Crystal structure of 5, 7-Dimethyl-4-p-chloro phenoxy methyl coumarin (C_{18} H_{15} Cl O_3)

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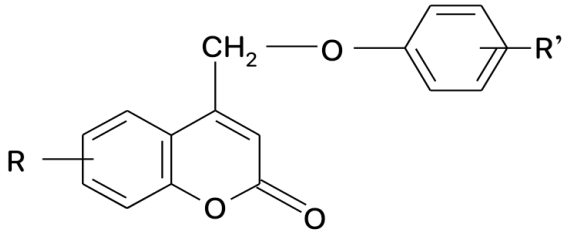
Abstract **- Crystal structure of coumarins has been of great interest in recent years especially in investigating the solid-state photochemical dimerization reactions. Coumarin itself crystallizes in the form of orthorhombic crystals and does not undergo photochemical dimerization in the solid state. Different types of packing of the crystal due to substitutions at different positions would affect their solid-state reactivity. Many substituted coumarins were studied for photodimerization due to the inertness of coumarin in solid state and also the role of packing of crystals as their solid-state activity were also studied. X-ray crystal structure analysis of Introduction of Cl at C4 makes the molecule photostable whereas at C6 and C7 it makes the molecule photoreactive though in all cases the crystal system is monoclinic. Methoxy group at C4, C6 and C7 gives rise to different crystal packing systems and different reactivities. Acetoxy group acts as steering agent in solid state reactions, many substituted coumarins were studied for photodimerization due to the inertness of coumarin in solid state and also the role of packing and presence of weak interactions in the following coumarin.**

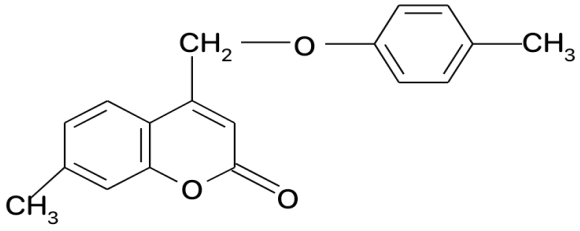
Index Terms **- coumarins, Dimethyl, crystal x-ray study, Molecular Packing and hydrogen bonding.**

I.INTRODUCTION

4-aryloxy methyl coumarins were mainly of mechanistic interest and they were investigated for a possible Claisen rearrangement by Bheemarao et al[1]. Further structure activity relation studies in this class of compounds revealed the anti-microbial property of various 4-aryloxy methyl coumarins (Kulkarni et al [2].



A diffraction study of one of the above compounds revealed the Centro symmetric nature of these compounds in the solid state.



A study of the packing has shown that in the solid state the two molecules are oriented anti-to each other. With a view of study, the possible changes due to the introduction of the chloro group the crystal structure of the following compound has been investigated.

II. EXPERIMENTAL

The Title compound has been synthesised by the reaction of p-chlorophenol with 5,7-dimethyl-4-bromomethylcoumarin. Crystals suitable for diffraction studies have been grown from ethanol by slow evaporation technique. With a view to find out the proffered conformer in the solid state the structure of the title compound schematic view of the molecule shown in the Fig. 1 has been studied during the present investigation.

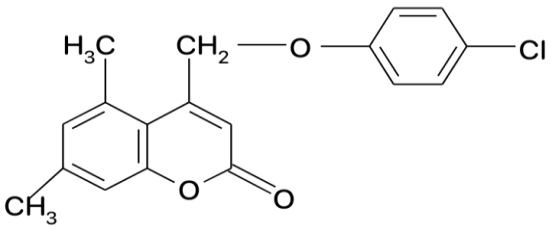


Fig .1

III.CRYSTALLIZATION

Compound has been grown by slow evaporation technique using acetic acid. Colourless plate like single crystals suitable for X-ray diffraction were obtained. The density of the crystal was measured by flotation technique using potassium iodide solution. The measure density agreed with the calculated density for Z=2.

