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3,3,6,6-Tetrakis(hydroxymethyl)-1,2,4,5-tetrazinane tetrahydrate

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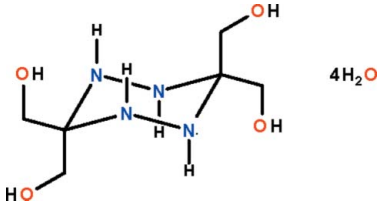
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.001 Å; R factor = 0.042; wR factor = 0.137; data-to-parameter ratio = 37.1.

In the title compound, $C_6H_{16}N_4O_4\cdot4H_2O$, the tetrazinane molecule lies across an inversion centre. The tetrazinane ring adopts a chair conformation, and all imino H atoms occupy axial positions. In the crystal, adjacent molecules are linked through O—H···O, O—H···N and N—H···O hydrogen bonds with water molecules generating a three-dimensional network.

Related literature

For the synthesis of hexahydro-1,2,4,5-tetrazine derivatives by condensing aldehydes with hydrazine, see: Skorianetz & Kovats (1970). For the synthesis of the 3,6-dimethyl homolog, see: Sun *et al.* (2003); Zhou *et al.* (1999).



Experimental

Crystal data

$C_6H_{16}N_4O_4\cdot4H_2O$
M_r = 280.29
Triclinic, $P\overline{1}$
a = 6.3067 (1) Å
b = 7.0317 (2) Å
c = 8.4015 (2) Å
α = 71.010 (1)°
β = 74.424 (1)°
γ = 85.055 (1)°
V = 339.36 (1) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 296 K
0.40 × 0.40 × 0.40 mm

Data collection

Bruker SMART APEXII diffractometer
Absorption correction: none
10198 measured reflections
4231 independent reflections
3630 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.137
S = 1.01
4231 reflections
114 parameters
8 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.93 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O1W	0.85 (1)	1.87 (1)	2.704 (1)	166 (2)
O2—H2O···O2W^{i}	0.86 (1)	1.87 (1)	2.723 (1)	171 (2)
N1—H1N···O2^{ii}	0.86 (1)	2.23 (1)	3.036 (1)	155 (1)
N2—H2N···O1W^{iii}	0.87 (1)	2.36 (1)	3.130 (1)	148 (1)
O1W—H1$W1$···O2W^{iv}	0.86 (1)	1.92 (1)	2.782 (1)	172 (2)
O1W—H1$W2$···N2^{v}	0.86 (1)	2.03 (1)	2.869 (1)	166 (2)
O2W—H2$W1$···O1	0.84 (1)	1.92 (1)	2.759 (1)	175 (2)
O2W—H2$W2$···N1^{vi}	0.84 (1)	2.02 (1)	2.853 (1)	171 (2)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2961).

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supporting information

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S1. Experimental

Dihydroxyacetone (0.90 g, 10 mmol) and hydrazine hydrate (0.49 ml, 10 mmol) in ethanol (50 ml) were heated for 12 h. Slow evaporation of the solvent gave colourless crystals in 80% yield. The formulation of the organic molecule was established by ^{1}H and ^{13}C NMR as well as by mass spectroscopies.

S2. Refinement

The amino and water H-atoms were located in a difference Fourier map, and were refined with a distance restraint of N-H = O-H = 0.85 (1) Å; their U_{iso} parameters were freely refined. Carbon-bound H-atoms were placed in calculated positions (C-H = 0.97 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The highest peak and the deepest hole are located 0.73 and 0.58 Å from O1W. Although the displacement parameters of atom O1W are relatively large, no disorder is expected as its H-atoms could be located and refined.

