

(1*SR*,2*SR*,3*SR*,4*RS*,5*RS*,6*RS*,7*SR*,8*RS*)-  
7,8-Dichlorobicyclo[4.2.0]octa-  
2,3,4,5-tetrayl tetraacetate

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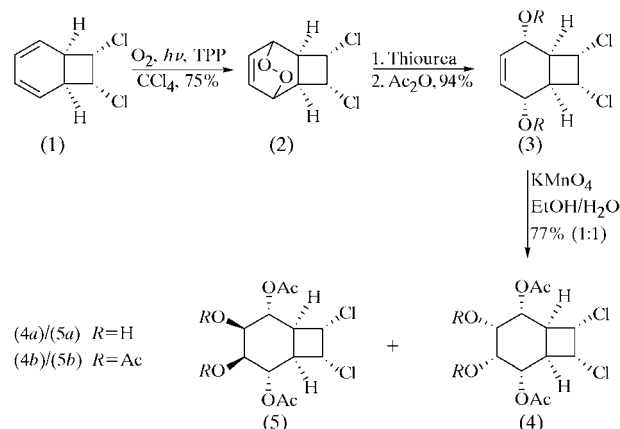
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In the title compound, C<sub>16</sub>H<sub>20</sub>Cl<sub>2</sub>O<sub>8</sub>, the bicyclic system contains a central non-planar cyclohexane ring which is fused to a cyclobutane moiety. The cyclohexane ring has a chair conformation and the whole system adopts a *syn* conformation. The structure provides information on the stereochemical course of the chlorination, photo-oxidation and hydroxylation steps of the reaction.

Comment

Carbohydrates are densely functionalized molecules and, as a result, their synthesis often requires many reaction steps, usually including the manipulation of different protecting groups. There are many synthetic strategies leading to the various conduritol isomers and their derivatives (Gültekin *et al.*, 2004). We have previously used a photo-oxygenation reaction to introduce two oxygen functionalities in the 1,4-positions of the appropriate dienes, followed by cleavage of the peroxide linkage (Sütbeyaz *et al.*, 1990; Seçen *et al.*, 1990, 1992, 1993; Salamci *et al.*, 1997; Kara & Balci, 2003). *cis*-Dichlorobicyclooctadiene, (1), was synthesized as described in the literature (Gözel *et al.*, 1991). Photooxidation of (1) with singlet oxygen gave the expected endoperoxide, (2) (see scheme) (Reppe *et al.*, 1948). Reduction of the peroxide bond in (2) was performed with thiourea under very mild conditions to give the diol, (3*a*) (Kelebekli *et al.*, 2005; Balci, 1981). For further proof of the structure, (3*a*) was converted into the corresponding diacetate, (3*b*), which was fully characterized by spectroscopic methods. *cis*-Hydroxylation of (3*b*) with KMnO<sub>4</sub> at 263 K gave a mixture of diols (4*a*) and (5*a*) in a ratio of 1:1. These were converted into the tetraacetate derivatives, (4*b*) and (5*b*), which were separated by fractional crystallization from hexane-CH<sub>2</sub>Cl<sub>2</sub>. The title isomer (4*b*) crystallized out first (Kelebekli *et al.*, 2005). The exact configuration of compound (4*b*) has now been determined by X-ray diffraction analysis. The structure provides information

on the stereochemical course of the chlorination, photo-oxidation and hydroxylation stages of the reaction.



Isomer (4*b*) crystallizes in the space group *P* $\bar{1}$ , with *Z* = 2. It contains a central non-planar cyclohexane ring with a cyclobutane ring fused to it. Each C atom is tetrahedral. The all-*cis* stereochemistry of the four acetate groups was determined unequivocally. The same *cis* stereochemistry was also seen in the dibromotetraacetate compound (Kara *et al.*, 1994), but there the Br atoms had a *trans* conformation.