IV.X-RAY DATA COLLECTION

The three dimensional intensity data were collected using a single crystal of approximate size 0.30 x 0.20 x 0.20 mm mounted on CCD diffractometer[3]. with graphite monochromated MoK_α radiation of wavelength 0.71073 Å in fine focused sealed tube. The intensities of reflections 6766 were collected in the 2θ range 1.88 to 24.71. The data was collected using ω and ϕ scans mode with h, -9 to 9, k, -10 to 10 and l, -13 to 13. The intensities were corrected for Lorentz and polarization effects has 2498 unique reflections of which 2084 $F_0>4\sigma(F_0)$ were observed. The space group *P-1* assigned from systematic absences. The cell parameters are a = 8.387(3) Å, b = 8.612(3) Å, c = 11.542(4) Å, α = 75.58(5)^0, β = 71.48(5)^0, γ = 70.35(5)^0 and V = 734.8(8) Å^3. The multi-scan absorption was carried out using SADABS[4]. The calculated absorption coefficient was 0.27 mm^{-1}.

Structure solution and Refinement

The structure was solved by direct methods using SHELXS-97[5]. The position of all non-hydrogen atoms were revealed in the best E-map. Then refined using SHELXL-97 by the full matrix least squares refinement. All non-hydrogen atoms treated isotropically and refined till R-value converged at R(F) = 0.493, wR(F^2) =0.1117. The difference Fourier map further revealed all H-atoms. All the hydrogen atoms parameters were included in the final steps of with weight assigned to a structure factor calculations using the scheme $w = 1/[\sigma^2(F_0^2)+(0.1851P)^2+5.624P]$ where $P = (F_0^2+2F_c^2)/3$. The parameters at the end of final refinement were R(F) = 0.0414, wR(F^2) = 0.1049. The minimum and maximum electron densities from difference Fourier map are -0.32 and 0.26e.A^{-3} respectively.

VI. RESULTS AND DISCUSSIONS

The crystallographic refinement data is given in the Table 1.. The bond lengths and bond angles for non-hydrogen atoms are listed in the Table 2 and Table 3. Table 4. Gives torsion angles involving non-hydrogen atoms[6]. A perspective view of a Ortep plot of the molecule [7] with 50% probability thermal ellipsoids with atomic numbering is shown in Fig. 1. Fig .2 shows the single molecule in a unit cell. Fig.3 shows packing of molecules with C-H…O contacts and the packing of the molecule in the unit cell [8]. Fig. 4 packing diagram showing C-H…O contacts. Packing diagram viewed down, a-axis, b-axis and c-axis are shown in Fig. 5. The least square planes and dihedral angles[9] are listed in Table 5. The distance and angles between the atoms involved in intra and inter-molecular hydrogen bonding are listed in Table 6.

Conformation of the molecule

The molecule adopts a planar arrangement. The aryloxy moiety is oriented cis with respect to the C_3-C_4 double bond of coumarin. This is similar to that observed in the case of 7-methyl-4-(p-tolyloxymethyl) coumarin reported by Puttaraja et al [10].

Bond angles, Molecular Packing

All the C-C bond lengths are in the normal range of Sp^2 carbons. The $C_{10}Sp^3$-O bond length is 1.412 Å. The O-$C_{11}Sp^2$ bond length is expectedly less than C_{10}-O_1 i.e., 1.368 Å. A comparison of the bond lengths of peri carbons C_{10} and C_{19} with C_3 and C_4 indicates that the C_4-C_{19} bond length is greater by 0.013 Å (C_3-C_{10} = 1.49 Å). This would reduce the non-bonded interactions with the methyl and methylene hydrogen.

VII.ACKNOWLEDGMENT

The authors thank Instrumentation and Service Unit, Indian Institute of Science, Bangalore-560 012 for data collection.

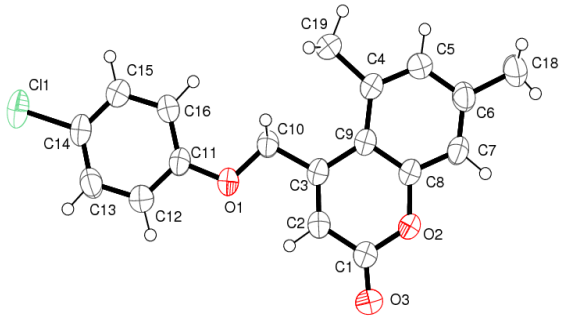


Fig.1 *ORTEP* diagram of the title molecule with 50% probability displacement ellipsoids for non-H atoms.

