

3-*exo*-Chloro-8-oxabicyclo[3.2.1]oct-6-ene-2,4-diol chloroform 0.33-solvate

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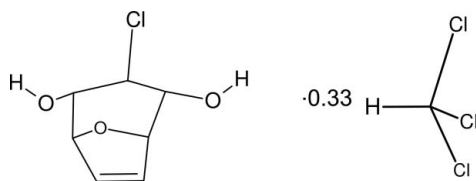
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.054; wR factor = 0.168; data-to-parameter ratio = 14.3.

The title compound, $3\text{C}_7\text{H}_9\text{ClO}_3 \cdot \text{CHCl}_3$, crystallizes with molecules of 3-*exo*-chloro-8-oxabicyclo[3.2.1]oct-6-ene-2,4-diol (*A*) and chloroform in a 3:1 ratio, in the space group $R\bar{3}m$. Molecules of *A* straddle a crystallographic mirror plane, whereas the chloroform molecules (*C* and *H* atoms) lie additionally on the threefold axis. The molecules of *A* are linked into right- and left-helical chains by means of $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, thus forming columns running along the *c* axis. Six interpenetrated columns form a channel in which the solvent molecules (chloroform) are located.

Related literature

Inositetriphosphates analogues are potential prospective antitumoral compounds, see: Piettre *et al.* (1997); Miller & Allemann (2007).



Experimental

Crystal data

$3\text{C}_7\text{H}_9\text{ClO}_3 \cdot \text{CHCl}_3$

$M_r = 649.16$

Hexagonal, $R\bar{3}m$

$a = 18.687$ (5) Å

$c = 6.8723$ (16) Å

$V = 2078.3$ (9) Å³

$Z = 3$

Cu $K\alpha$ radiation

$\mu = 6.09$ mm⁻¹

$T = 295$ K

$0.1 \times 0.07 \times 0.06$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer

Absorption correction: ψ scan (North *et al.*, 1968)

$T_{\min} = 0.530$, $T_{\max} = 0.694$

1832 measured reflections

987 independent reflections

966 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

2 standard reflections

frequency: 120 min

intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.168$

$S = 1.18$

987 reflections

69 parameters

1 restraint

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.28$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.51$ e Å⁻³

Absolute structure: Flack (1983),

481 Friedel pairs

Flack parameter: -0.01 (2)

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H11...O1 ⁱ	0.77 (7)	1.98 (7)	2.723 (3)	162 (7)

Symmetry code: (i) $-x + y + \frac{2}{3}, -x + \frac{1}{3}, z + \frac{1}{3}$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2178).

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supplementary materials

Acta Cryst. (2009). E65, o1580 [doi:10.1107/S1600536809021898]

3-*exo*-Chloro-8-oxabicyclo[3.2.1]oct-6-ene-2,4-diol chloroform 0.33-solvate

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Comment

It is known (Piettre *et al.*, (1997); Miller & Allemann, (2007)) that the analogous of inositetriphosphates are potential prospective antitumoral compounds. As we assume that the polyhydroxycycloheptanes are able to act like inositemonophosphate inhibitors, so the 3-*exo*-chloro-8-oxa-bicyclo[3.2.1]oct-6-en-2,4-diendo-diol was synthesized. The elemental analysis of the compound we obtained, were in good agreement with the title compound, but ^1H NMR data did not allow us to clarify the relative oxy-groups arrangement in the molecule. To determine the structure of the compound, we carried out an X-ray crystallographic analysis. Molecule of (A) (Fig. 1) straddle a crystallographic mirror plane m passing through atoms C11, C1, H1, endocyclic oxygen O2, the midpoint of the double bond C4/C4ⁱⁱ, whereas the chloroform molecules (carbon C5 and hydrogen H5 atoms) lie additionally on the threefold axis. The 6-membered cycle of the molecule adopts a chair conformation, with atoms O2 and C1 displaced out of plane defined by the atoms C2/C2ⁱⁱ/C3/C3ⁱⁱ (plane 1) by -0.848 (3) and 0.543 (2) Å. Atoms O1, C4, C11, H1 (attached to C1) displaced out of plane 1 by 0.797 (2), 1.329 (3), 0.1990 (1), 1.44 (2) Å, while atoms H2 and H3 (attached to C2 and C3) by -0.90 (3), -0.37 (3) Å, respectively. The packing motif, as shown in Fig. 2 can be described as follows: the molecules (A) are linked into the interpenetrated right- and left-helical chains by means of O1—H···O1* hydrogen bonds thus to form columns, running along the c axis. The six interpenetrated columns form channels, where solvent molecules (chloroform) are located.

