organic compounds

(+)-(1R,2S,3S,4S)-2-Chloro-3-(phenyl-selanyl)cyclohexane-1,4-diol

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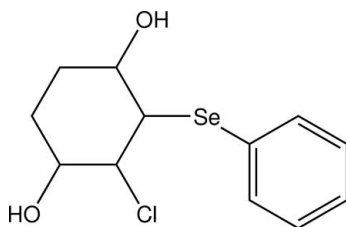Correspondence e-mail: edward.tiekink@utsa.edu

The cyclohexyl ring in the title compound, $C_{12}H_{15}ClO_2Se$, has a chair conformation with the 4-hydroxy group occupying an axial position; the other non-H substituents occupy equatorial positions. Molecules aggregate *via* O—H···O hydrogen bonds into a supramolecular helical chain.

Related literature

For related literature, see: Clive *et al.* (1977); Engman (1989); Greatrex *et al.* (2003); Ho & Kolt (1982); Nicolaou *et al.* (1979); Robinson *et al.* (2006); Tiecco *et al.* (1988); Toshimitsu *et al.* (1981, 1985).

Experimental

Crystal data

$C_{12}H_{15}ClO_2Se$	$V = 1231.16$ (15) Å^3
$M_r = 305.65$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 13.5529$ (10) Å	$\mu = 3.25$ mm^{-1}
$b = 7.0627$ (5) Å	$T = 223$ (2) K
$c = 12.9203$ (9) Å	$0.47 \times 0.18 \times 0.16$ mm
$\beta = 95.443$ (1)°	

Data collection

Bruker SMART CCD diffractometer	Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.857$, $T_{max} = 1$ (expected range = 0.510–0.595)	2832 independent reflections
8348 measured reflections	2524 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	147 parameters
$wR(F^2) = 0.077$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{max} = 0.61$ e Å^{-3}
2832 reflections	$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4[i]	0.83	1.91	2.737 (2)	174
O4—H4···O1[ii]	0.83	1.91	2.744 (2)	178

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

References

Altomare, A., Cascarano, M., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–435.

Brandenburg, K. (2006). *DIAMOND*. Release 3.1. Crystal Impact GbR, Bonn, Germany.

Bruker (2000). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, U. S. A.

Clive, D. L. J., Chittattu, G., Curtis, N. J., Kiel, W. A. & Wong, C. K. (1977). *Chem. Commun.* pp. 725–727.

Engman, L. (1989). *J. Org. Chem.* **54**, 884–890.

Greatrex, B. W., Jenkins, N. F., Taylor, D. K. & Tiekink, E. R. T. (2003). *J. Org. Chem.* **68**, 5205–5210.

Ho, P. T. & Kolt, R. J. (1982). *Can. J. Chem.* **1982**, 60, 663–666.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Nicolaou, K. C., Claremon, D. A., Barnette, W. E. & Seitz, S. P. (1979). *J. Am. Chem. Soc.* **101**, 3704–3706.

Robinson, T. V., Taylor, D. K. & Tiekink, E. R. T. (2006). *J. Org. Chem.* **71**, 7236–7244.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Tiecco, M., Testaferri, L., Tingoli, M., Chianelli, D. & Bartoli, D. (1988). *Tetrahedron*, **44**, 2261–2272.

Toshimitsu, A., Aoai, T., Owada, H., Uemura, S. & Okana, M. (1981). *J. Org. Chem.* **1981**, 46, 4727–4733.

Toshimitsu, A., Aoai, T., Owada, H., Uemura, S. & Okana, M. (1985). *Tetrahedron*, **41**, 5301–5306.

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supplementary materials

(+)-(1*R*,2*S*,3*S*,4*S*)-2-Chloro-3-(phenylselanyl)cyclohexane-1,4-diol

T. V. Robinson, D. K. Taylor and **E. R. T. Tiekink**

Comment

Recently, we reported the application of epoxidation and dihydroxylation to the olefinic portion of 1,2-dioxines, giving modified 1,2-dioxines, which were subsequently converted into novel epoxy hydroxy ketones, and sugar-type derivatives (Greatrex *et al.*, 2003; Robinson *et al.*, 2006). In the course of investigating other useful electrophilic additions, we attempted addition of phenylselenenyl chloride across the alkene of the bicyclic peroxide 2,3-dioxa-bicyclo[2.2.2]oct-7-ene. Such additions have been well documented on other alkene bearing organic compounds (Engman, 1989; Toshimitsu *et al.*, 1981, 1985), generally giving *trans*-1,2-phenylselenyl chloro adducts (Ho & Kolt, 1982; Clive *et al.*, 1977), or in the presence of other nucleophiles, such as water or methanol, phenylselenenly alkoxide adducts can be formed (Nicolaou *et al.*, 1979; Tiecco *et al.*, 1988). Interestingly, addition of phenylselenenyl chloride to the peroxide was accompanied by simultaneous reduction of the peroxide bond to give the cyclohexyl-1,4-diol, (I). Also, even though the reaction was performed in methanol, no displacement of the halogen was observed.

