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Dodecahydroxycyclohexane dihydrate

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In the commercially available title compound, $C_6H_{12}O_{12}\cdot 2H_2O$, the dodecahydroxycyclohexane molecule has an inversion center. The crystal packing is characterized by a strong O—H···O hydrogen bond involving the water molecules, and the dodecahydroxycyclohexane molecules are additionally linked by O—H···O hydrogen bonds of the hydroxyl groups, resulting in the formation of a three-dimensional network.

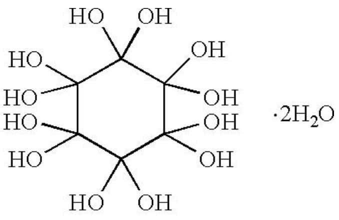
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.033
wR factor = 0.091
Data-to-parameter ratio = 9.7

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

Comment

For a long time, the molecular structure of the commercially available 'hexaketocyclohexane octahydrate', the title compound, (I), has been the cause of controversial discussions and it is amazing that until now no X-ray structure determination has been carried out. Interestingly, the triquinoyl ring of this compound appears from the spectroscopic characterization to be dodecahydroxycyclohexane $C_6(OH)_{12}$ (West & Niu, 1970), but the products of amine condensation reactions, as well as an oxidation reaction with metallic copper, shows that the chemistry of (I) follows the path of hexaketocyclohexane C_6O_6 (Catalano *et al.*, 1994; Speier *et al.*, 1997). In order to unearth the truth, the structure of (I) has been determined.



(I)

The molecular structure of (I) is shown in Fig. 1. The cyclohexane ring lies about an inversion center and exhibits an undistorted chair conformation with 12 OH groups, six in axial and six in equatorial positions. All C—C bonds and bond angles (Table 1) fall in the expected ranges derived from other cyclohexanols. The C—O bonds are about 0.025 Å shorter than the typical value for such bonds in a similar environment (Linden, 1995). There are seven intermolecular and one intramolecular hydrogen bond (Table 2), with O···O in the range 2.704 (2)–2.916 (2) Å. All the hydroxyl groups except O1 act as hydrogen-bond donors and acceptors, either with other hydroxyl groups or with the water molecules, forming a three-dimensional network (Fig. 2). The hydrogen bond between O4 and O2 is intramolecular and a closer inspection of the intermolecular bond patterns reveals that O1, accepting

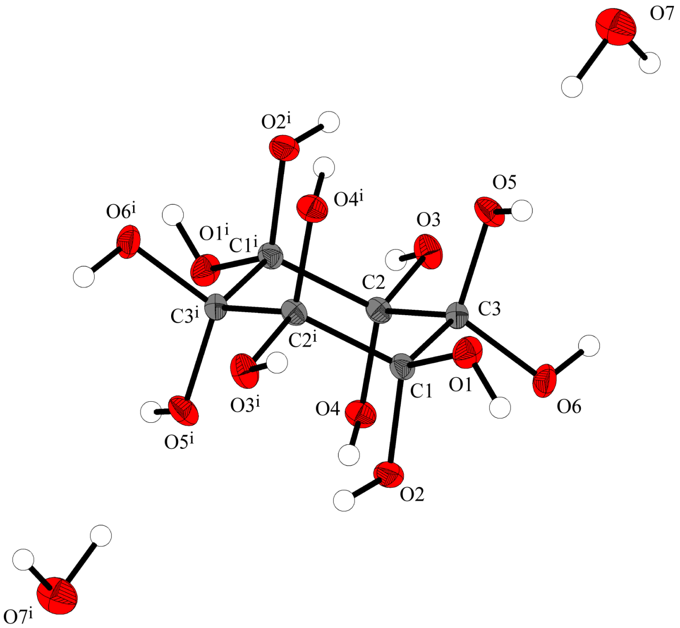


Figure 1
A view of the molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $1-x$, $1-y$, $1-z$.]