All the substituents, including the acetoxy and chloro groups, are on the same side of the bicycle (*syn* conformation). In addition to this, the Cl atoms have *cis* stereochemistry. The six-membered ring adopts a chair conformation, with puckering parameters (Cremer & Pople, 1975) *Q*<sub>T</sub> = 0.525 (2) Å,  $\theta$  = 151.1 (2)° and  $\varphi$  = 185.7 (5)° (Fig. 1).

The cyclobutane moiety is appreciably distorted, with C—C distances in the range 1.534 (3)–1.567 (3) Å. The strong electronegativity of the Cl atoms along the C3—C7—Cl1 and C4—C8—Cl2 chains causes elongation of the C3—C4 bond.

Intermolecular C—H...O hydrogen bonds between cyclohexane H atoms of the cyclic system and the acetyl O atom are

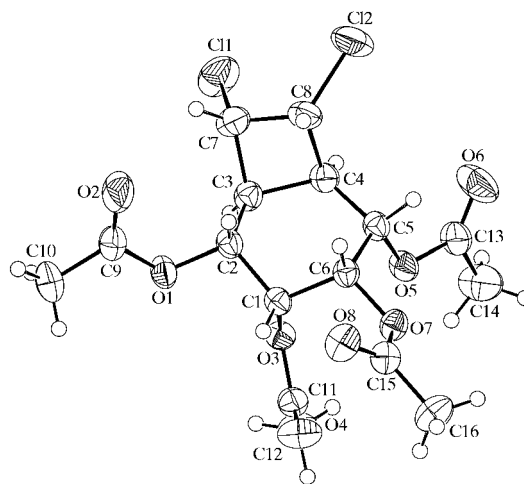
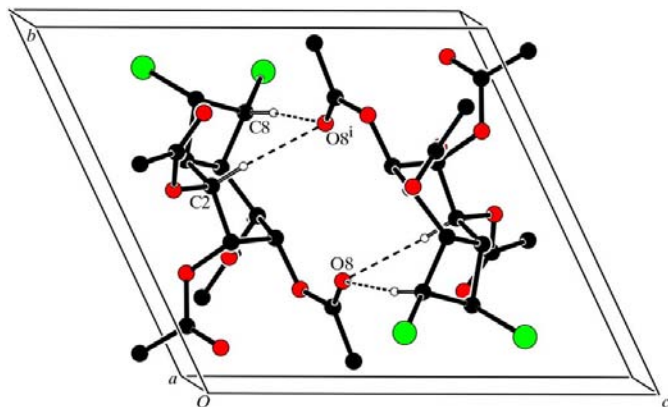


Figure 1  
A drawing of the title molecule, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**

The crystal structure of (4b), viewed down the *a* axis. Hydrogen bonds are indicated by dashed lines. H atoms not involved in the hydrogen bonding have been omitted for clarity. [Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .]

effective in determining the molecular conformation of (4b) [ $C2 \cdots O8^i = 3.279$  (2) Å and  $C8 \cdots O8^i = 3.339$  (3) Å; symmetry code: (i)  $1 - x, 1 - y, 1 - z$ ]. The molecules are elongated approximately parallel to the (001) plane and are stacked approximately along the *a* direction (Fig. 2).

## Experimental

For the preparation of (2) (Gözel *et al.*, 1991), tetraphenylporphyrin (TPP; 30 mg) was added to a stirred solution of the dichlorodiene, (1) (Reppe *et al.*, 1948) (3.0 g, 17 mmol), in  $CCl_4$  (100 ml). The resulting mixture was irradiated with a projection lamp (500 W) while oxygen was passed through the solution, and the mixture was stirred at room temperature for 8 h. Evaporation of the solvent (303 K, 20 mm Hg; 1 mm Hg = 133.322 Pa) and chromatography of the residue on a silica-gel column (50 g) eluted with hexane- $CH_2Cl_2$  (1:1) gave pure endoperoxide (2) (2.67 g, 75%, m.p. 364–365 K). The compound was recrystallized from  $CHCl_3$ -hexane (1:2 *v/v*).