Experimental

1M hexane solution of DIBAL-H (6 ml) was added (Fig. 3) dropwise during 20 min at 213 K to a solution of compound (1) 3-chloro-8-oxabicyclo[3.2.1]-6-en-2,4-dione (5.75 mmol, 1000 mg) in 40 ml of dry THF under argon atmosphere. Reaction quenched with methanol and the mixture stirred for 4–5 h, concentrated to 20–30 ml, filtered through silica gel (2 cm, 60/200 μ), evaporated to dryness to yield compound 2 as yellow oil which was used for preparing of compound (3) without further purification. 1M hexane solution of DIBAL-H (6 ml) was added dropwise during 20 min at 213 K to a solution of compound (2) (1.72 mmol, 300 mg) in 20 ml of dry THF under argon atmosphere. The reaction was quenched with methanol (15 ml) and the mixture was stirred for 4–5 h, concentrated to 10 ml, filtered through silica gel (2 cm, 60/200 μ), evaporated to dryness to yield compound (3) as a colorless solid (280 mg) which was flesh-chromatographed on silica gel (40/60 μ , CH₂Cl₂ Et₂O: 2:1, gradient 1:5) to give diol (3) (150 mg), Crystals suitable for diffraction analysis were obtained by slow diffusion of petroleum ether vapour into a CHCl₃ solution.

Refinement

The positions of the H atoms were determined from Fourier difference maps; H atoms attached to carbons were then placed in calculated positions and allowed to ride on their parent atoms [C—H = 0.93–0.98 Å. $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{parent atom})$, where $x = 1.2$.] Hydrogen attached to oxygen was refined freely.

Figures

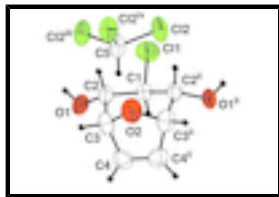


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. Symmetry codes: (ii) $x, x-y, z$; (iii) $-y+1, x-y, z$; (iv) $1-x+y, -x+1, z$.

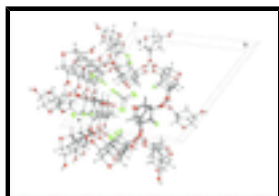


Fig. 2. The packing motif of the crystal structure. Symmetry codes: (i) $-x+y+2/3, -x+1/3, z+1/3$

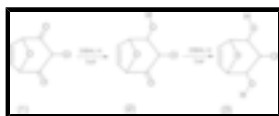


Fig. 3. Reaction scheme.

3-*exo*-Chloro-8-oxabicyclo[3.2.1]oct-6-ene-2,4-diol chloroform 0.33-solvate

Crystal data

$3C_7H_9ClO_3 \cdot CHCl_3$

$M_r = 649.16$

Hexagonal, $R3m$

Hall symbol: $R\ 3\ -2$

$a = 18.687\ (5)\ \text{\AA}$

$b = 18.687\ (5)\ \text{\AA}$

$c = 6.8723\ (16)\ \text{\AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 120^\circ$

$V = 2078.3\ (9)\ \text{\AA}^3$

$Z = 3$

$F_{000} = 1002$

$D_x = 1.556\ \text{Mg m}^{-3}$

Melting point: decomposition K

Cu $K\alpha$ radiation

$\lambda = 1.54184\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 32\text{--}45^\circ$

$\mu = 6.09\ \text{mm}^{-1}$

$T = 295\ \text{K}$

Prism, colourless

$0.1 \times 0.07 \times 0.06\ \text{mm}$

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 291\ \text{K}$

Nonprofiled ω scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.530, T_{\max} = 0.694$

1832 measured reflections

$R_{\text{int}} = 0.036$

$\theta_{\max} = 71.9^\circ$

$\theta_{\min} = 4.7^\circ$

$h = -22 \rightarrow 0$

$k = 0 \rightarrow 22$

$l = -8 \rightarrow 8$

2 standard reflections

every 120 min

987 independent reflections
 966 reflections with $I > 2\sigma(I)$
 intensity decay: none

Refinement

Refinement on F^2 Hydrogen site location: inferred from neighbouring sites
 Least-squares matrix: full H atoms treated by a mixture of independent and constrained refinement
 $R[F^2 > 2\sigma(F^2)] = 0.054$ $w = 1/[\sigma^2(F_o^2) + (0.021P)^2 + 2.2041P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.168$ $(\Delta/\sigma)_{\max} = 0.001$
 $S = 1.18$ $\Delta\rho_{\max} = 0.28 \text{ e } \text{Å}^{-3}$
 987 reflections $\Delta\rho_{\min} = -0.51 \text{ e } \text{Å}^{-3}$
 69 parameters Extinction correction: SHELXL97 (Sheldrick, 2008),
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 1 restraint Extinction coefficient: 0.0016 (4)
 Primary atom site location: structure-invariant direct methods Absolute structure: Flack (1983), 481 Friedel pairs
 Secondary atom site location: difference Fourier map Flack parameter: -0.01 (2)

Special details

Experimental. As the solvent molecules release from the crystal at ambient air, so the experiment was carried out from the crystal placed in a glass capillary.

