# 5,5-Dihydroxybarbituric acid monohydrate (alloxan dihydrate)

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The title compound, $C_4H_4N_2O_5 \cdot H_2O$, was crystallized from both tetrahydrofuran and 1,4-dioxane solutions of alloxan as part of an experimental polymorph screen on alloxan.

Comment

It has previously been reported that alloxan has two hydrates, *viz.* 5,5-dihydroxybarbituric acid (Singh, 1965; Harrowfield *et al.*, 1989) and 5,5-dihydroxybarbituric acid trihydrate (Mootz & Jeffrey, 1965). The crystal structure of a new hydrate of alloxan, namely 5,5-dihydroxybarbituric acid monohydrate, (I), has one organic molecule and one water molecule in the asymmetric unit (Fig. 1). The heterocyclic ring has an envelope conformation with the flap at C5, with the angle between the mean C4/N3/C2/N1/C6 and C4/C5/C6 planes being 20.1 (2)°. The C—N bond lengths are in the range 1.360 (2)–1.378 (2) Å, with the bond lengths associated with the sp^3-hybridized carbon being 1.536 (2) and 1.527 (2) Å for C4—C5 and C5—C6, respectively.

(I)
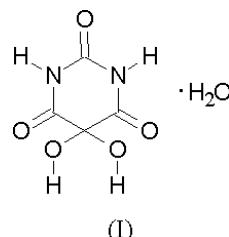
The crystal packing (Fig. 2) consists of a series of ribbon motifs arranged in an overall sheet structure. Water molecules lie in the sheets and between the ribbons. Each water molecule acts as a hydrogen-bond donor to a carbonyl group in the same sheet and to a hydroxyl group on a molecule in the adjacent sheet. Each water molecule also acts as a hydrogen-bond acceptor for a hydroxyl group on a molecule in the same sheet. The axial hydroxyl group on each molecule acts as a hydrogen-bond donor to the unique carbonyl of a molecule in an adjacent sheet. The $D \cdots A$ distances within the sheets are in the range 2.6380 (19)–2.9516 (19) Å, whilst the distances between the sheets are 2.6958 (17) and 2.9973 (19) Å. All potential hydrogen-bond acceptors and donors participate in the hydrogen bonding.

Experimental

5,5-Dihydroxybarbituric acid monohydrate was crystallized over a number of weeks by slow evaporation of tetrahydrofuran and 1,4-dioxane solutions of alloxan (0.002–0.03 mol dm^{-3}) at room temperature, forming colourless plate crystals.

Crystal data

$C_4H_4N_2O_5 \cdot H_2O$
$M_r = 178.11$
Triclinic, $P\bar{1}$
$a = 6.6730\ (11)$ Å
$b = 7.5834\ (13)$ Å
$c = 7.6157\ (13)$ Å
$\alpha = 105.401\ (3)°$
$\beta = 93.134\ (3)°$
$\gamma = 115.089\ (2)°$
$V = 330.26\ (10)$ Å^3

$Z = 2$
$D_x = 1.791$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 712
reflections
$\theta = 2.8$–$25.0°$
$\mu = 0.17$ mm^{-1}
$T = 150\ (2)$ K
Plate, colourless
$0.23 \times 0.11 \times 0.07$ mm

Data collection

Bruker SMART APEX
diffractometer
Narrow-frame ω scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)
$T_{min} = 0.962$, $T_{max} = 0.988$
2972 measured reflections

1536 independent reflections
1274 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 28.3°$
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.102$
$S = 1.07$
1536 reflections
133 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.0119P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O6^i	0.89 (2)	1.95 (2)	2.8366 (18)	170.7 (19)
N3—H3$\cdots$O4^{ii}	0.81 (2)	2.11 (2)	2.8736 (18)	157 (2)
O7—H7$\cdots$O2^{iii}	0.87 (2)	1.83 (3)	2.6958 (17)	173 (2)
O8—H8$\cdots$O1W^{iii}	0.80 (2)	1.87 (2)	2.6380 (19)	161 (2)
O1W—H1W$\cdots$O6^{iv}	0.92 (3)	2.04 (3)	2.9516 (19)	173 (2)
O1W—H2W$\cdots$O7^{ii}	0.82 (3)	2.28 (3)	2.9973 (19)	147 (3)

