# organic compounds

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

**S. Kongsutjarit,[a] P. Thamyongkit,[a] N. Muangsin,[a] N. Chaichit,[b] Amorn Petsom[a] and Seik Weng Ng[c]***

[a]Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand, [b]Department of Physics, Faculty of Science and Technology, Thammasart University, Pathum Thani 12121, Thailand, and [c]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia
Correspondence e-mail: seikweng@um.edu.my

In the title compound, $C_6H_{16}N_4O_4 \cdot 4H_2O$, 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).
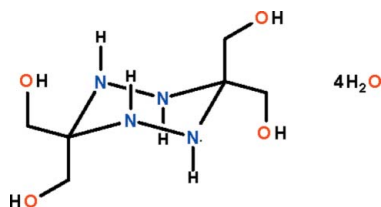


## Experimental

### Crystal data

| | |
|---|---|
| $C_6H_{16}N_4O_4 \cdot 4H_2O$ | $b$ = 7.0317 (2) Å |
| $M_r$ = 280.29 | $c$ = 8.4015 (2) Å |
| Triclinic, $P\bar{1}$ | $\alpha$ = 71.010 (1)° |
| $a$ = 6.3067 (1) Å | $\beta$ = 74.424 (1)° |
| $\gamma$ = 85.055 (1)° | $\mu$ = 0.12 mm$^{-1}$ |
| $V$ = 339.36 (1) Å$^3$ | $T$ = 296 K |
| $Z$ = 1 | $0.40 \times 0.40 \times 0.40$ mm |
| Mo $K\alpha$ radiation | |

### Data collection

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

### Refinement

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

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

| $D$—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$W^i$ | 0.86 (1) | 1.87 (1) | 2.723 (1) | 171 (2) |
| N1—H1$N$···O2$^{ii}$ | 0.86 (1) | 2.23 (1) | 3.036 (1) | 155 (1) |
| N2—H2$N$···O1$W^{iii}$ | 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) $-x + 1, -y, -z + 1$; (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).

## References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2005). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Skorianetz, W. & Kovats, E. Sz. (1970). *Helv. Chim. Acta*, **53**, 251–262.
Sun, Y.-Q., Hu, W.-X. & Yuan, Q. (2003). *Synth. Commun.* **33**, 2769–2775.
Westrip, S. P. (2009). *publCIF*. In preparation.
Zhou, M., Cai, Z.-B., Yang, Z.-Y. & Hu, W.-X. (1999). *Jingxi Huagong*, **16**, 1–4.

**supplementary materials**

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

**S. Kongsutjarit, P. Thamyongkit, N. Muangsin, N. Chaichit, A. Petsom and S. W. Ng**

### 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.

### 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.
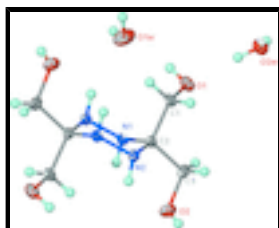
### Figures



Fig. 1. Displacement ellipsoid plot (Barbour, 2001) of $C_6H_{16}N_4O_4$·$4H_2O$ 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*

| | |
|---|---|
| $C_6H_{16}N_4O_4$·$4H_2O$ | $Z = 1$ |
| $M_r = 280.29$ | $F_{000} = 152$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.371$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 6.3067$ (1) Å | Cell parameters from 6318 reflections |
| $b = 7.0317$ (2) Å | $\theta = 3.1–40.2°$ |
| $c = 8.4015$ (2) Å | $\mu = 0.12$ mm$^{-1}$ |
| $\alpha = 71.010$ (1)° | $T = 296$ K |
| $\beta = 74.424$ (1)° | Cube, colourless |
| $\gamma = 85.055$ (1)° | $0.40 \times 0.40 \times 0.40$ mm |
| $V = 339.364$ (14) Å$^3$ | |

## Data collection

| | |
|---|---|
| Bruker SMART APEXII diffractometer | 3630 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int} = 0.018$ |
| Monochromator: graphite | $\theta_{max} = 40.2°$ |
| $T = 296$ K | $\theta_{min} = 3.1°$ |
| φ and ω scans | $h = -11 \rightarrow 11$ |
| Absorption correction: None | $k = -12 \rightarrow 12$ |
| 10198 measured reflections | $l = -15 \rightarrow 15$ |
| 4231 independent reflections | |

## Refinement

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.137$ | $w = 1/[\sigma^2(F_o^2) + (0.0853P)^2 + 0.0377P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.01$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 4231 reflections | $\Delta\rho_{max} = 0.93$ e Å$^{-3}$ |
| 114 parameters | $\Delta\rho_{min} = -0.63$ e Å$^{-3}$ |
| 8 restraints | Extinction correction: none |
| Primary atom site location: structure-invariant direct methods | |

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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 ($Å^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, °)*

| | | | |
|---|---|---|---|
| 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 codes: (i) −x+1, −y, −z+2.

*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$^{ii}$ | 0.86 (1) | 1.87 (1) | 2.723 (1) | 171 (2) |
| N1—H1N···O2$^{iii}$ | 0.86 (1) | 2.23 (1) | 3.036 (1) | 155 (1) |
| N2—H2N···O1W$^i$ | 0.87 (1) | 2.36 (1) | 3.130 (1) | 148 (1) |
| O1W—H1W1···O2W$^{iv}$ | 0.86 (1) | 1.92 (1) | 2.782 (1) | 172 (2) |
| O1W—H1W2···N2$^v$ | 0.86 (1) | 2.03 (1) | 2.869 (1) | 166 (2) |
| O2W—H2W1···O1 | 0.84 (1) | 1.92 (1) | 2.759 (1) | 175 (2) |
| O2W—H2W2···N1$^{vi}$ | 0.84 (1) | 2.02 (1) | 2.853 (1) | 171 (2) |

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

**Fig. 1**