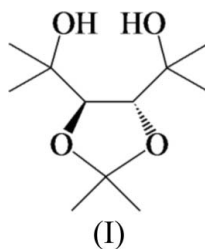


**(4*R*,5*R*)-Bis(hydroxydimethylmethyl)-2,2-dimethyl-1,3-dioxolane****Grant A. Boyle,<sup>a</sup> Hendrik G. Kruger,<sup>a</sup> Glenn E. M. Maguire<sup>a</sup> and Melanie Rademeyer<sup>b\*</sup>**<sup>a</sup>School of Chemistry, University of KwaZulu-Natal, Howard College, Durban 4041, South Africa, and <sup>b</sup>School of Chemistry, University of KwaZulu-Natal, Pietermaritzburg Campus, Private Bag X01, Scottsville 3209, South AfricaCorrespondence e-mail:  
rademeyerm@ukzn.ac.za**Key indicators**Single-crystal X-ray study  
*T* = 150 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
*R* factor = 0.046  
*wR* factor = 0.134  
Data-to-parameter ratio = 14.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound,  $\text{C}_{11}\text{H}_{22}\text{O}_4$ , certain C—C bond lengths are shorter than expected. As a result of the synthetic precursor being enantiomerically pure, only the *R,R* enantiomer occurs in the structure. There are two molecules in the asymmetric unit. Both intra- and intermolecular hydrogen bonds are present between the hydroxyl groups, resulting in a one-dimensional hydrogen-bonding network.

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The present study is part of an ongoing investigation into the synthesis of chiral pentacycloundecane macrocycles. The title compound, (I), has been used as a chiral unit in macrocycles that have been synthesized for U-tube transport studies involving chiral organic ammonium salts (Marchand *et al.*, 2001). Derivatives of (I) have been used as chiral catalysts in Michael reactions (Belokon', Kochetkov, Churkina, Chesnokov *et al.*, 1998) and alkylation reactions (Belokon', Kochetkov, Churkina, Ikonnikov *et al.*, 1998).

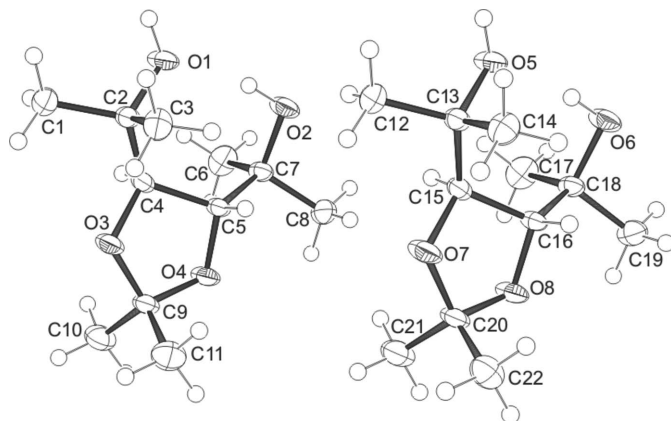


Compound (I) was synthesized from *L*-tartaric acid, in which both chiral centres adopt the *R* configuration. The *R* configuration is retained at both chiral centres in (I), resulting in an enantiomerically pure structure. The asymmetric unit comprises two crystallographically independent molecules, with four molecules in the unit cell. Fig. 1 illustrates the molecular geometry and atomic labelling scheme employed.

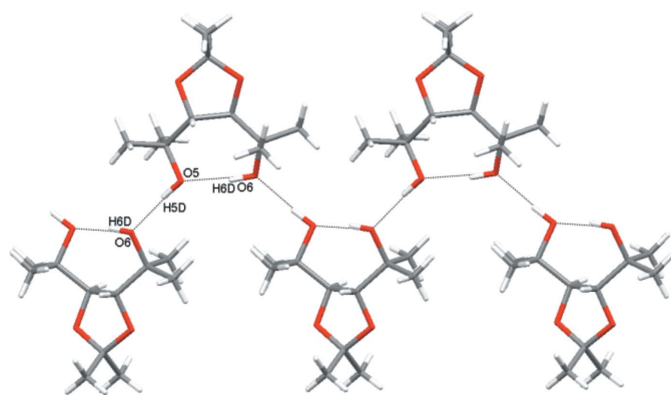
The title compound exhibits a shortening of the C—C bonds between C9 and C10/C11, and C20 and C21/C22, with values of 1.516 (2), 1.504 (2), 1.513 (2) and 1.508 (3) Å, respectively. These bonds are significantly shorter than normal carbon—carbon bonds (1.54 Å). This shortening is also observed for similar molecules of this type (Goldberg *et al.*, 1990; Ito *et al.*, 1994). A number of other C—C bonds are also shorter than normal, and are listed in Table 1.