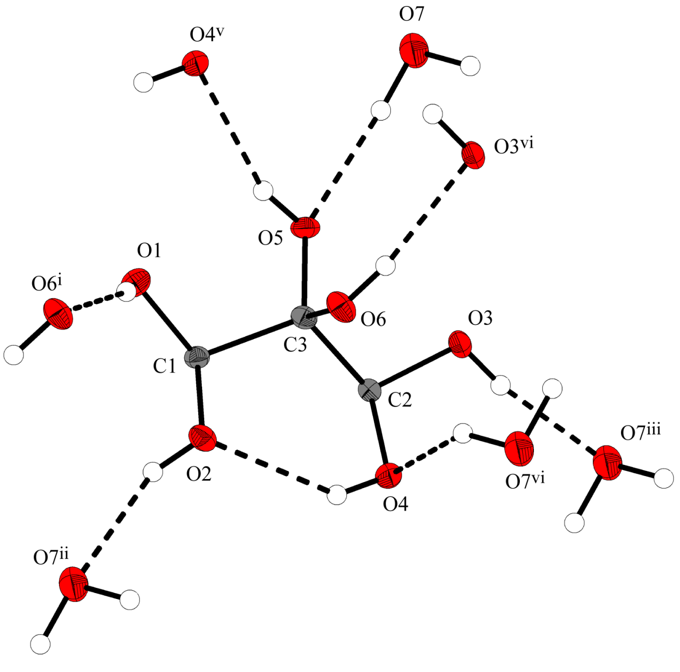


Figure 2
he hydrogen-bonding scheme in (I), showing the asymmetric unit of the organic molecule with its surroundings. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. [Symmetry codes: (i) x, $y-1$, z; (ii) $2-x$, $-y$, $2-z$; (iii) $x-1$, y, z; (iv) $1-x$, $1-y$, $1-z$; (v) $1+x$, y, z; (vi) $1-x$, $1-y$, $2-z$.]

a hydrogen bond from O6, does not serve as an intermolecular hydrogen-bond donor. The water accepts and donates two hydrogen bonds. Its fourfold coordination shell (Fig. 3), formed by atoms O2, O3, O4 and O5, can be approximated by a very distorted tetrahedron.

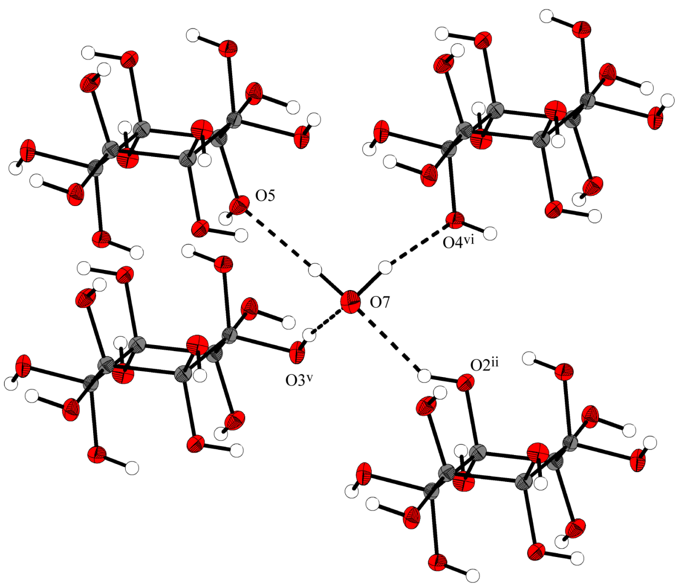


Figure 3
Distorted tetrahedral coordination shell of the water molecule in (I). [Symmetry codes: (ii) $2-x$, $-y$, $2-z$; (v) $1+x$, y, z; (vi) $1-x$, $1-y$, $2-z$.]

Experimental

In a typical reaction, powdered sodium tetrahydroxyquinone (16.2 g, 50 mmol; Fatiadi & Sager, 1983) was added in portions over a period of 10 min to a stirred solution of 25% HNO_3 (38 ml). The temperature of the vigorous reaction was controlled at 318±5 K using an ice bath. Compound (I) crystallized from the resulting yellow solution as colorless plates suitable for an X-ray structure determination [yield 17.55 g, 80%; m.p. 367–369 K (decomposition)].