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.

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 $F^2 > \sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.29956 (13)	0.14978 (7)	0.6438 (3)	0.0671 (7)
Cl2	0.61527 (5)	0.38473 (5)	0.7368 (3)	0.0619 (6)
O1	0.3605 (3)	0.0525 (2)	0.3740 (6)	0.0560 (10)
O2	0.5272 (3)	0.26359 (14)	0.3179 (9)	0.0583 (13)
C1	0.3610 (3)	0.18052 (16)	0.4256 (8)	0.0341 (12)
H1	0.3232	0.1616	0.3143	0.041*
C2	0.4122 (3)	0.1378 (2)	0.4156 (6)	0.0397 (10)
H2	0.4393	0.1436	0.5414	0.048*
C3	0.4782 (3)	0.1795 (3)	0.2586 (8)	0.0510 (12)
H3	0.5115	0.1527	0.2434	0.061*

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C4	0.4419 (4)	0.1856 (3)	0.0684 (8)	0.0543 (12)
H4	0.4228	0.1467	-0.0311	0.065*
C5	0.6667	0.3333	0.654 (2)	0.048 (3)
H5	0.6667	0.3333	0.5111	0.058*
H11	0.361 (4)	0.024 (4)	0.453 (10)	0.063 (19)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0535 (11)	0.0777 (11)	0.0619 (10)	0.0268 (5)	0.0216 (8)	0.0108 (4)
Cl2	0.0497 (8)	0.0497 (8)	0.0932 (14)	0.0300 (8)	0.0052 (4)	-0.0052 (4)
O1	0.077 (3)	0.0298 (16)	0.058 (2)	0.0241 (18)	-0.0182 (19)	-0.0027 (15)
O2	0.026 (2)	0.054 (2)	0.085 (3)	0.0128 (11)	0.001 (2)	0.0003 (11)
C1	0.026 (3)	0.033 (2)	0.040 (3)	0.0132 (13)	-0.002 (2)	-0.0012 (11)
C2	0.039 (2)	0.0310 (19)	0.052 (2)	0.0196 (17)	-0.0126 (18)	-0.0054 (17)
C3	0.039 (2)	0.052 (3)	0.071 (3)	0.029 (2)	0.004 (2)	-0.003 (2)
C4	0.054 (3)	0.061 (3)	0.051 (2)	0.031 (2)	0.013 (2)	0.000 (2)
C5	0.033 (3)	0.033 (3)	0.078 (8)	0.0166 (16)	0.000	0.000

Geometric parameters (\AA , $^\circ$)

Cl1—C1	1.799 (6)	C2—C3	1.526 (7)
Cl2—C5	1.759 (5)	C2—H2	0.9800
O1—C2	1.420 (5)	C3—C4	1.503 (8)
O1—H11	0.77 (7)	C3—H3	0.9800
O2—C3 ⁱ	1.426 (6)	C4—C4 ⁱ	1.320 (11)
O2—C3	1.426 (6)	C4—H4	0.9300
C1—C2	1.524 (5)	C5—Cl2 ⁱⁱ	1.759 (5)
C1—C2 ⁱ	1.524 (5)	C5—Cl2 ⁱⁱⁱ	1.759 (5)
C1—H1	0.9800	C5—H5	0.9800
C2—O1—H11	114 (5)	O2—C3—C2	105.7 (4)
C3 ⁱ —O2—C3	102.6 (5)	C4—C3—C2	111.9 (4)
C2—C1—C2 ⁱ	113.8 (5)	O2—C3—H3	111.8
C2—C1—Cl1	109.8 (3)	C4—C3—H3	111.8
C2 ⁱ —C1—Cl1	109.8 (3)	C2—C3—H3	111.8
C2—C1—H1	107.7	C4 ⁱ —C4—C3	107.6 (3)
C2 ⁱ —C1—H1	107.7	C4 ⁱ —C4—H4	126.2
Cl1—C1—H1	107.7	C3—C4—H4	126.2
O1—C2—C1	110.1 (4)	Cl2 ⁱⁱ —C5—Cl2 ⁱⁱⁱ	110.0 (4)
O1—C2—C3	110.7 (4)	Cl2 ⁱⁱ —C5—Cl2	110.0 (4)
C1—C2—C3	108.8 (4)	Cl2 ⁱⁱⁱ —C5—Cl2	110.0 (4)
O1—C2—H2	109.1	Cl2 ⁱⁱ —C5—H5	108.9
C1—C2—H2	109.1	Cl2 ⁱⁱⁱ —C5—H5	108.9
C3—C2—H2	109.1	Cl2—C5—H5	108.9
O2—C3—C4	103.3 (4)		

Symmetry codes: (i) $x, x-y, z$; (ii) $-x+y+1, -x+1, z$; (iii) $-y+1, x-y, z$.

