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4,6-Dihydroxy-4,6-dimethyl-1,3-diazinane-2-thione

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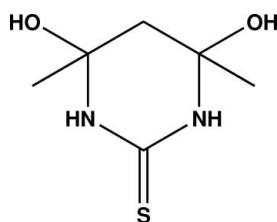
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.029; wR factor = 0.080; data-to-parameter ratio = 17.3.

In the title compound, $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_2\text{S}$, the heterocyclic ring has a sofa conformation. The molecular conformation is stabilized by an intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bond interaction with graph-set motif $S(6)$. In the crystal, molecules are linked by $\text{O}-\text{H}\cdots\text{S}$, $\text{N}-\text{H}\cdots\text{S}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bond interactions, forming an extended two-dimensional framework parallel to the ac plane.

Related literature

For the preparation of pyrimidines by reactions of 1,3-dicarbonyl compounds (e.g. ethyl acetoacetate, acetylacetone) with urea, thiourea, guanidine, see: Barton & Ollis (1979). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For ring conformations, see: Cremer & Pople (1975).



Experimental

Crystal data

 $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ $M_r = 176.24$ Triclinic, $P\bar{1}$ $a = 5.2425$ (4) Å $b = 8.7047$ (6) Å $c = 9.4370$ (7) Å
 $\alpha = 74.812$ (1)°
 $\beta = 88.670$ (1)°
 $\gamma = 79.708$ (1)°
 $V = 408.80$ (5) Å³
 $Z = 2$
Mo $K\alpha$ radiation $\mu = 0.35$ mm⁻¹ $T = 296$ K $0.30 \times 0.20 \times 0.20$ mm

Data collection

 Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.903$, $T_{\max} = 0.934$

 4260 measured reflections
 1760 independent reflections
 1557 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.080$
 $S = 1.00$
 1760 reflections

 102 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1O}\cdots\text{O2}$	0.88	1.98	2.727 (2)	143
$\text{O2}-\text{H2O}\cdots\text{S1}^{\text{i}}$	0.88	2.37	3.249 (1)	173
$\text{N1}-\text{H1N}\cdots\text{S1}^{\text{ii}}$	0.92	2.60	3.414 (1)	149
$\text{N2}-\text{H2N}\cdots\text{O1}^{\text{iii}}$	0.92	2.18	3.074 (2)	164

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5602).

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supplementary materials

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4,6-Dihydroxy-4,6-dimethyl-1,3-diazinane-2-thione

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Comment

The biological activity of pyrimidine derivatives attracts great interest to their synthesis. Their derivatives play important part in the functions of the human body. Pyrimidine structural fragment is included into quite a number of natural substances (nucleic acids, vitamin B1), into synthetic medicinals (barbiturates), into chemotherapeutic preparations (fluorouracil). In preparation of pyrimidines are widely used reactions of 1,3-dicarbonyl compounds (*e.g.* ethyl acetoacetate, acetylacetone) with urea, thiourea, guanidine *etc* (Barton & Ollis, 1979). In the title compound (I), C₆H₁₂N₂O₂S, the heterocyclic ring has a sofa conformation, ($Q_T = 0.459(13)$ Å, $\theta = 127.52(7)^\circ$, $\varphi_2 = 59.54(4)^\circ$, (Cremer & Pople, 1975). The molecular conformation is stabilized by one intramolecular O—H...O hydrogen-bond interaction with set graph motif S(6) (Bernstein, *et al.* 1995). In the crystal the molecules are linked by O—H...S, N—H...S, N—H...O hydrogen-bond interactions forming an extended two-dimensional framework parallel to *ab* plane, Table 1, Fig. 2.

Experimental

On the anhydrous ethanol (40 ml) added 18 gram (0.783 mol) small pieces of metallic sodium and was vigorously stirred until sodium fully reacted with ethanol. Then on the obtained solution was added 10 gram (0.1 mol) of acetylacetone and 7.4 gram (0.1 mol) of thiourea. Reaction mixture was stirred two hours in room temperature. Then 120 ml distilled water added on reaction mixture and neutralized with 5 ml of glacial acetic acid. Precipitated unreacted part of thiourea was filtered off and the obtained filtrate stayed in -10 °C. After two days obtained single crystals of 4,6-dihydroxy-4,6-dimethyltetrahydropyrimidine-2(1*h*)-thione was collected. Yield 6 gram (42%), m.p. 254–255 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 1.32 (s, 6H, 2CH₃), 1.71–2.05 (m, 2H, CH₂), 3.52 (s, 2H, 2OH), 6.16 (s, 1H, NH), 8.67 (s, 1H, NH). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 28.40, 43.63, 78.98, 79.07, 175.23, 175.31

Refinement

All H-atoms were placed in calculated positions [C—H = 0.96 to 0.97 Å, $U_{iso}(H) = 1.2$ to $1.5 U_{eq}(C)$, O—H = 0.88 Å, $U_{iso}(H) = 1.5 U_{eq}(O)$ and N—H = 0.92 Å, $U_{iso}(H) = 1.2 U_{eq}(N)$] and were included in the refinement in the riding model approximation.