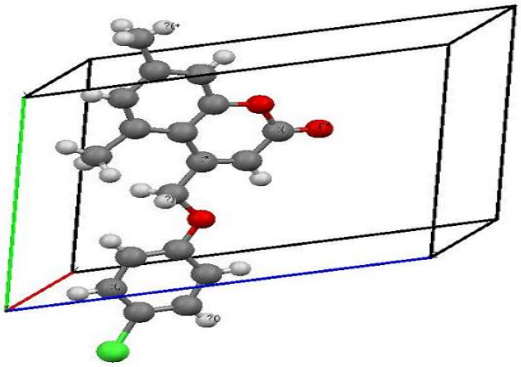


Fig .2 Single molecules in a unit cell

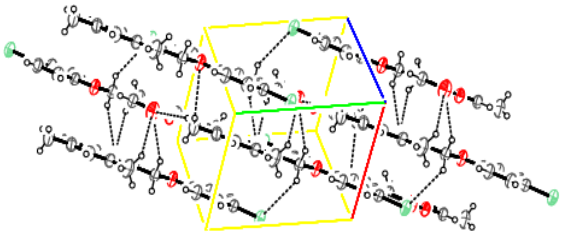


Fig.3 Packing diagram of the molecule in a crystal showing C-H hydrogen bonding.

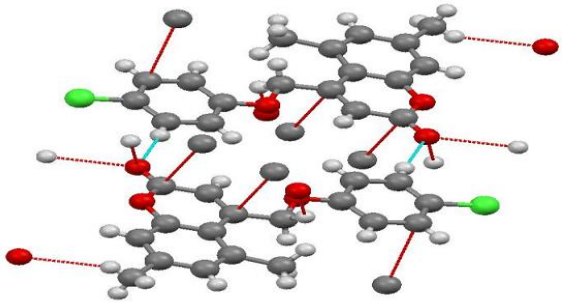
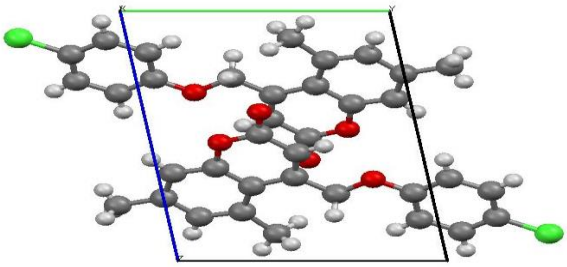
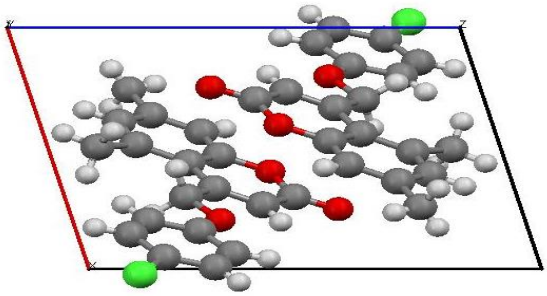


Fig. 4 Diagram of the molecule in a crystal showing C-H….O hydrogen bonding.

(a)



(b)



(c)

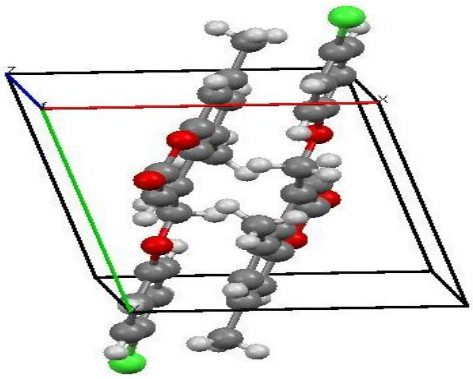


Fig. 5 (a), (b) and (c)Packing diagram of the molecule in a crystal viewed down a-axis, b-axis and c-axis

Table 1. Crystal data and structure refinement

DATA	COMPOUND
Chemical formula	$C_{18}H_{15}ClO_3$
M_r	314.75
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
a, *b*, *c* (Å)	8.387 (3), 8.612 (3), 11.542 (4)
α, β, γ (°)	75.578 (5), 71.481 (5), 70.351 (5)
V (Å^3)	735.0 (4)
Z	2
F(000)	328
D_x (Mg m^{-3})	1.422
Radiation type	Mo *K*α, (λ = 0.71073 Å)

