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rac-3,4-trans-Dichloro-1,2,3,4-tetrahydro-2-naphthyl acetate

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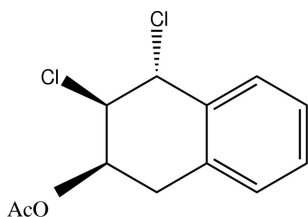
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.063; wR factor = 0.154; data-to-parameter ratio = 24.8.

The title compound, $\text{C}_{12}\text{H}_{12}\text{Cl}_2\text{O}_2$, has a bicyclic skeleton containing cyclohexene and benzene fragments. The cyclohexene ring adopts a half-chair conformation with displacements of two atoms out of the least-squares plane of 0.311 (2) and -0.336 (2) Å. The Cl atoms are *trans*-positioned.

Related literature

For related literature, see: Frimer (1985*a,b*); March & Smith (2001); McBride *et al.* (1999); Metha & Ramesh (2003, 2005); Metha *et al.* (2003); Patai (1983); Ros *et al.* (2006); Wasserman & Murray (1979). For related structures, see: Kishali *et al.* (2006*a,b*).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{12}\text{Cl}_2\text{O}_2$
 $M_r = 259.12$
 Monoclinic, $P2_1/c$
 $a = 12.931$ (5) Å
 $b = 12.478$ (5) Å
 $c = 7.441$ (4) Å
 $\beta = 101.040$ (5)°

$V = 1178.4$ (9) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.53$ mm⁻¹
 $T = 293$ (2) K
 $0.2 \times 0.2 \times 0.2$ mm

Data collection

Rigaku R-AXIS conversion diffractometer
 Absorption correction: multi-scan (Blessing, 1995)
 $T_{\min} = 0.897$, $T_{\max} = 0.898$
 34473 measured reflections

3627 independent reflections
 2486 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.083$
 25 standard reflections every 200 reflections
 intensity decay: 3%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.154$
 $S = 1.09$
 3627 reflections

146 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.21$ e Å⁻³
 $\Delta\rho_{\min} = -0.34$ e Å⁻³

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2181).

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***rac*-3,4-*trans*-Dichloro-1,2,3,4-tetrahydro-2-naphthyl acetate**

Ertan Şahin, Nurhan Kishali and Yunus Kara

S1. Comment

Oxyfunctionalization of organic unsaturated molecules are efficiently performed by an oxygen atom. It has been reported that the main reactions of singlet oxygen are cycloaddition and ene-reaction (Frimer, 1985*a,b*; Patai 1983; Wasserman & Murray, 1979). We have successively used isotetralin (1,4,5,8-tetrahydronaphthalene) for a short and stereocontrolled synthesis of a new class of bis-endoperoxide (Kishali *et al.*, 2006*a*) and the interesting chlorination product, (2*S**,3*S**,4*S**)-3,4-dichloro-1,2,3,4,5,8-hexahydro naphthalen-2-yl acetate (Kishali *et al.*, 2006*b*), *cf.* Fig. 3). A multistep procedure for the preparation of a new family of annulated inositols from tetrahydronaphthalene has been developed (Metha & Ramesh, 2003, 2005; Metha *et al.*, 2003). Vicinal halohydrins are versatile building blocks and key intermediates for the synthesis of many bioactive molecules (Ros *et al.*, 2006).

We aimed to synthesize the polyhydroxyhalohidrins from (2*S**, 3*S**, 4*S**)-3, 4-dichloro-1, 2, 3, 4, 5, 8-hexahydro-naphthalen-2-yl acetate with KMnO₄, but reaction of (2*S**, 3*S**, 4*S**)-3, 4-dichloro-1, 2, 3, 4, 5, 8-hexahydro-naphthalen-2-yl acetate with KMnO₄ gave a very interesting and unexpected product (I) including an aromatic ring.