The geometry of both molecules is such that the hydroxyl groups all lie approximately in the plane of the ring, while all the methyl groups are axial to the ring.

Both independent molecules in the asymmetric unit display the same hydrogen-bonding interactions, namely one intra-



**Figure 1**  
The asymmetric unit of (I), showing the atomic numbering scheme and ellipsoids at the 50% probability level.

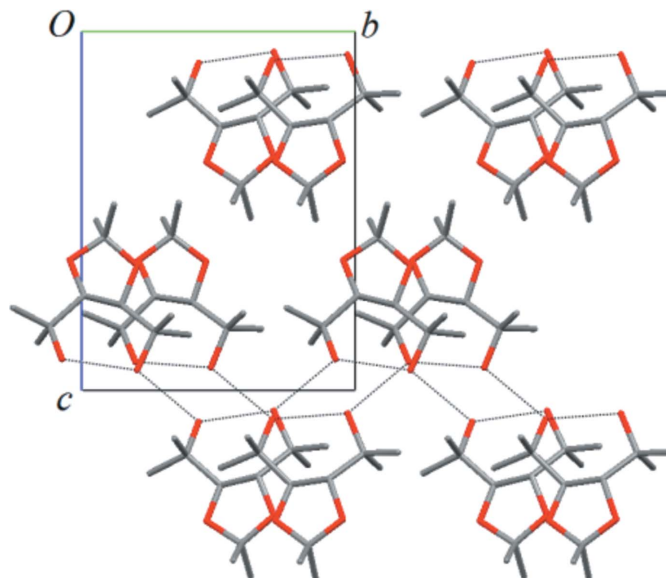


**Figure 2**  
The one-dimensional hydrogen-bonding arrangement, showing intra- and intermolecular hydrogen bonds (dashed lines).

molecular interaction ( $O2-H2D \cdots O1$  and  $O6-H6D \cdots O5$ ) and one intermolecular hydrogen bridge ( $O1-H1D \cdots O2^i$  and  $O5-H5D \cdots O6^{ii}$ ) per molecule (Table 2). The result is one-dimensional two-molecule-wide hydrogen-bonded chains of symmetry-equivalent molecules parallel to the *b* axis (Fig. 2). Hydrogen-bonded chains interact with neighbouring symmetry-equivalent hydrogen-bonded chains through hydrophilic contacts along the *c*-axis direction, forming two-dimensional sheets, each consisting of one independent molecule, parallel to the *bc* plane. The alternating stacking of sheets of the two independent molecules along the *a* axis gives the three-dimensional structure.

Hydrogen-bonding interactions and parameters are listed in Table 2. The intramolecular hydrogen bonding may serve to fix the conformation as described by preventing any rotation around C2, C7, C13 or C18. This hydrogen bonding is also observed in similar compounds of this type (Ito *et al.*, 1994). However, steric factors may also contribute to the observed conformation.

The molecular packing and hydrogen-bonding interactions are illustrated in Fig. 3. A layered structure consisting of



**Figure 3**  
The molecular packing, viewed down the *a* axis, showing the layered structure and hydrogen-bonding interactions (dashed lines). H atoms have been omitted.

alternating hydrophobic and hydrophilic layers is formed. The hydrophilic layer contains the hydroxyl groups which interact *via* hydrogen bonds. Pairs of molecules that alternate in orientation pack in two neighbouring layers, forming the hydrophilic layer.