μ (mm^{-1})	0.27
Crystal size (mm)	0.30×0.20×0.20
Absorption correction	0.27 mm^{-1}
Calculated density	1.42 mg/m^3
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6766, 2498, 2083
R_{int}	0.096
θ values (°)	θ_{max} = 24.7, θ_{min} = 1.9
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.588
Range of *h*, *k*, *l*	h = -9→9, k = -10→10, l = -13→13
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.112, 1.05
No. of reflections	2498
No. of parameters	259
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.0989P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	2.442
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e $Å^{-3}$)	0.26, -0.32

Table 2.List of Bond lengths (Å), esd's given in the parentheses

Atom1-Atom2	Distance	Atom1-Atom2	Distance
C18—C6	1.502 (3)	C3—C2	1.330 (3)
C18—H13	0.790 (5)	C3—C10	1.497 (2)
C18—H14	0.800 (4)	C16—C15	1.380 (3)
C18—H16	0.910 (5)	C16—H11	0.950 (2)
C19—C4	1.510 (2)	C14—C15	1.354 (3)
C19—H4	0.930 (3)	C14—C13	1.364 (3)
C19—H7	1.030 (3)	C12—C13	1.377 (3)
C19—H8	0.980 (3)	C12—H10	0.944 (2)
Cl1—C14	1.742 (2)	C15—H9	0.950 (2)
O1—C11	1.368 (2)	C6—C7	1.360 (3)
O1—C10	1.412 (2)	C6—C5	1.393 (3)
O2—C1	1.360 (2)	C1—C2	1.439 (2)
O2—C8	1.365 (2)	C7—H3	0.924 (2)
O3—C1	1.190 (2)	C2—H6	0.940 (2)
C9—C8	1.397 (2)	C4—C5	1.367 (3)
C9—C4	1.411 (3)	C5—H5	0.930 (2)
C9—C3	1.457 (2)	C10—H1	1.001 (2)
C8—C7	1.376 (2)	C10—H2	1.030 (2)
C11—C16	1.368 (3)	C13—H12	0.900 (2)
C11—C12	1.372 (3)		

Table 3. List of Bond angles (º), esd's given in the parentheses

Atom-Atom2-Atom3	Angle	Atom-Atom2-Atom3	Angle
C6—C18—H13	120.00 (3)	C11—C12—H10	117.80 (1)
C6—C18—H14	105.00 (3)	C13—C12—H10	121.70 (1)
H13—C18—H14	110.00 (4)	C14—C15—C16	119.85 (2)
C6—C18—H16	108.00 (3)	C14—C15—H9	120.10 (1)
H13—C18—H16	111.00 (4)	C16—C15—H9	120.10 (1)
H14—C18—H16	101.00 (3)	C7—C6—C5	117.44 (2)
C4—C19—H4	111.50 (2)	C7—C6—C18	122.42 (2)
C4—C19—H7	111.30 (1)	C5—C6—C18	120.14 (2)
H4—C19—H7	114.00 (2)	O3—C1—O2	117.07 (2)
C4—C19—H8	109.30 (1)	O3—C1—C2	126.61 (2)
H4—C19—H8	104.00 (2)	O2—C1—C2	116.27 (2)
H7—C19—H8	107.00 (2)	C6—C7—C8	120.01 (2)
C11—O1—C10	116.10 (1)	C6—C7—H3	122.40 (1)
C1—O2—C8	122.51 (1)	C8—C7—H3	117.50 (1)
C8—C9—C4	116.17 (2)	C3—C2—C1	122.89 (2)
C8—C9—C3	115.78 (2)	C3—C2—H6	123.40 (1)
C4—C9—C3	128.05 (1)	C1—C2—H6	113.70 (1)
O2—C8—C7	114.19 (1)	C5—C4—C9	119.05 (2)
O2—C8—C9	122.30 (2)	C5—C4—C19	116.35 (2)
C7—C8—C9	123.51 (2)	C9—C4—C19	124.57 (2)
O1—C11—C16	124.53 (2)	C4—C5—C6	123.80 (2)
O1—C11—C12	115.61 (2)	C4—C5—H5	120.40 (1)
C16—C11—C12	119.86 (2)	C6—C5—H5	115.80 (1)
C2—C3—C9	120.15 (2)	O1—C10—C3	109.78 (1)
C2—C3—C10	119.14 (2)	O1—C10—H1	108.60 (1)
C9—C3—C10	120.71 (2)	C3—C10—H1	109.20 (1)
C11—C16—C15	119.63 (2)	O1—C10—H2	108.80 (1)
C11—C16—H11	123.40 (1)	C3—C10—H2	109.50 (1)
C15—C16—H11	117.00 (1)	H1—C10—H2	110.90 (2)
C15—C14—C13	121.39 (2)	C14—C13—C12	118.79 (2)
C15—C14—Cl1	118.72 (2)	C14—C13—H12	124.70 (1)
C13—C14—Cl1	119.89 (2)	C12—C13—H12	116.50 (1)
C11—C12—C13	120.47 (2)		