Potassium permanganate, a very oxidizing agent can be used to oxidize alkenes to diols (March & Smith, 2001). Limiting the reaction to hydroxylation alone is often difficult, and it is usually attempted by using a cold, diluted and basic KMnO₄ solution. Potassium permanganate, when supported on alumina and used in acetone, reacts very differently than potassium permanganate in aqueous solution. The synthesis of benzene derivatives from 1,4-cyclohexadienes by using KMnO₄—Al₂O₃ is already known in the literature (McBride *et al.*, 1999). (2*S**, 3*S**, 4*S**)-3, 4-dichloro-1, 2, 3, 4, 5, 8-hexahydronaphthalen-2-yl acetate was synthesized as described in the literature (Kishali *et al.*, 2006*b*). We expected the formation of a diol from reaction of (2*S**, 3*S**, 4*S**)-3, 4-dichloro-1, 2, 3, 4, 5, 8-hexahydronaphthalen-2-yl acetate with KMnO₄, but instead the formation of (I) was detected.

The bicyclic skeleton contains a cyclohexene and a benzene ring sharing a common C?C bond [C1—C6=1.400 (3) Å] (Fig. 1). The Cl atoms are *trans*-positioned. C10—C11 and C9—C12 bond lengths are 1.827 (3) and 1.802 (3) Å, respectively. The three stereogenic centres C2, C3, and C4 are of the same configuration; during crystallization the racemization occurred. All these values are comparable with our previous structure (C₁₂H₁₄O₂Cl₂) (Kishali *et al.*, 2006*b*), in which, only the difference, hexadien moiety exists instead of benzene in the carbocyclic ring. Crystal packing is dominated by van der Waals contacts.

S2. Experimental

3,4-Dichloro-1, 2, 3, 4-tetrahydro-naphthalen-2-yl acetate was prepared as follows. To a magnetically stirred acetone solution (25 ml of (2*S**, 3*S**, 4*S**)-3, 4-dichloro-1, 2, 3, 4, 5, 8-hexahydronaphthalen-2-yl acetate (260 mg, 1 mmol) was added a solution of KMnO₄ (158 mg, 1 mmol) and MgSO₄ (144 mg, 1.2 mmol) in water (20 ml) at 253 K during 5 h. After the addition was completed, the reaction mixture was stirred for an additional 15 h at the given temperature and then filtered. The filtrate was concentrated to 20 ml by evaporation. The aqueous solution was extracted with ethyl

acetate (3x30 ml) and the extract were dried (Na_2SO_4). Evaporation of the solvent gave racemic mixture of compound I. It was separated by column chromatography, eluting with ethylacetate/hexanes (120 mg, 42%, colourless solid). Colourless solid from CH_2Cl_2 /hexane. m. p: 348–349 K. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , p.p.m.): 7.39–7.12 (m, 4H), 5.78 (m, $1\text{H-C}_{(2)}$), 5.35 (d, $J = 3.3$, $1\text{H-C}_{(4)}$), 4.74 (t, $J = 2.9$, $1\text{H-C}_{(3)}$), 3.2 (m, $2\text{H-C}_{(1)}$), 2.14 (s, $3\text{H-C}_{(\text{Ac})}$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , p.p.m.): 170.4, 132.9, 131.7, 130.9, 129.5, 129.3, 127.6, 67.3, 61.3, 60.1, 30.2, 30.0, 21.3. calcd C 55.62, H 4.67; found C 55.87, H 4.89.

S3. Refinement

H atoms were placed in geometrically idealized positions ($\text{C-H} = 0.93\text{--}0.98 \text{ \AA}$) and treated as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (for methine and methylene) or $1.5U_{\text{eq}}(\text{methyl C})$.