## Experimental

Dimethyl 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate was prepared by heating a mixture of dimethyl *L*-tartrate (35.6 g, 0.20 mol), 2,2-dimethoxypropane (31.4 g, 0.30 mol) and *p*-toluenesulfonic acid monohydrate (0.121 g, 0.64 mmol) in benzene (800 ml) under reflux in a Soxhlet extractor containing fresh 4 Å molecular sieves for 3 h (Musich & Rapoport, 1978). Anhydrous  $K_2CO_3$  (0.2 g) was added and the solution stirred at room temperature for 4 h. The solution was filtered and the solvent removed under reduced pressure. The residue was taken up in diethyl ether and washed with saturated aqueous sodium bicarbonate (50 ml) and saturated NaCl (50 ml). The solvent was evaporated and the residue was vacuum distilled (0.2 m mHg) at 386 K to yield 38.5 g (88%) of the product.

The ester (10.9 g, 50.0 mmol) in dry tetrahydrofuran (100 ml) was then added dropwise to a solution of methylmagnesium bromide (500 ml) in dry THF under nitrogen at 273 K. The ice bath was removed and the solution was allowed to warm gradually to room temperature and was then stirred at ambient temperature overnight under nitrogen. The reaction was quenched *via* the addition of saturated aqueous ammonium chloride. The layers were separated and the aqueous layer was extracted with ethyl acetate ( $2 \times 100$  ml). The combined organic layers were dried over anhydrous sodium sulfate and the solvent removed *in vacuo* to yield the product as a microcrystalline solid (yield 8.0 g, 74%). Colourless crystals suitable for X-ray diffraction were obtained by evaporation of an ethyl acetate solution of the product at room temperature over a period of 2 d.

## Crystal data

$C_{11}H_{22}O_4$   
 $M_r = 218.29$   
 Monoclinic,  $P2_1$   
 $a = 11.521$  (3) Å  
 $b = 9.072$  (4) Å  
 $c = 12.535$  (3) Å  
 $\beta = 108.24$  (2)°  
 $V = 1244.4$  (7) Å<sup>3</sup>

$Z = 4$   
 $D_x = 1.165$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 Block, colourless  
 $0.6 \times 0.5 \times 0.4$  mm

## Data collection

Oxford Excalibur2 diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: none  
 12554 measured reflections

4144 independent reflections  
 3688 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.038$   
 $\theta_{max} = 31.9^\circ$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.134$   
 $S = 1.09$   
 4144 reflections  
 287 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0883P)^2 + 0.0449P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.31$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.23$  e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

C7—C6	1.524 (2)	C2—C1	1.527 (2)
C7—C8	1.524 (2)	C2—C4	1.529 (2)
C7—C5	1.534 (2)	C18—C17	1.522 (2)
C13—C12	1.526 (2)	C18—C19	1.523 (2)
C13—C14	1.526 (2)	C18—C16	1.533 (2)
C13—C15	1.532 (2)	C5—C4	1.535 (2)
C2—C3	1.526 (2)	C16—C15	1.531 (2)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H6D $\cdots$ O5	0.89 (3)	1.82 (3)	2.701 (2)	170 (2)
O2—H2D $\cdots$ O1	0.89 (3)	1.82 (3)	2.690 (2)	166 (2)
O1—H1D $\cdots$ O2 <sup>i</sup>	0.91 (3)	1.86 (3)	2.7652 (18)	172 (2)
O5—H5D $\cdots$ O6 <sup>ii</sup>	0.91 (3)	1.88 (3)	2.7862 (18)	175 (3)

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

H atoms involved in hydrogen bonding were placed as observed in a Fourier map, thus resulting in the best placement of the atoms in the hydrogen-bonding network. All other H atoms were placed in calculated positions, with methyl C—H = 0.96 Å, methylene C—H = 0.97 Å and methine C—H = 0.98 Å, and were refined using a riding model, with  $U_{iso}(H) = 1.2U_{eq}(\text{parent})$  or  $1.5U_{eq}(\text{methyl C})$ . Since the chirality of the molecule could not be determined from the data the Friedel pairs were merged for the refinement.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *PLATON* (Spek, 2003) and *WinGX* (Farrugia, 1999).

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