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

H atoms were refined freely with an isotropic model.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL*97.
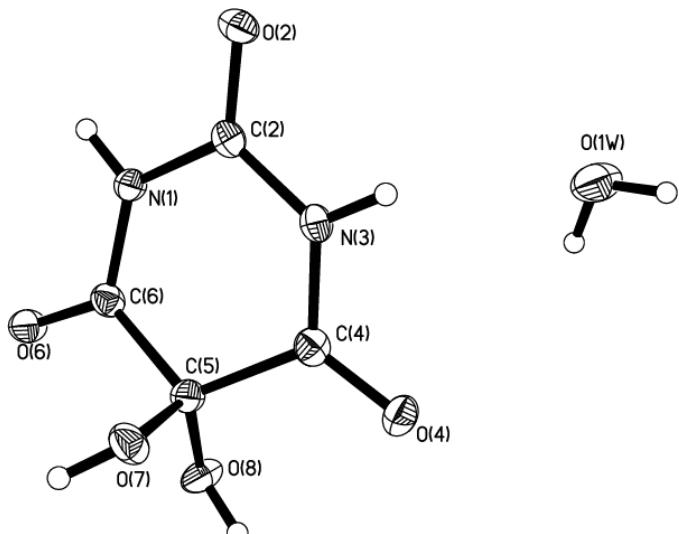
Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.
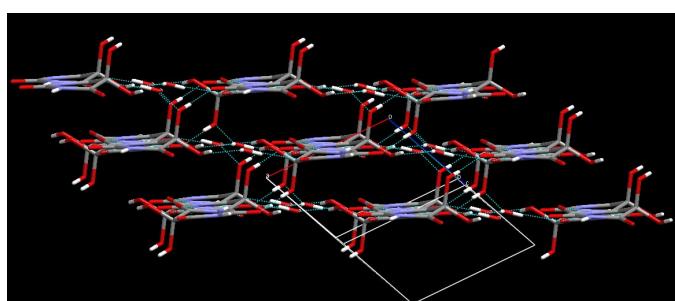
Figure 2
The crystal packing of (I), showing the N—H$\cdots$O and O—H$\cdots$O hydrogen-bonding interactions as dashed lines; the view is approximately on to the $(01\bar{1})$ plane.

References

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supporting information

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Triclinic, $P\bar{1}$	$D_x = 1.791$ Mg m^{-3}
$a = 6.6730$ (11) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 7.5834$ (13) Å	Cell parameters from 712 reflections
$c = 7.6157$ (13) Å	$\theta = 2.8$–25.0°
$\alpha = 105.401$ (3)°	$\mu = 0.17$ mm^{-1}
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$\gamma = 115.089$ (2)°	Plate, colourless
$V = 330.26$ (10) Å^3	$0.23 \times 0.11 \times 0.07$ mm

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Bruker SMART APEX diffractometer	2972 measured reflections
Radiation source: fine-focus sealed tube	1536 independent reflections
Graphite monochromator	1274 reflections with $I > 2\sigma(I)$
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Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{max} = 28.3°$, $\theta_{min} = 2.8°$
	$h = -8 \rightarrow 8$
	$k = -9 \rightarrow 9$
$T_{min} = 0.962$, $T_{max} = 0.988$	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.043$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.102$	
$S = 1.07$	All H-atom parameters refined
1536 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.0119P]$
133 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.34$ e Å^{-3}
	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
O2	0.2526 (2)	0.32902 (18)	0.90727 (17)	0.0200 (3)
O4	0.6356 (2)	0.34785 (19)	0.43384 (16)	0.0214 (3)
O6	0.7119 (2)	0.02976 (19)	0.86645 (17)	0.0207 (3)
O7	0.9445 (2)	0.42247 (18)	0.76705 (17)	0.0194 (3)
O8	0.7906 (2)	0.09757 (19)	0.54162 (17)	0.0204 (3)
O1W	0.0411 (3)	0.1981 (2)	0.2940 (2)	0.0339 (4)
N1	0.4853 (2)	0.1829 (2)	0.8839 (2)	0.0160 (3)
N3	0.4626 (2)	0.3615 (2)	0.6818 (2)	0.0171 (3)
C2	0.3919 (3)	0.2946 (2)	0.8279 (2)	0.0156 (4)
C4	0.6073 (3)	0.3162 (2)	0.5801 (2)	0.0160 (4)
C5	0.7514 (3)	0.2387 (2)	0.6700 (2)	0.0155 (4)
C6	0.6456 (3)	0.1366 (2)	0.8121 (2)	0.0154 (3)
H1	0.421 (4)	0.128 (3)	0.969 (3)	0.033 (6)*
H3	0.398 (4)	0.416 (3)	0.641 (3)	0.035 (6)*
H7	1.035 (4)	0.383 (4)	0.813 (3)	0.046 (7)*
H8	0.859 (4)	0.149 (3)	0.472 (3)	0.034 (6)*
H1W	0.107 (5)	0.117 (4)	0.244 (4)	0.059 (8)*
H2W	0.030 (5)	0.268 (4)	0.232 (4)	0.072 (10)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0185 (6)	0.0251 (7)	0.0231 (7)	0.0143 (5)	0.0074 (5)	0.0101 (5)
O4	0.0264 (7)	0.0273 (7)	0.0190 (7)	0.0157 (6)	0.0081 (5)	0.0136 (5)
O6	0.0236 (7)	0.0270 (7)	0.0256 (7)	0.0179 (6)	0.0120 (5)	0.0175 (5)
O7	0.0158 (6)	0.0205 (7)	0.0262 (7)	0.0093 (5)	0.0038 (5)	0.0121 (5)
O8	0.0292 (7)	0.0213 (7)	0.0204 (7)	0.0161 (6)	0.0143 (5)	0.0116 (5)
O1W	0.0465 (9)	0.0343 (8)	0.0412 (9)	0.0277 (8)	0.0276 (8)	0.0235 (7)
N1	0.0171 (7)	0.0204 (7)	0.0173 (7)	0.0110 (6)	0.0068 (6)	0.0116 (6)
N3	0.0198 (7)	0.0201 (7)	0.0191 (7)	0.0133 (6)	0.0049 (6)	0.0106 (6)
C2	0.0155 (8)	0.0151 (8)	0.0173 (8)	0.0079 (7)	0.0019 (6)	0.0056 (7)
C4	0.0171 (8)	0.0128 (8)	0.0192 (8)	0.0068 (7)	0.0033 (6)	0.0068 (6)
C5	0.0162 (8)	0.0170 (8)	0.0172 (8)	0.0090 (7)	0.0054 (6)	0.0084 (7)
C6	0.0144 (8)	0.0155 (8)	0.0186 (9)	0.0075 (7)	0.0038 (6)	0.0077 (7)