The molecular structure of (I) (Fig. 1) shows the cyclohexyl ring to adopt a chair conformation with the Se, Cl, O1 and O4 substituents occupying equatorial, equatorial, equatorial, and axial positions, respectively. The Se—C_{phenyl} bond is shorter than the Se—$C_{methine}$ bond and the geometry about the Se atom is bent (Table 1). Molecules aggregate in the crystal structure *via* O—H···O hydrogen bonds to form a supramolecular chain (Table 2). The chain is propagated by the screw axis and thus has a helical topology (Fig. 2). Interactions between chains are of the type π···π. Phenyl substituents are interdigitated along the *b* axis; the *Cg*···*Cg* distance is 3.7545 (14) Å for symmetry operation −*x*, −*y*, −*z*. However, as seen from Fig. 3, the aromatic rings overlap only partially with the closest approach involving the C31 and C33 atoms at 3.369 (3) Å.

Experimental

To a stirred solution of 2,3-dioxa-bicyclo[2.2.2]oct-7-ene (100 mg, 0.9 mmol) in anhydrous methanol (5 ml) was added phenylselenenyl chloride (205 mg, 1.08 mmol) and the solution stirred under an atmosphere of N_2 until reaction was complete, by TLC (*ca* 16 h). The reaction mixture was then diluted with dichloromethane (50 ml), washed with sat. sodium bicarbonate solution (2 *x* 25 ml), followed by brine (20 ml) and dried (Na_2SO_4). The solvent was removed *in vacuo*, and the residue purified by flash chromatography to give (I) as a white solid. The pure material was recrystallized from a slowly evaporating mixture of 1:1 dichloromethane/heptane to give colourless prisms (204 mg, 75%); m.p. 381–382 K. R_f 0.26 (2:3 ethyl acetate/hexane). Elemental analysis found: C 47.15, H, 4.95%; $C_{12}H_{15}ClO_2Se$ requires: C 47.26, H, 5.02%. IR (nujol) 3297, 1581, 1506, 1330, 1046, 1000 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.49–1.55 (m, 1H), 1.87–1.95 (m, 2H), 2.05 (dddd, *J* = 3.6, 3.6, 7.8, 14.4 Hz, 1H), 2.46 (br s, 2H), 3.44 (dd, *J* = 2.4, 11.4 Hz, 1H), 3.65 (ddd, *J* = 6.3, 9.0, 10.2 Hz, 1H), 3.85 (ddd, *J* = 2.4, 2.4, 3.6 Hz, 1H), 4.13 (dd, *J* = 9.0, 11.4 Hz, 1H), 7.29–7.36 (m, 3H), 7.63–7.66 (m, 2H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 25.7, 28.6, 56.9, 66.1, 66.1, 75.4, 127.6, 128.5, 129.5, 137.2. MS m/*z* (+EI): 308 (*M*$^+$, ^{37}Cl, 23), 306 (*M*$^+$, ^{35}Cl, 52), 158 (100), 131 (31), 113 (24), 77 (61), 67 (84).

supplementary materials

Refinement

All H atoms were included in the riding-model approximation, with C—H = 0.94 to 0.99 Å and O—H = 0.83 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ and $U_{iso}(H) = 1.5U_{eq}(O)$.
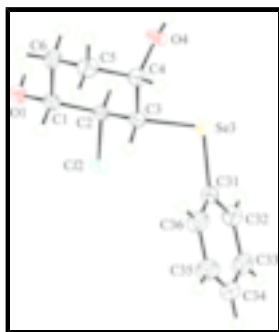
Figures

Fig. 1. Molecular structure of (I) showing atom-labelling scheme and displacement ellipsoids at the 50% probability level.
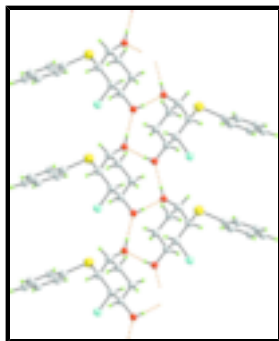

Fig. 2. View of the supramolecular chain in (I) mediated by hydrogen bonds, shown as orange-dashed lines. Colour code: yellow (selenium), cyan (chloride), red (oxygen), grey (carbon) and green (hydrogen).

Fig. 3. View of the unit-cell contents of (I) down the *b* axis. Hydrogen bonding (O—H···O) contacts are shown as orange-dashed lines.