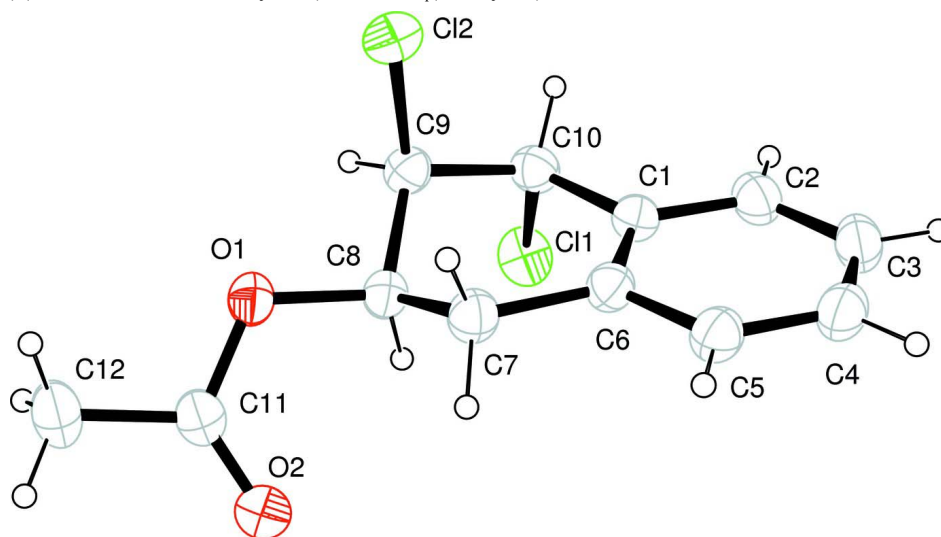


Figure 1

Molecular structure of I with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

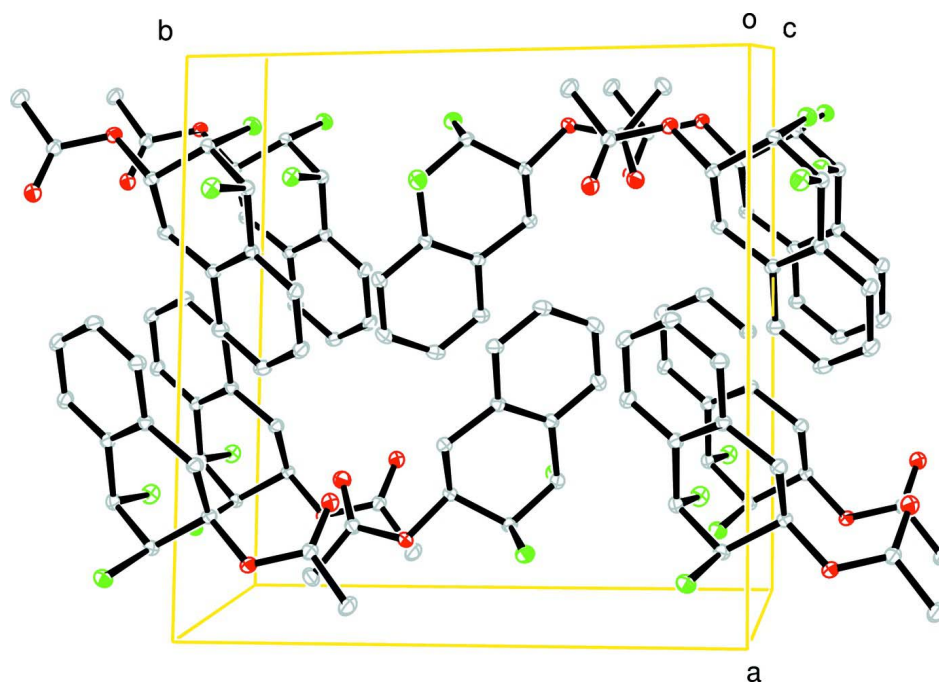


Figure 2

A packing diagram. H atoms have been omitted for clarity.

