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(1*R**,2*S**,4*S**,5*S**)-Cyclohexane-1,2,4,5-tetrol

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.002 Å
R factor = 0.029
wR factor = 0.081
Data-to-parameter ratio = 8.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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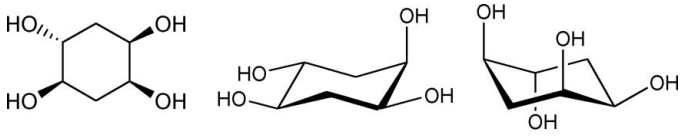
The title compound, $C_6H_{12}O_4$, exists in a chair form, with three of the four OH groups equatorially disposed. All four hydroxy groups participate in extensive intermolecular O—H···O hydrogen bonding.

Comment

The title compound, (1), is one of the five possible geometrical isomers of 1,2,4,5-cyclohexanetetrol. Compound (1) can be conveniently prepared from 1,4-cyclohexadiene *via* a selective epoxidation–hydrolysis–osmylation strategy (McCasland *et al.*, 1963) and is the only readily obtainable configurational isomer of 1,2,4,5-cyclohexanetetrol capable of existing in two energetically different conformational isomers, (1*a*) and (1*b*). While conformer (1*a*) has three of the four hydroxy groups equatorial and is capable of solely intermolecular O—H···O hydrogen bonding, conformer (1*b*), with two *syn*-diaxial hydroxy groups, can be stabilized through an intramolecular O—H···O hydrogen bond (Girling *et al.*, 1974; Panagiotopoulos *et al.*, 1974; James *et al.*, 1978).



(1) (1*a*) (1*b*)

Experimentally, the hydroxy groups in (1) were found to adopt the spatial disposition present in (1*a*) (Fig. 1). Molecules of (1) pack in a herringbone-type arrangement in the non-centrosymmetric space group $P2_12_12_1$ (Fig. 2). Each tetrol molecule is linked to six nearest neighbors by intermolecular O—H···O hydrogen bonds (Table 2). The puckering parameters (Cremer & Pople, 1975) for the cyclohexane ring [q_2 = 0.026 (2) Å, q_3 = −0.582 (2) Å, φ_2 = −17 (4)°, Q_T = 0.585 (2) Å and θ_2 = 177.2 (2)°] describe a slightly distorted chair conformation. The total puckering amplitude Q_T is only