(+)-(1*R*,2*S*,3*S*,4*S*)-2-Chloro-3-(phenylselanyl)cyclohexane-1,4-diol

Crystal data

$C_{12}H_{15}ClO_2Se$	$F_{000} = 616$
$M_r = 305.65$	$D_x = 1.649$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
Hall symbol: -P 2ybc	Cell parameters from 2654 reflections
$a = 13.5529$ (10) Å	$\theta = 2.3–29.0º$
$b = 7.0627$ (5) Å	$\mu = 3.25$ mm^{-1}

$c = 12.9203\ (9)$ Å	$T = 223\ (2)$ K
$\beta = 95.443\ (1)°$	Block, colourless
$V = 1231.16\ (15)$ Å^3	$0.47 \times 0.18 \times 0.16$ mm
$Z = 4$	

Data collection

Bruker SMART CCD diffractometer	2832 independent reflections
Radiation source: fine-focus sealed tube	2524 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.025$
$T = 223(2)$ K	$\theta_{max} = 27.5°$
ω scans	$\theta_{min} = 1.5°$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$h = -17 \rightarrow 17$
$T_{min} = 0.857$, $T_{max} = 1$	$k = -9 \rightarrow 7$
8348 measured reflections	$l = -14 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.029$	H-atom parameters constrained
$wR(F^2) = 0.077$	$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 0.3384P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
2832 reflections	$\Delta\rho_{max} = 0.61$ e Å^{-3}
147 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2sigma(F^2)$ 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	$U_{iso}*/U_{eq}$
Se3	0.223073 (15)	0.05198 (3)	0.126906 (17)	0.02977 (9)

Cl2	0.26790 (4)	0.52886 (7)	0.17758 (4)	0.03242 (13)
O1	0.44699 (11)	0.57891 (19)	0.33447 (12)	0.0285 (3)
H1	0.4960	0.5419	0.3061	0.043*
O4	0.40103 (11)	−0.05964 (19)	0.26849 (13)	0.0302 (3)
H4	0.4139	−0.1691	0.2890	0.045*
C1	0.38350 (15)	0.4218 (3)	0.34966 (16)	0.0247 (4)
H1A	0.3289	0.4669	0.3891	0.030*
C2	0.33780 (14)	0.3428 (3)	0.24551 (15)	0.0220 (4)
H2	0.3920	0.3041	0.2038	0.026*
C3	0.27180 (14)	0.1719 (3)	0.25939 (15)	0.0232 (4)
H3	0.2138	0.2144	0.2944	0.028*
C4	0.32598 (15)	0.0194 (3)	0.32663 (17)	0.0264 (4)
H4A	0.2783	−0.0814	0.3407	0.032*
C5	0.37069 (17)	0.1005 (3)	0.42939 (17)	0.0314 (4)
H5A	0.4083	0.0014	0.4689	0.038*
H5B	0.3173	0.1422	0.4702	0.038*
C6	0.43905 (16)	0.2672 (3)	0.41313 (16)	0.0296 (4)
H6A	0.4651	0.3184	0.4808	0.035*
H6B	0.4952	0.2238	0.3769	0.035*
C31	0.09343 (14)	0.1616 (3)	0.10249 (16)	0.0270 (4)
C32	0.06268 (16)	0.2203 (3)	0.00253 (17)	0.0319 (5)
H32	0.1073	0.2192	−0.0489	0.038*
C33	−0.03398 (17)	0.2810 (3)	−0.02180 (18)	0.0372 (5)
H33	−0.0550	0.3189	−0.0901	0.045*
C34	−0.09930 (17)	0.2861 (3)	0.05327 (19)	0.0374 (5)
H34	−0.1647	0.3281	0.0366	0.045*
C35	−0.06820 (17)	0.2291 (4)	0.15351 (19)	0.0412 (6)
H35	−0.1124	0.2341	0.2053	0.049*
C36	0.02774 (17)	0.1648 (4)	0.17807 (18)	0.0371 (5)
H36	0.0481	0.1234	0.2459	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Se3	0.02667 (13)	0.02833 (14)	0.03375 (14)	0.00167 (8)	−0.00011 (9)	−0.00736 (8)
Cl2	0.0381 (3)	0.0241 (3)	0.0338 (3)	0.0085 (2)	−0.0032 (2)	0.0045 (2)
O1	0.0286 (7)	0.0197 (7)	0.0374 (8)	−0.0010 (6)	0.0037 (6)	−0.0028 (6)
O4	0.0291 (8)	0.0170 (7)	0.0455 (9)	0.0032 (5)	0.0093 (7)	0.0031 (6)
C1	0.0271 (10)	0.0206 (9)	0.0263 (10)	0.0002 (7)	0.0022 (8)	0.0000 (7)
C2	0.0227 (9)	0.0176 (9)	0.0256 (9)	0.0036 (7)	0.0020 (7)	0.0014 (7)
C3	0.0213 (8)	0.0217 (9)	0.0265 (9)	0.0001 (7)	0.0024 (7)	−0.0015 (7)
C4	0.0245 (9)	0.0214 (9)	0.0338 (11)	−0.0019 (8)	0.0056 (8)	0.0041 (8)
C5	0.0364 (11)	0.0289 (10)	0.0284 (11)	0.0004 (9)	0.0008 (9)	0.0084 (9)
C6	0.0336 (11)	0.0267 (10)	0.0267 (10)	−0.0010 (8)	−0.0061 (8)	0.0018 (8)
C31	0.0237 (9)	0.0242 (10)	0.0326 (10)	−0.0014 (8)	−0.0005 (8)	−0.0034 (8)
C32	0.0332 (11)	0.0314 (11)	0.0311 (11)	−0.0013 (9)	0.0025 (9)	0.0006 (9)
C33	0.0372 (12)	0.0383 (12)	0.0343 (12)	−0.0014 (10)	−0.0068 (10)	0.0013 (10)
C34	0.0286 (10)	0.0386 (13)	0.0436 (13)	0.0046 (9)	−0.0041 (9)	−0.0071 (10)