Table 4. List of Torsion angles (º), esd's given in the parentheses

Atom1-Atom2-Atom3-Atom4	Angle	Atom1-Atom2-Atom3-Atom4	Angle

C1—O2—C8—C7	-177.38 (2)	C18—C6—C7—C8	-179.00 (2)
C1—O2—C8—C9	2.90 (3)	O2—C8—C7—C6	178.48 (2)
C4—C9—C8—O2	-179.45 (2)	C9—C8—C7—C6	-1.80 (3)
C3—C9—C8—O2	-0.30 (2)	C9—C3—C2—C1	2.60 (3)
C4—C9—C8—C7	0.80 (3)	C10—C3—C2—C1	-176.85 (2)
C3—C9—C8—C7	179.93 (2)	O3—C1—C2—C3	177.30 (2)
C10—O1—C11—C16	0.40 (3)	O2—C1—C2—C3	-0.10 (3)
C10—O1—C11—C12	179.92 (2)	C8—C9—C4—C5	0.70 (3)
C8—C9—C3—C2	-2.30 (3)	C3—C9—C4—C5	-178.24 (2)
C4—C9—C3—C2	176.69 (2)	C8—C9—C4—C19	-177.20 (2)
C8—C9—C3—C10	177.12 (2)	C3—C9—C4—C19	3.80 (3)
C4—C9—C3—C10	-3.90 (3)	C9—C4—C5—C6	-1.40 (3)
O1—C11—C16—C15	178.59 (2)	C19—C4—C5—C6	176.70 (2)
C12—C11—C16—C15	-1.00 (3)	C7—C6—C5—C4	0.50 (3)
O1—C11—C12—C13	-178.24 (2)	C18—C6—C5—C4	-179.50 (2)
C16—C11—C12—C13	1.30 (3)	C11—O1—C10—C3	-178.23 (1)
C13—C14—C15—C16	1.00 (3)	C2—C3—C10—O1	3.20 (2)
Cl1—C14—C15—C16	-178.75 (2)	C9—C3—C10—O1	-176.18 (2)
C11—C16—C15—C14	-0.20 (3)	C15—C14—C13—C12	-0.60 (3)
C8—O2—C1—O3	179.70 (2)	Cl1—C14—C13—C12	179.14 (2)
C8—O2—C1—C2	-2.60 (3)	C11—C12—C13—C14	-0.60 (3)
C5—C6—C7—C8	1.10 (3)		