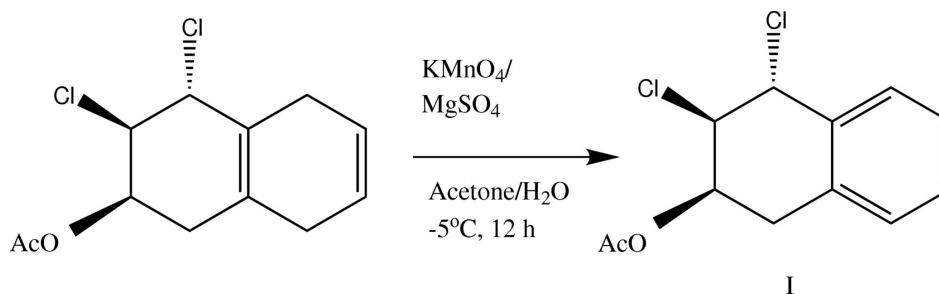


Figure 3

The preparation of the title compound.

rac-3,4-*trans*-Dichloro-1,2,3,4-tetrahydro-2-naphthyl acetate

Crystal data

$C_{12}H_{12}Cl_2O_2$

$M_r = 259.12$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 12.931(5)\ \text{\AA}$

$b = 12.478(5)\ \text{\AA}$

$c = 7.441(4)\ \text{\AA}$

$\beta = 101.040(5)^\circ$

$V = 1178.4(9)\ \text{\AA}^3$

$Z = 4$

$F(000) = 536$

$D_x = 1.461\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 6382 reflections

$\theta = 2.3\text{--}30.6^\circ$

$\mu = 0.53\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Needle, pale white

$0.2 \times 0.2 \times 0.2\ \text{mm}$

Data collection

Rigaku R-Axis conversion diffractometer	2486 reflections with $I > 2\sigma(I)$
dtprofit.ref scans	$R_{\text{int}} = 0.083$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{\text{max}} = 30.7^\circ$, $\theta_{\text{min}} = 2.3^\circ$
$T_{\text{min}} = 0.897$, $T_{\text{max}} = 0.898$	$h = -18 \rightarrow 18$
34473 measured reflections	$k = -17 \rightarrow 17$
3627 independent reflections	$l = -10 \rightarrow 10$
	25 standard reflections every 200 reflections
	intensity decay: 3%

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.063$	$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.2956P]$
$wR(F^2) = 0.154$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3627 reflections	$\Delta\rho_{\text{max}} = 0.21 \text{ e } \text{\AA}^{-3}$
146 parameters	$\Delta\rho_{\text{min}} = -0.34 \text{ e } \text{\AA}^{-3}$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.22319 (6)	0.59964 (5)	0.18471 (9)	0.0666 (2)
C12	0.12465 (5)	0.59224 (5)	0.70388 (10)	0.0667 (2)
O1	0.13535 (12)	0.35895 (13)	0.5577 (2)	0.0535 (4)
O2	0.23303 (14)	0.22818 (15)	0.4683 (3)	0.0722 (5)
C1	0.34102 (17)	0.62147 (18)	0.5296 (3)	0.0486 (5)
C2	0.40917 (19)	0.7052 (2)	0.5078 (3)	0.0580 (6)
H2	0.3843	0.7623	0.4315	0.07*
C3	0.5123 (2)	0.7044 (2)	0.5973 (4)	0.0646 (7)
H3	0.5573	0.7601	0.5804	0.078*
C4	0.5489 (2)	0.6200 (2)	0.7129 (4)	0.0636 (7)
H4	0.6184	0.6197	0.7756	0.076*
C5	0.48316 (19)	0.5365 (2)	0.7357 (3)	0.0577 (6)
H5	0.5089	0.4802	0.8135	0.069*
C6	0.37804 (17)	0.53492 (18)	0.6436 (3)	0.0478 (5)
C7	0.30921 (18)	0.44074 (19)	0.6704 (3)	0.0533 (5)
H7A	0.3489	0.3748	0.6696	0.064*
H7B	0.2883	0.4467	0.7884	0.064*
C8	0.21251 (17)	0.43671 (18)	0.5214 (3)	0.0483 (5)
H8	0.2343	0.4166	0.4069	0.058*
C9	0.15676 (17)	0.54420 (18)	0.4929 (3)	0.0496 (5)
H9	0.0921	0.5369	0.4005	0.06*
C10	0.22906 (18)	0.62559 (18)	0.4281 (3)	0.0512 (5)
H10	0.2012	0.6975	0.4416	0.061*