C35	0.0312 (11)	0.0530 (15)	0.0401 (13)	0.0021 (11)	0.0066 (10)	−0.0037 (11)
C36	0.0332 (11)	0.0472 (14)	0.0305 (11)	0.0009 (10)	0.0004 (9)	0.0007 (10)

Geometric parameters (Å, °)

Se3—C3	1.9669 (19)	C5—C6	1.525 (3)
Se3—C31	1.919 (2)	C5—H5A	0.9800
C2—Cl2	1.7990 (19)	C5—H5B	0.9800
C1—O1	1.429 (2)	C6—H6A	0.9800
O1—H1	0.8300	C6—H6B	0.9800
C4—O4	1.434 (3)	C31—C32	1.383 (3)
O4—H4	0.8300	C31—C36	1.383 (3)
C1—C6	1.521 (3)	C32—C33	1.386 (3)
C1—C2	1.532 (3)	C32—H32	0.9400
C1—H1A	0.9900	C33—C34	1.374 (3)
C2—C3	1.523 (3)	C33—H33	0.9400
C2—H2	0.9900	C34—C35	1.383 (3)
C3—C4	1.527 (3)	C34—H34	0.9400
C3—H3	0.9900	C35—C36	1.386 (3)
C4—C5	1.518 (3)	C35—H35	0.9400
C4—H4A	0.9900	C36—H36	0.9400
C3—Se3—C31	101.31 (8)	C6—C5—H5A	109.3
C1—O1—H1	109.5	C4—C5—H5B	109.3
C4—O4—H4	109.5	C6—C5—H5B	109.3
O1—C1—C6	110.96 (16)	H5A—C5—H5B	108.0
O1—C1—C2	111.13 (16)	C1—C6—C5	110.63 (17)
C6—C1—C2	110.52 (16)	C1—C6—H6A	109.5
O1—C1—H1A	108.0	C5—C6—H6A	109.5
C6—C1—H1A	108.0	C1—C6—H6B	109.5
C2—C1—H1A	108.0	C5—C6—H6B	109.5
C3—C2—C1	112.21 (16)	H6A—C6—H6B	108.1
C3—C2—Cl2	110.39 (13)	C32—C31—C36	119.85 (19)
C1—C2—Cl2	108.25 (13)	C32—C31—Se3	117.70 (16)
C3—C2—H2	108.6	C36—C31—Se3	122.11 (16)
C1—C2—H2	108.6	C31—C32—C33	119.9 (2)
Cl2—C2—H2	108.6	C31—C32—H32	120.0
C2—C3—C4	111.71 (15)	C33—C32—H32	120.0
C2—C3—Se3	113.03 (13)	C34—C33—C32	120.4 (2)
C4—C3—Se3	107.17 (13)	C34—C33—H33	119.8
C2—C3—H3	108.3	C32—C33—H33	119.8
C4—C3—H3	108.3	C33—C34—C35	119.6 (2)
Se3—C3—H3	108.3	C33—C34—H34	120.2
O4—C4—C5	111.15 (17)	C35—C34—H34	120.2
O4—C4—C3	107.65 (16)	C36—C35—C34	120.4 (2)
C5—C4—C3	111.23 (17)	C36—C35—H35	119.8
O4—C4—H4A	108.9	C34—C35—H35	119.8
C5—C4—H4A	108.9	C35—C36—C31	119.8 (2)
C3—C4—H4A	108.9	C35—C36—H36	120.1
C4—C5—C6	111.59 (17)	C31—C36—H36	120.1

C4—C5—H5A	109.3

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O4[i]	0.83	1.91	2.737 (2)	174
O4—H4⋯O1[ii]	0.83	1.91	2.744 (2)	178

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

Fig. 1

Fig. 2

Fig. 3