Geometric parameters (Å, º)

O2—C2	1.2171 (19)	N1—C6	1.360 (2)
O4—C4	1.209 (2)	N1—C2	1.378 (2)
O6—C6	1.2188 (19)	N1—H1	0.89 (2)

O7—C5	1.405 (2)	N3—C4	1.368 (2)
O7—H7	0.87 (2)	N3—C2	1.368 (2)
O8—C5	1.3706 (19)	N3—H3	0.81 (2)
O8—H8	0.80 (2)	C4—C5	1.536 (2)
O1W—H1W	0.92 (3)	C5—C6	1.527 (2)
O1W—H2W	0.82 (3)		
C5—O7—H7	104.6 (16)	O4—C4—N3	123.23 (15)
C5—O8—H8	109.7 (16)	O4—C4—C5	120.38 (15)
H1W—O1W—H2W	115 (3)	N3—C4—C5	116.18 (14)
C6—N1—C2	126.62 (15)	O8—C5—O7	115.10 (14)
C6—N1—H1	119.2 (13)	O8—C5—C6	106.53 (13)
C2—N1—H1	113.9 (13)	O7—C5—C6	107.51 (13)
C4—N3—C2	125.45 (14)	O8—C5—C4	112.19 (14)
C4—N3—H3	116.6 (15)	O7—C5—C4	102.10 (12)
C2—N3—H3	117.1 (16)	C6—C5—C4	113.50 (13)
O2—C2—N3	123.04 (15)	O6—C6—N1	121.83 (15)
O2—C2—N1	119.95 (15)	O6—C6—C5	121.52 (14)
N3—C2—N1	117.00 (15)	N1—C6—C5	116.49 (14)
C4—N3—C2—O2	−175.55 (16)	O4—C4—C5—C6	−159.76 (15)
C4—N3—C2—N1	4.2 (2)	N3—C4—C5—C6	25.3 (2)
C6—N1—C2—O2	−178.33 (16)	C2—N1—C6—O6	−177.16 (16)
C6—N1—C2—N3	1.9 (2)	C2—N1—C6—C5	7.3 (2)
C2—N3—C4—O4	166.85 (16)	O8—C5—C6—O6	40.3 (2)
C2—N3—C4—C5	−18.4 (2)	O7—C5—C6—O6	−83.59 (19)
O4—C4—C5—O8	−38.9 (2)	C4—C5—C6—O6	164.28 (15)
N3—C4—C5—O8	146.15 (14)	O8—C5—C6—N1	−144.19 (14)
O4—C4—C5—O7	84.86 (18)	O7—C5—C6—N1	91.92 (17)
N3—C4—C5—O7	−90.07 (16)	C4—C5—C6—N1	−20.2 (2)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O6[i]	0.89 (2)	1.95 (2)	2.8366 (18)	170.7 (19)
N3—H3···O4[ii]	0.81 (2)	2.11 (2)	2.8736 (18)	157 (2)
O7—H7···O2[iii]	0.87 (2)	1.83 (3)	2.6958 (17)	173 (2)
O8—H8···O1W[iii]	0.80 (2)	1.87 (2)	2.6380 (19)	161 (2)
O1W—H1W···O6[iv]	0.92 (3)	2.04 (3)	2.9516 (19)	173 (2)
O1W—H2W···O7[ii]	0.82 (3)	2.28 (3)	2.9973 (19)	147 (3)

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