.5
C2—C3—H3	108.4	C7—C11—H11C	109.5
C9—C4—C5	118.7 (3)	H11A—C11—H11C	109.5
C9—C4—C3	121.0 (3)	H11B—C11—H11C	109.5
C5—C4—C3	120.2 (3)	C13—C12—C17	117.7 (3)

O3—C5—C4	121.1 (4)	C13—C12—C3	121.3 (3)
O3—C5—C6	120.8 (4)	C17—C12—C3	121.0 (3)
C4—C5—C6	117.9 (3)	C14—C13—C12	121.9 (3)
C5—C6—C7	114.3 (3)	C14—C13—H13	119.1
C5—C6—H6A	108.7	C12—C13—H13	119.1
C7—C6—H6A	108.7	C15—C14—C13	119.2 (4)
C5—C6—H6B	108.7	C15—C14—H14	120.4
C7—C6—H6B	108.7	C13—C14—H14	120.4
H6A—C6—H6B	107.6	C16—C15—C14	121.2 (4)
C8—C7—C6	110.1 (3)	C16—C15—Cl1	120.2 (3)
C8—C7—C11	110.9 (3)	C14—C15—Cl1	118.6 (4)
C6—C7—C11	111.2 (3)	C15—C16—C17	119.8 (4)
C8—C7—C10	109.3 (3)	C15—C16—H16	120.1
C6—C7—C10	108.8 (3)	C17—C16—H16	120.1
C11—C7—C10	106.5 (3)	C16—C17—C12	120.2 (4)
C9—C8—C7	114.1 (3)	C16—C17—H17	119.9
C9—C8—H8A	108.7	C12—C17—H17	119.9
C7—C8—H8A	108.7		

C9—O1—C1—O2	169.1 (3)	C5—C4—C9—O1	−172.3 (3)
C9—O1—C1—C2	−12.9 (5)	C3—C4—C9—O1	3.8 (5)
O2—C1—C2—C3	−138.5 (4)	C5—C4—C9—C8	2.4 (5)
O1—C1—C2—C3	43.7 (5)	C3—C4—C9—C8	178.5 (3)
C1—C2—C3—C4	−48.0 (5)	C1—O1—C9—C4	−12.2 (5)
C1—C2—C3—C12	75.9 (4)	C1—O1—C9—C8	172.4 (3)
C12—C3—C4—C9	−97.0 (4)	C7—C8—C9—C4	16.7 (5)
C2—C3—C4—C9	26.0 (5)	C7—C8—C9—O1	−168.1 (3)
C12—C3—C4—C5	79.1 (4)	C4—C3—C12—C13	35.1 (5)
C2—C3—C4—C5	−157.9 (3)	C2—C3—C12—C13	−86.0 (4)
C9—C4—C5—O3	−179.1 (4)	C4—C3—C12—C17	−146.4 (3)
C3—C4—C5—O3	4.7 (5)	C2—C3—C12—C17	92.5 (4)
C9—C4—C5—C6	6.0 (5)	C17—C12—C13—C14	−0.3 (5)
C3—C4—C5—C6	−170.1 (3)	C3—C12—C13—C14	178.2 (4)
O3—C5—C6—C7	152.0 (4)	C12—C13—C14—C15	1.3 (6)
C4—C5—C6—C7	−33.1 (5)	C13—C14—C15—C16	−1.6 (6)
C5—C6—C7—C8	49.9 (5)	C13—C14—C15—Cl1	177.7 (3)
C5—C6—C7—C11	173.2 (4)	C14—C15—C16—C17	0.9 (6)
C5—C6—C7—C10	−69.9 (5)	Cl1—C15—C16—C17	−178.3 (3)
C6—C7—C8—C9	−41.4 (4)	C15—C16—C17—C12	0.0 (6)
C11—C7—C8—C9	−164.8 (3)	C13—C12—C17—C16	−0.3 (5)
C10—C7—C8—C9	78.1 (4)	C3—C12—C17—C16	−178.8 (3)