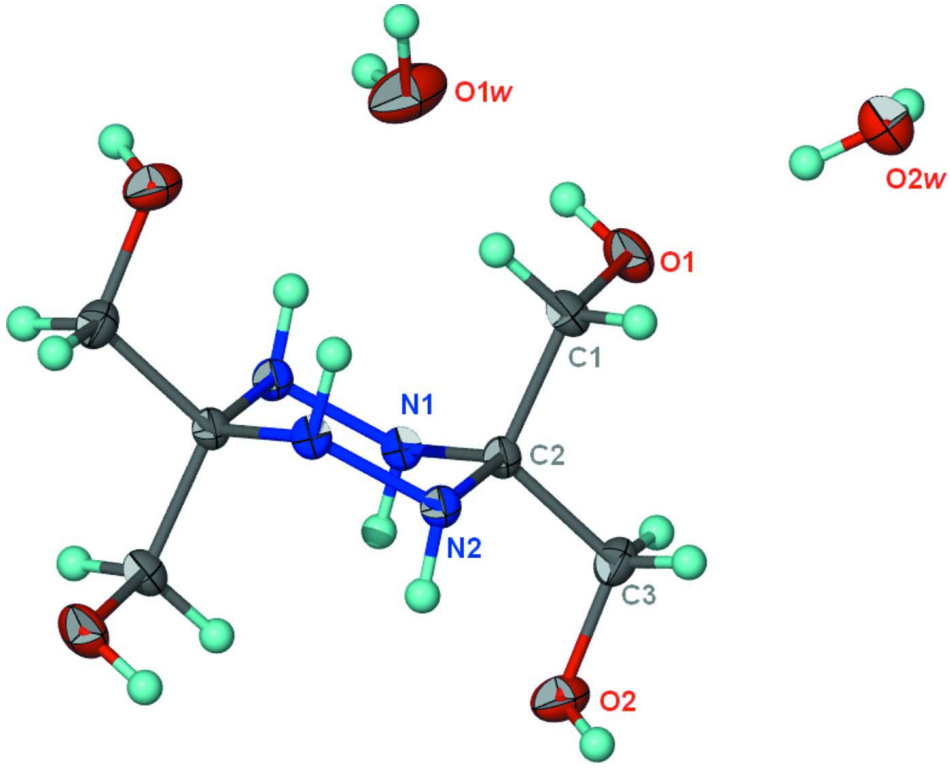

Figure 1

Displacement ellipsoid plot (Barbour, 2001) of $C_6H_{16}N_4O_4{\cdot}4H_2O$ at the 50% probability level. H atoms are drawn as spheres of arbitrary radius. Unlabelled atoms in the tetrazinane derivative are related to labelled atoms by the symmetry operation (1-x, -y, 2-z). Two symmetry related water molecules are not shown.

3,3,6,6-Tetrakis(hydroxymethyl)-1,2,4,5-tetrazinane tetrahydrate

Crystal data

$C_6H_{16}N_4O_4{\cdot}4H_2O$
$M_r = 280.29$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.3067\ (1)$ Å
$b = 7.0317\ (2)$ Å
$c = 8.4015\ (2)$ Å
$\alpha = 71.010\ (1)°$
$\beta = 74.424\ (1)°$
$\gamma = 85.055\ (1)°$
$V = 339.36\ (1)$ Å^3
$Z = 1$
$F(000) = 152$
$D_x = 1.371$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6318 reflections
$\theta = 3.1–40.2°$
$\mu = 0.12$ mm^{-1}
$T = 296$ K
Cube, colourless
0.40 × 0.40 × 0.40 mm

Data collection

Bruker SMART APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
10198 measured reflections
4231 independent reflections
3630 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 40.2°$, $\theta_{min} = 3.1°$
$h = -11\rightarrow11$
$k = -12\rightarrow12$
$l = -15\rightarrow15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.137$
$S = 1.01$
4231 reflections
114 parameters
8 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0853P)^2 + 0.0377P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.93$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.62982 (10)	0.32676 (8)	0.59353 (6)	0.03101 (11)
O2	0.12442 (8)	−0.12559 (9)	0.85708 (8)	0.03186 (11)
O1W	0.74166 (12)	0.53141 (12)	0.78141 (13)	0.0496 (2)
O2W	0.81111 (10)	0.46492 (8)	0.23874 (7)	0.03194 (11)
N1	0.35398 (7)	0.15628 (7)	0.93656 (6)	0.01863 (8)
N2	0.53643 (7)	−0.16882 (6)	0.93673 (6)	0.01882 (8)
C3	0.30946 (11)	−0.01190 (10)	0.73791 (8)	0.02651 (11)
H3A	0.2599	0.1154	0.6697	0.032*
H3B	0.3856	−0.0844	0.6586	0.032*
C1	0.67667 (9)	0.13379 (9)	0.69956 (7)	0.02297 (10)
H1A	0.7819	0.1472	0.7609	0.028*
H1B	0.7435	0.0517	0.6262	0.028*
C2	0.46871 (8)	0.02767 (7)	0.83271 (6)	0.01806 (9)
H1O	0.661 (3)	0.409 (2)	0.640 (2)	0.051 (4)*
H2O	0.140 (3)	−0.2396 (16)	0.839 (2)	0.052 (4)*
H1W1	0.8827 (15)	0.535 (3)	0.765 (2)	0.057 (4)*
H1W2	0.688 (3)	0.6353 (19)	0.810 (2)	0.055 (4)*
H2W1	0.753 (2)	0.430 (2)	0.3464 (12)	0.053 (4)*
H2W2	0.754 (3)	0.5766 (18)	0.198 (3)	0.069 (5)*
H1N	0.2237 (14)	0.1097 (17)	0.9941 (14)	0.026 (2)*
H2N	0.4192 (16)	−0.2420 (16)	0.9932 (15)	0.027 (2)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0395 (3)	0.0239 (2)	0.02234 (19)	−0.00194 (17)	−0.00506 (17)	0.00069 (15)
O2	0.02304 (19)	0.0353 (2)	0.0423 (3)	−0.00251 (16)	−0.00474 (17)	−0.0211 (2)
O1W	0.0348 (3)	0.0488 (4)	0.0794 (6)	0.0026 (3)	−0.0098 (3)	−0.0437 (4)
O2W	0.0353 (2)	0.0254 (2)	0.0306 (2)	0.00639 (17)	−0.00462 (18)	−0.00747 (17)
N1	0.01946 (16)	0.01761 (16)	0.01842 (16)	0.00258 (12)	−0.00506 (12)	−0.00561 (12)
N2	0.02248 (17)	0.01557 (15)	0.01876 (16)	0.00090 (12)	−0.00525 (12)	−0.00611 (12)
C3	0.0297 (2)	0.0293 (3)	0.0242 (2)	−0.00180 (19)	−0.01135 (18)	−0.00917 (19)
C1	0.0244 (2)	0.0221 (2)	0.01861 (18)	−0.00032 (16)	−0.00180 (15)	−0.00427 (15)