C11	0.15545 (19)	0.25602 (19)	0.5198 (3)	0.0546 (6)
C12	0.0677 (2)	0.1837 (2)	0.5466 (4)	0.0707 (7)
H12A	0.0407	0.2066	0.6519	0.106*
H12B	0.0934	0.1116	0.5648	0.106*
H12C	0.0124	0.1865	0.4402	0.106*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0761 (5)	0.0694 (4)	0.0518 (4)	-0.0055 (3)	0.0059 (3)	0.0081 (3)
C12	0.0632 (4)	0.0683 (4)	0.0735 (5)	0.0053 (3)	0.0256 (3)	-0.0070 (3)
O1	0.0468 (9)	0.0490 (9)	0.0664 (10)	-0.0052 (7)	0.0152 (8)	0.0032 (7)
O2	0.0656 (11)	0.0582 (11)	0.0966 (15)	-0.0020 (9)	0.0247 (10)	-0.0128 (10)
C1	0.0485 (12)	0.0474 (11)	0.0511 (12)	-0.0018 (9)	0.0125 (10)	-0.0053 (9)
C2	0.0639 (15)	0.0509 (13)	0.0615 (14)	-0.0085 (11)	0.0179 (12)	-0.0030 (11)
C3	0.0614 (15)	0.0659 (16)	0.0701 (16)	-0.0204 (12)	0.0216 (13)	-0.0162 (13)
C4	0.0460 (13)	0.0794 (18)	0.0653 (16)	-0.0074 (12)	0.0108 (12)	-0.0163 (13)
C5	0.0487 (13)	0.0634 (15)	0.0601 (14)	0.0002 (11)	0.0082 (11)	-0.0047 (11)
C6	0.0444 (11)	0.0518 (12)	0.0482 (12)	-0.0019 (9)	0.0114 (9)	-0.0028 (9)
C7	0.0474 (12)	0.0509 (12)	0.0605 (14)	0.0011 (10)	0.0076 (11)	0.0062 (11)
C8	0.0430 (11)	0.0455 (11)	0.0579 (13)	-0.0031 (9)	0.0131 (10)	0.0016 (10)
C9	0.0438 (11)	0.0513 (12)	0.0532 (12)	0.0022 (9)	0.0083 (10)	-0.0018 (10)
C10	0.0533 (13)	0.0455 (11)	0.0544 (13)	0.0019 (9)	0.0094 (10)	0.0015 (10)
C11	0.0545 (13)	0.0508 (13)	0.0566 (14)	-0.0052 (10)	0.0055 (11)	0.0025 (10)
C12	0.0676 (16)	0.0600 (16)	0.0823 (19)	-0.0171 (13)	0.0092 (14)	0.0069 (14)

Geometric parameters (Å, °)

C11—C10	1.827 (3)	C7—H7A	0.97
C12—C9	1.802 (3)	C7—H7B	0.97
O1—C11	1.351 (3)	C8—H8	0.98
O1—C8	1.454 (3)	C10—H10	0.98
C9—C8	1.518 (3)	C4—C5	1.376 (4)
C9—C10	1.520 (3)	C4—C3	1.385 (4)
C9—H9	0.98	C4—H4	0.93
C6—C1	1.400 (3)	C5—H5	0.93
C6—C5	1.401 (3)	C2—C3	1.372 (4)
C6—C7	1.510 (3)	C2—H2	0.93
C1—C2	1.396 (3)	C3—H3	0.93
C1—C10	1.500 (3)	C12—H12A	0.96
O2—C11	1.192 (3)	C12—H12B	0.96
C11—C12	1.493 (3)	C12—H12C	0.96
C7—C8	1.504 (3)		
C11—O1—C8	115.45 (18)	C7—C8—H8	108.2
C8—C9—C10	109.28 (18)	C9—C8—H8	108.2
C8—C9—C12	110.77 (17)	C1—C10—C9	114.21 (19)
C10—C9—C12	108.22 (16)	C1—C10—C11	110.26 (16)