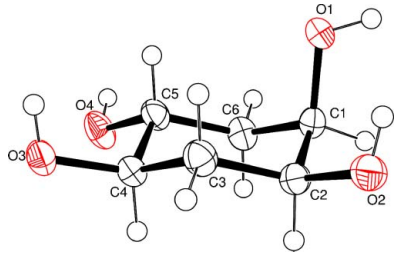


Figure 1
View of (1), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

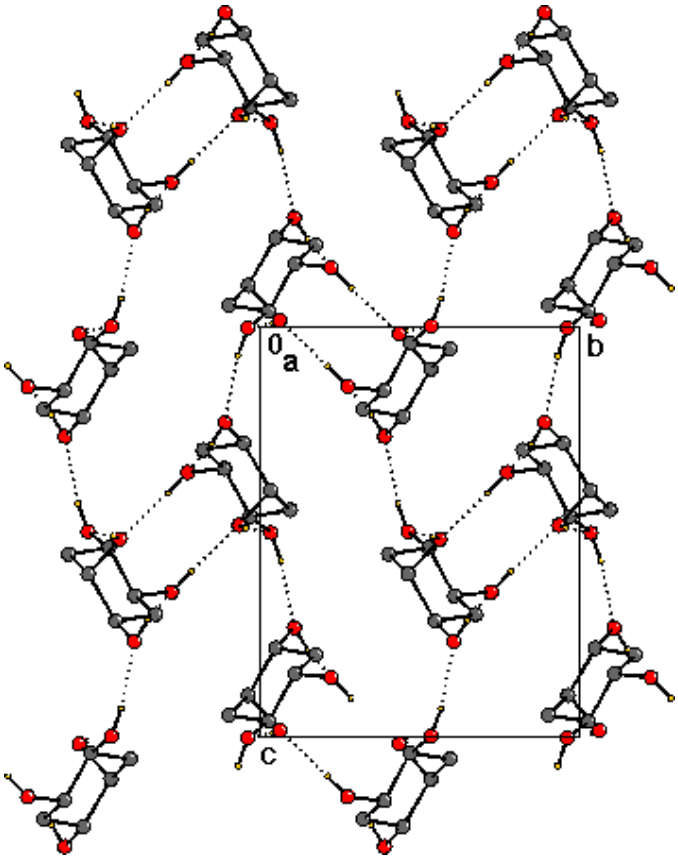


Figure 2
The molecular packing of (1), viewed along the *a* axis. H atoms bonded to C atoms have been omitted for clarity. Dotted lines indicate hydrogen bonds.

slightly smaller than that for an ideal chair (0.63 Å). φ_2 is close to 0°, which corresponds to a boat conformation. Therefore the cyclohexane ring is distorted from an ideal chair conformation and is flattened at C6, allowing the C1—C6—C5 angle to increase to 112.86 (13)°, while the other internal ring angles remain close to the tetrahedral values. The flattening of the cyclohexane ring at C6 can be ascribed to the non-bonding (1,3-diaxial) interaction between the atom O1 and H atoms bonded to atoms C3 and C5.

Experimental

Compound (1) was prepared by a modification of the procedure described by McCasland *et al.* (1963). 1,4-Cyclohexadiene (0.5 ml, 5.3 mmol) in dichloromethane (3 ml) was treated with *m*-chloroperbenzoic acid (70% purity, 1.4 g) in dichloromethane (5 ml) at 273 K. The monoepoxide thus obtained was heated with a 0.2 *M* aqueous solution of Na_2CO_3 (5 ml) at 368 K to obtain *trans*-4-cyclohexene-1,2-diol (0.36 g) in 70% yield (Michaud & Viala, 1999). The diol (0.20 g, 1.8 mmol), upon *cis*-dihydroxylation with catalytic osmium tetroxide (0.5 mol%) and *N*-methylmorpholine-*N*-oxide (50% solution in water, 0.40 ml) in 4:1 acetone–water (0.5 ml), gave the tetrol (1) (0.21 g) in 80% yield. Suitable crystals of (1) were obtained by slow evaporation of its solution in 1:2 dry ethyl acetate–methanol.

Crystal data

$C_6H_{12}O_4$
M_r = 148.16
Orthorhombic, $P2_12_12_1$
a = 6.756 (2) Å
b = 8.783 (3) Å
c = 11.271 (4) Å
V = 668.8 (4) Å^3
Z = 4
D_x = 1.471 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 700 reflections
θ = 2.9–27.0°
μ = 0.12 mm^{-1}
T = 296 (2) K
Block, colorless
0.40 × 0.35 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.922, T_{max} = 0.964
5158 measured reflections
814 independent reflections
800 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 26.4°
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.081
S = 1.18
814 reflections
95 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 0.064P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Selected bond angles (°).

C1—C2—C3	111.04 (13)	C4—C5—C6	109.96 (13)
C1—C6—C5	112.86 (13)	C5—C4—C3	109.68 (12)
C4—C3—C2	111.01 (13)	C6—C1—C2	109.83 (12)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O4^{i}	0.82	1.89	2.705 (2)	172
O2—H2O···O3^{i}	0.82	2.01	2.765 (2)	153
O3—H3O···O1^{ii}	0.82	1.92	2.742 (2)	176
O4—H4O···O2^{iii}	0.82	1.94	2.752 (2)	169

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

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.97–0.98 Å and U_{iso}(H) = 1.2U_{eq}(C), and O—H distances fixed at 0.82 Å and U_{iso}(H) = 1.5U_{eq}(O). Though (1) is obtained in a racemic form through synthesis, its chiral structure in the solid state appears to have resulted from a spontaneous resolution during crystallization. However, owing to the absence of any heavy atom (Z > Si) in (1), the absolute configuration could not be refined. Friedel pairs (539) were averaged prior to merging of data in $P2_12_12_1$; the reported value of R_{int} corresponds to subsequent merging of equivalent reflections in this space group.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et*

al., 1993); software used to prepare material for publication: *PLATON* (Spek, 2003).

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