For the preparation of (3a), a solution of endoperoxide (2) (1.20 g, 5.79 mmol) in  $CHCl_3$  (30 ml) was added to a magnetically stirred slurry of thiourea (0.44 g, 5.79 mmol) in methanol (30 ml) at room temperature. After completion of the addition (*ca* 10 min), the mixture was stirred for 1 h and the solid was removed by filtration. Evaporation of the solvent gave diol (3a) (1.15 g, 95%) as a colourless oil.

For the preparation of (3b), diol (3a) (0.81 g, 3.87 mmol) was dissolved in acetyl chloride (10 ml) and the resulting solution was stirred at room temperature overnight. The excess unreacted acetyl chloride was evaporated (333 K, 20 mm Hg). The residue was dissolved in  $CHCl_3$  and filtered through silica gel. Evaporation of the solvent gave (3b) (1.08 g, 94%, m.p. 327–328 K). The compound was recrystallized from  $CHCl_3$ -hexane (1:1 *v/v*).

For the preparation of (4b)/(5b) (Kelebekli *et al.*, 2005), a solution of  $KMnO_4$  (0.3 g, 1.88 mmol) and  $MgSO_4$  (0.23 g, 1.88 mmol) in water (20 ml) was added to a stirred solution of dichlorodiacetate (3b) (0.55 g, 1.88 mmol) in EtOH (50 ml) at 263 K over a period of 5 h. After completion of the addition, the reaction mixture was stirred for an additional 15 h at 268 K and then filtered. The precipitate was washed several times with hot water. The combined filtrates were concentrated to 20 ml by rotary evaporation (333 K, 20 mm Hg). The

aqueous solution was extracted with ethyl acetate (3 × 75 ml) and the extracts were dried ( $Na_2SO_4$ ). After removal of the solvent, the crude mixture was acetylated as described above to give compounds (5b) and (4b) in a 1:1 ratio (according to  $^1H$  NMR) (0.59 g, 77%). Compounds (4b) and (5b) were separated by recrystallization from hexane- $CH_2Cl_2$  (2:1 *v/v*). The title compound, (4b), formed colourless crystals from hexane- $CH_2Cl_2$  (2:1 *v/v*) (m.p. 444–446 K).

## Crystal data

$C_{16}H_{20}Cl_2O_8$	$V = 936.70$ (10) Å <sup>3</sup>
$M_r = 411.22$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.458$ Mg m <sup>-3</sup>
$a = 8.9489$ (5) Å	Mo $K\alpha$ radiation
$b = 11.0230$ (8) Å	$\mu = 0.39$ mm <sup>-1</sup>
$c = 11.2885$ (7) Å	$T = 295$ (2) K
$\alpha = 111.427$ (2)°	Block, white
$\beta = 98.2810$ (10)°	$0.32 \times 0.21 \times 0.20$ mm
$\gamma = 108.8340$ (10)°	

## Data collection

Rigaku R-Axis RAPID S diffractometer	64683 measured reflections
Oscillation scans	7145 independent reflections
Absorption correction: multi-scan (Blessing, 1995)	6532 reflections with $I > 2\sigma(I)$
$T_{min} = 0.909, T_{max} = 0.926$	$R_{int} = 0.045$
	$\theta_{max} = 33.2^\circ$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.3756P]$
$R[F^2 > 2\sigma(F^2)] = 0.076$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.190$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.32$	$\Delta\rho_{max} = 0.33$ e Å <sup>-3</sup>
7145 reflections	$\Delta\rho_{min} = -0.26$ e Å <sup>-3</sup>
271 parameters	
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C2-H2 \cdots O8^i$	1.00 (2)	2.31 (2)	3.279 (2)	161 (2)
$C8-H8 \cdots O8^i$	0.89 (3)	2.50 (3)	3.339 (3)	158 (2)

Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .

Methyl atoms were positioned geometrically, with  $C-H = 0.96$  Å, and constrained to ride on their parent atoms, with  $U_{iso}(H) = 1.5U_{eq}(C)$ . All other H atoms were located in a difference synthesis and refined isotropically [ $C-H = 0.89$  (3)–1.00 (2) Å].

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3010). Services for accessing these data are described at the back of the journal.

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