C8—C9—H9	109.5	C9—C10—C11	106.55 (16)
C10—C9—H9	109.5	C1—C10—H10	108.6
C12—C9—H9	109.5	C9—C10—H10	108.6
C1—C6—C5	118.2 (2)	C11—C10—H10	108.6
C1—C6—C7	122.58 (19)	C5—C4—C3	120.4 (2)
C5—C6—C7	119.2 (2)	C5—C4—H4	119.8
C2—C1—C6	119.8 (2)	C3—C4—H4	119.8
C2—C1—C10	119.1 (2)	C4—C5—C6	121.0 (2)
C6—C1—C10	121.1 (2)	C4—C5—H5	119.5
O2—C11—O1	123.5 (2)	C6—C5—H5	119.5
O2—C11—C12	125.1 (2)	C3—C2—C1	121.0 (2)
O1—C11—C12	111.4 (2)	C3—C2—H2	119.5
C8—C7—C6	110.88 (19)	C1—C2—H2	119.5
C8—C7—H7A	109.5	C2—C3—C4	119.5 (2)
C6—C7—H7A	109.5	C2—C3—H3	120.3
C8—C7—H7B	109.5	C4—C3—H3	120.3
C6—C7—H7B	109.5	C11—C12—H12A	109.5
H7A—C7—H7B	108.1	C11—C12—H12B	109.5
O1—C8—C7	112.88 (18)	H12A—C12—H12B	109.5
O1—C8—C9	106.93 (17)	C11—C12—H12C	109.5
C7—C8—C9	112.26 (19)	H12A—C12—H12C	109.5
O1—C8—H8	108.2	H12B—C12—H12C	109.5
C5—C6—C1—C2	1.2 (3)	C2—C1—C10—C9	-167.4 (2)
C7—C6—C1—C2	-178.7 (2)	C6—C1—C10—C9	13.3 (3)
C5—C6—C1—C10	-179.4 (2)	C2—C1—C10—C11	72.7 (2)
C7—C6—C1—C10	0.6 (3)	C6—C1—C10—C11	-106.6 (2)
C8—O1—C11—O2	3.4 (3)	C8—C9—C10—C1	-43.7 (3)
C8—O1—C11—C12	-175.2 (2)	C12—C9—C10—C1	77.0 (2)
C1—C6—C7—C8	17.2 (3)	C8—C9—C10—C11	78.3 (2)
C5—C6—C7—C8	-162.8 (2)	C12—C9—C10—C11	-161.00 (12)
C11—O1—C8—C7	-79.8 (2)	C3—C4—C5—C6	-0.2 (4)
C11—O1—C8—C9	156.3 (2)	C1—C6—C5—C4	-1.0 (3)
C6—C7—C8—O1	-170.16 (18)	C7—C6—C5—C4	179.0 (2)
C6—C7—C8—C9	-49.2 (3)	C6—C1—C2—C3	-0.3 (4)
C10—C9—C8—O1	-172.10 (18)	C10—C1—C2—C3	-179.6 (2)
C12—C9—C8—O1	68.8 (2)	C1—C2—C3—C4	-0.9 (4)
C10—C9—C8—C7	63.6 (2)	C5—C4—C3—C2	1.2 (4)
C12—C9—C8—C7	-55.5 (2)		