Table.5 List of Bond angles (º), esd's given in the parentheses

Atom-Atom2-Atom3	Angle	Atom-Atom2-Atom3	Angle
C6—C18—H13	120.00 (3)	C11—C12—H10	117.80 (1)
C6—C18—H14	105.00 (3)	C13—C12—H10	121.70 (1)
H13—C18—H14	110.00 (4)	C14—C15—C16	119.85 (2)
C6—C18—H16	108.00 (3)	C14—C15—H9	120.10 (1)
H13—C18—H16	111.00 (4)	C16—C15—H9	120.10 (1)
H14—C18—H16	101.00 (3)	C7—C6—C5	117.44 (2)
C4—C19—H4	111.50 (2)	C7—C6—C18	122.42 (2)
C4—C19—H7	111.30 (1)	C5—C6—C18	120.14 (2)
H4—C19—H7	114.00 (2)	O3—C1—O2	117.07 (2)
C4—C19—H8	109.30 (1)	O3—C1—C2	126.61 (2)
H4—C19—H8	104.00 (2)	O2—C1—C2	116.27 (2)
H7—C19—H8	107.00 (2)	C6—C7—C8	120.01 (2)
C11—O1—C10	116.10 (1)	C6—C7—H3	122.40 (1)
C1—O2—C8	122.51 (1)	C8—C7—H3	117.50 (1)
C8—C9—C4	116.17 (2)	C3—C2—C1	122.89 (2)
C8—C9—C3	115.78 (2)	C3—C2—H6	123.40 (1)
C4—C9—C3	128.05 (1)	C1—C2—H6	113.70 (1)
O2—C8—C7	114.19 (1)	C5—C4—C9	119.05 (2)
O2—C8—C9	122.30 (2)	C5—C4—C19	116.35 (2)
C7—C8—C9	123.51 (2)	C9—C4—C19	124.57 (2)
O1—C11—C16	124.53 (2)	C4—C5—C6	123.80 (2)
O1—C11—C12	115.61 (2)	C4—C5—H5	120.40 (1)
C16—C11—C12	119.86 (2)	C6—C5—H5	115.80 (1)
C2—C3—C9	120.15 (2)	O1—C10—C3	109.78 (1)
C2—C3—C10	119.14 (2)	O1—C10—H1	108.60 (1)
C9—C3—C10	120.71 (2)	C3—C10—H1	109.20 (1)
C11—C16—C15	119.63 (2)	O1—C10—H2	108.80 (1)
C11—C16—H11	123.40 (1)	C3—C10—H2	109.50 (1)
C15—C16—H11	117.00 (1)	H1—C10—H2	110.90 (2)
C15—C14—C13	121.39 (2)	C14—C13—C12	118.79 (2)
C15—C14—Cl1	118.72 (2)	C14—C13—H12	124.70 (1)
C13—C14—Cl1	119.89 (2)	C12—C13—H12	116.50 (1)

C11—C12—C13	120.47 (2)		

Table 6 List of Torsion angles (º), esd's given in the parentheses

Atom1-Atom2-Atom3-Atom4	Angle	Atom1-Atom2-Atom3-Atom4	Angle
C1—O2—C8—C7	-177.38 (2)	C18—C6—C7—C8	-179.00 (2)
C1—O2—C8—C9	2.90 (3)	O2—C8—C7—C6	178.48 (2)
C4—C9—C8—O2	-179.45 (2)	C9—C8—C7—C6	-1.80 (3)
C3—C9—C8—O2	-0.30 (2)	C9—C3—C2—C1	2.60 (3)
C4—C9—C8—C7	0.80 (3)	C10—C3—C2—C1	-176.85 (2)
C3—C9—C8—C7	179.93 (2)	O3—C1—C2—C3	177.30 (2)
C10—O1—C11—C16	0.40 (3)	O2—C1—C2—C3	-0.10 (3)
C10—O1—C11—C12	179.92 (2)	C8—C9—C4—C5	0.70 (3)
C8—C9—C3—C2	-2.30 (3)	C3—C9—C4—C5	-178.24 (2)
C4—C9—C3—C2	176.69 (2)	C8—C9—C4—C19	-177.20 (2)
C8—C9—C3—C10	177.12 (2)	C3—C9—C4—C19	3.80 (3)
C4—C9—C3—C10	-3.90 (3)	C9—C4—C5—C6	-1.40 (3)
O1—C11—C16—C15	178.59 (2)	C19—C4—C5—C6	176.70 (2)
C12—C11—C16—C15	-1.00 (3)	C7—C6—C5—C4	0.50 (3)
O1—C11—C12—C13	-178.24 (2)	C18—C6—C5—C4	-179.50 (2)
C16—C11—C12—C13	1.30 (3)	C11—O1—C10—C3	-178.23 (1)
C13—C14—C15—C16	1.00 (3)	C2—C3—C10—O1	3.20 (2)
Cl1—C14—C15—C16	-178.75 (2)	C9—C3—C10—O1	-176.18 (2)
C11—C16—C15—C14	-0.20 (3)	C15—C14—C13—C12	-0.60 (3)
C8—O2—C1—O3	179.70 (2)	Cl1—C14—C13—C12	179.14 (2)
C8—O2—C1—C2	-2.60 (3)	C11—C12—C13—C14	-0.60 (3)
C5—C6—C7—C8	1.10 (3)		

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