C2	0.02086 (18)	0.01704 (17)	0.01609 (16)	0.00065 (13)	−0.00472 (13)	−0.00510 (13)

Geometric parameters (Å, º)

O1—C1	1.4169 (7)	N1—H1N	0.86 (1)
O1—H1O	0.851 (9)	N2—N1^{i}	1.4441 (6)
O2—C3	1.4198 (9)	N2—C2	1.4724 (6)
O2—H2O	0.86 (1)	N2—H2N	0.87 (1)
O1W—H1W1	0.86 (1)	C3—C2	1.5305 (8)
O1W—H1W2	0.86 (1)	C3—H3A	0.97
O2W—H2W1	0.84 (1)	C3—H3B	0.97
O2W—H2W2	0.84 (1)	C1—C2	1.5382 (7)
N1—N2^{i}	1.4441 (6)	C1—H1A	0.97
N1—C2	1.4712 (7)	C1—H1B	0.97
C1—O1—H1O	105.1 (11)	C2—C3—H3B	109.4
C3—O2—H2O	104.1 (11)	H3A—C3—H3B	108.0
H1W1—O1W—H1W2	107.6 (16)	O1—C1—C2	112.12 (5)
H2W1—O2W—H2W2	105.0 (18)	O1—C1—H1A	109.2
N2^{i}—N1—C2	113.59 (4)	C2—C1—H1A	109.2
N2^{i}—N1—H1N	106.4 (8)	O1—C1—H1B	109.2
C2—N1—H1N	110.2 (8)	C2—C1—H1B	109.2
N1^{i}—N2—C2	113.72 (4)	H1A—C1—H1B	107.9
N1^{i}—N2—H2N	107.4 (8)	N1—C2—N2	114.01 (4)
C2—N2—H2N	108.2 (8)	N1—C2—C3	107.44 (4)
O2—C3—C2	111.33 (5)	N2—C2—C3	107.54 (4)
O2—C3—H3A	109.4	N1—C2—C1	110.36 (4)
C2—C3—H3A	109.4	N2—C2—C1	107.54 (4)
O2—C3—H3B	109.4	C3—C2—C1	109.89 (4)
N2^{i}—N1—C2—N2	47.54 (6)	O2—C3—C2—N1	−65.11 (6)
N2^{i}—N1—C2—C3	166.60 (4)	O2—C3—C2—N2	58.02 (6)
N2^{i}—N1—C2—C1	−73.60 (5)	O2—C3—C2—C1	174.80 (5)
N1^{i}—N2—C2—N1	−47.60 (6)	O1—C1—C2—N1	−54.32 (6)
N1^{i}—N2—C2—C3	−166.60 (4)	O1—C1—C2—N2	−179.24 (4)
N1^{i}—N2—C2—C1	75.09 (5)	O1—C1—C2—C3	63.98 (6)

Symmetry code: (i) −*x*+1, −*y*, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O1*W*	0.85 (1)	1.87 (1)	2.704 (1)	166 (2)
O2—H2*O*···O2*W*^{ii}	0.86 (1)	1.87 (1)	2.723 (1)	171 (2)
N1—H1*N*···O2^{iii}	0.86 (1)	2.23 (1)	3.036 (1)	155 (1)
N2—H2*N*···O1*W*^{i}	0.87 (1)	2.36 (1)	3.130 (1)	148 (1)
O1*W*—H1*W*1···O2*W*^{iv}	0.86 (1)	1.92 (1)	2.782 (1)	172 (2)
O1*W*—H1*W*2···N2^{v}	0.86 (1)	2.03 (1)	2.869 (1)	166 (2)

O2*W*—H2*W*1···O1	0.84 (1)	1.92 (1)	2.759 (1)	175 (2)
O2*W*—H2*W*2···N1^{vi}	0.84 (1)	2.02 (1)	2.853 (1)	171 (2)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+2; (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*, −*y*, −*z*+2; (iv) −*x*+2, −*y*+1, −*z*+1; (v) *x*, *y*+1, *z*; (vi) −*x*+1, −*y*+1, −*z*+1.