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H11\cdots O1^{iv}$	0.77 (7)	1.98 (7)	2.723 (3)	162 (7)

Symmetry codes: (iv) $-x+y+2/3, -x+1/3, z+1/3$.

Fig. 1

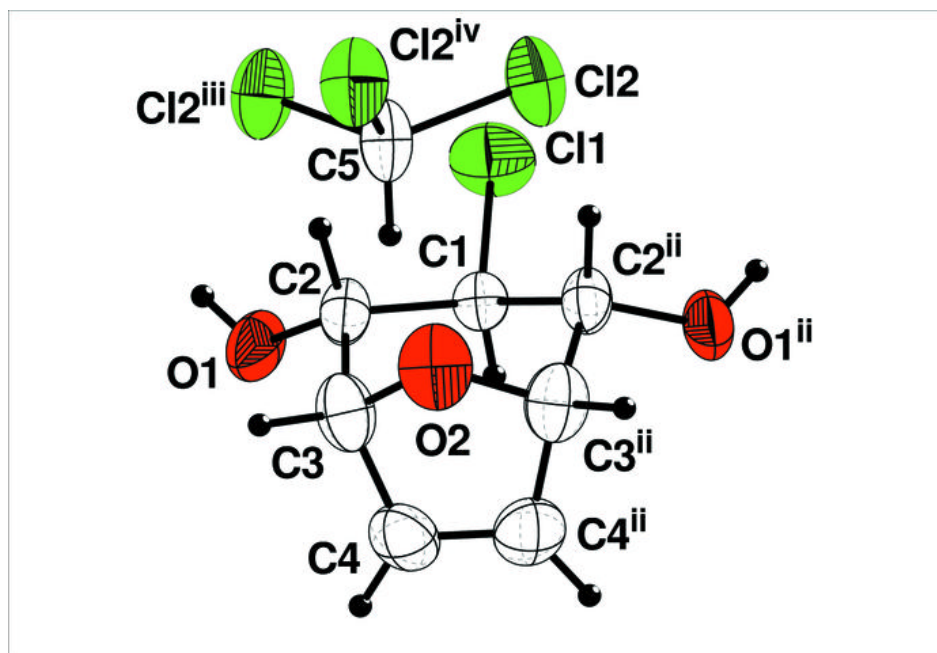


Fig. 2

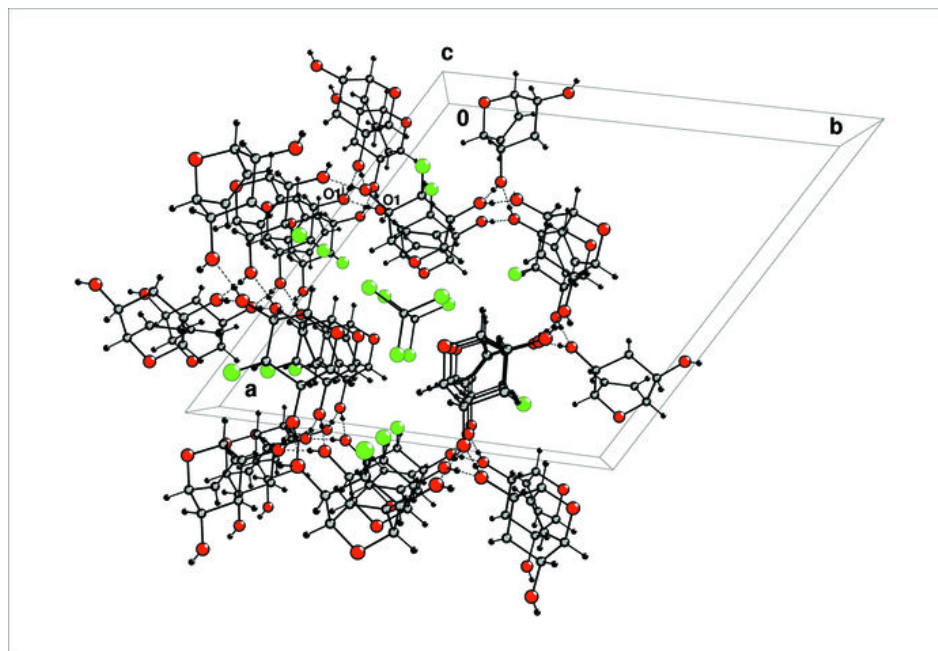


Fig. 3