Crystal data

$C_6H_{12}O_{12}\cdot 2H_2O$
$M_r = 312.19$
Triclinic, $P\overline{1}$
$a = 6.1829$ (8) Å
$b = 7.0696$ (8) Å
$c = 7.3023$ (6) Å
$\alpha = 70.443$ (8)°
$\beta = 80.153$ (8)°
$\gamma = 63.973$ (10)°
$V = 270.16$ (5) Å^3
$Z = 1$
$D_x = 1.919$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 9$–18°
$\mu = 0.20$ mm^{-1}
$T = 295$ (2) K
Plate, colourless
0.47 × 0.43 × 0.10 mm

Data collection

Nonius MACH3 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.945$, $T_{\max} = 0.976$
1046 measured reflections
948 independent reflections
893 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.010$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 7$
$k = -7 \rightarrow 8$
$l = -8 \rightarrow 8$
3 standard reflections
frequency: 120 min
intensity decay: 1.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.091$
$S = 1.10$
948 reflections
98 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.2382P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.155 (19)

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Table 1
Selected geometric parameters (Å, °).

O1—C1	1.402 (2)	O6—C3	1.408 (2)
O2—C1	1.397 (2)	C1—C3^{i}	1.553 (2)
O3—C2	1.393 (2)	C1—C2	1.562 (2)
O4—C2	1.416 (2)	C2—C3	1.554 (2)
O5—C3	1.390 (2)		
O2—C1—O1	111.93 (13)	O3—C2—C1	108.62 (13)
O2—C1—C3^{i}	106.13 (13)	O4—C2—C1	109.99 (13)
O1—C1—C3^{i}	109.27 (13)	C3—C2—C1	113.08 (13)
O2—C1—C2	111.45 (13)	O5—C3—O6	111.14 (13)
O1—C1—C2	105.63 (13)	O5—C3—C1^{i}	111.13 (14)
C3^{i}—C1—C2	112.52 (13)	O6—C3—C1^{i}	106.69 (13)
O3—C2—O4	107.37 (13)	O5—C3—C2	107.33 (13)
O3—C2—C3	107.66 (13)	O6—C3—C2	109.66 (13)
O4—C2—C3	109.92 (13)	C1^{i}—C3—C2	110.93 (13)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O6^{vii}	0.82	2.00	2.791 (2)	161
O2—H2···O7^{ii}	0.82	2.06	2.761 (2)	143
O3—H3···O7^{viii}	0.82	1.89	2.704 (2)	171
O4—H4···O2^{i}	0.82	2.09	2.768 (2)	140
O5—H5···O4^{v}	0.82	2.11	2.897 (2)	161
O6—H6···O3^{vi}	0.82	1.97	2.769 (2)	163
O7—H7*A*···O4^{vi}	0.96	2.05	2.877 (2)	143
O7—H7*B*···O5	0.95	1.96	2.916 (2)	175

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $2-x, -y, 2-z$; (v) $1+x, y, z$; (vi) $1-x, 1-y, 2-z$; (vii) $x, y-1, z$; (viii) $x-1, y, z$.

The water H atoms were located in difference density maps, while the H atoms of the hydroxyl groups were positioned geometrically. Restraints were applied to the bond lengths and to the distance between the H atoms of the hydroxyl groups to stabilize the structure during initial refinement. All non-H atoms were refined with anisotropic displacement parameters, employing a rigid-bond restaint to $U_{\rm ij}$ of pairs of bonded atoms (Rollett, 1970). The H atoms were allowed to ride on the coordinates of their parent atoms during the final refinement, with hydroxyl O—H = 0.82 Å and water O—H fixed at the values obtained in free refinement. The $U_{\rm iso}$(H) values were taken as $1.2U_{\rm eq}$(O). The hydroxyl groups were allowed to rotate around the C—O bonds.

Data collection: *CAD-4 Software* (Nonius, 1994); cell refinement: *CAD-4 Software*; data reduction: *OpenMoleN* (Nonius, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

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