Figures

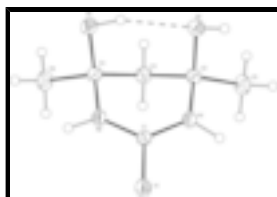


Fig. 1. The structure of (I) showing the atom numbering scheme. The hydrogen bond is showing as dotted line. Displacement ellipsoids are drawn at 30% probability level.

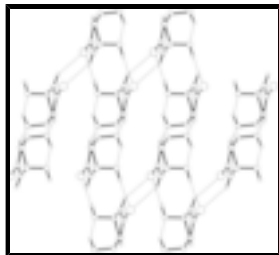


Fig. 2. Part of the crystal structure showing O—H···S; N—H···S & N—H···O hydrogen-bond interactions parallel to *ab* plane. The methyl groups and the H atoms on C3 atom have been omitted for clarity.

4,6-Dihydroxy-4,6-dimethyl-1,3-diazinane-2-thione

Crystal data

$C_6H_{12}N_2O_2S$

$M_r = 176.24$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 5.2425$ (4) Å

$b = 8.7047$ (6) Å

$c = 9.4370$ (7) Å

$\alpha = 74.812$ (1)°

$\beta = 88.670$ (1)°

$\gamma = 79.708$ (1)°

$V = 408.80$ (5) Å³

$Z = 2$

$F(000) = 188$

$D_x = 1.432$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2799 reflections

$\theta = 2.2$ – 28.4 °

$\mu = 0.35$ mm⁻¹

$T = 296$ K

Needle, colourless

$0.30 \times 0.20 \times 0.20$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2003)

$T_{\min} = 0.903$, $T_{\max} = 0.934$

4260 measured reflections

1760 independent reflections

1557 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.012$

$\theta_{\text{max}} = 27.0$ °, $\theta_{\text{min}} = 2.2$ °

$h = -6 \rightarrow 6$

$k = -11 \rightarrow 11$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.080$

$S = 1.00$

1760 reflections

102 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 0.0583P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.36$ e Å⁻³

0 restraints

$$\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	-0.13693 (17)	0.81379 (12)	0.96252 (10)	0.0356 (2)
H1O	-0.2022	0.8234	0.8749	0.053*
O2	-0.14367 (17)	0.74017 (12)	0.69909 (10)	0.0366 (2)
H2O	-0.1954	0.7791	0.6065	0.055*
N1	0.2210 (2)	0.86785 (12)	0.64127 (11)	0.0280 (2)
H1N	0.2746	0.8901	0.5457	0.034*
N2	0.2262 (2)	0.92771 (12)	0.86480 (11)	0.0279 (2)
H2N	0.2349	1.0033	0.9160	0.033*
S1	0.35950 (7)	1.14664 (4)	0.63906 (3)	0.03452 (13)
C1	0.2615 (2)	0.96882 (14)	0.72002 (13)	0.0244 (2)
C2	0.1320 (2)	0.71395 (14)	0.70201 (13)	0.0273 (3)
C3	0.2177 (2)	0.65313 (14)	0.86236 (13)	0.0285 (3)
H3A	0.4050	0.6213	0.8688	0.034*
H3B	0.1433	0.5581	0.9075	0.034*
C4	0.1366 (2)	0.78007 (15)	0.94675 (13)	0.0269 (3)
C5	0.2428 (3)	0.59777 (17)	0.61166 (16)	0.0391 (3)
H5A	0.1869	0.6437	0.5109	0.059*
H5B	0.1827	0.4971	0.6486	0.059*
H5C	0.4287	0.5790	0.6183	0.059*
C6	0.2540 (3)	0.72820 (18)	1.10103 (14)	0.0365 (3)
H6A	0.1999	0.8124	1.1494	0.055*
H6B	0.4397	0.7081	1.0962	0.055*
H6C	0.1966	0.6312	1.1551	0.055*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0260 (4)	0.0510 (6)	0.0316 (5)	-0.0065 (4)	0.0043 (4)	-0.0147 (4)
O2	0.0294 (5)	0.0502 (6)	0.0331 (5)	-0.0117 (4)	-0.0005 (4)	-0.0128 (4)
N1	0.0366 (5)	0.0270 (5)	0.0231 (5)	-0.0107 (4)	0.0039 (4)	-0.0081 (4)
N2	0.0347 (5)	0.0276 (5)	0.0236 (5)	-0.0084 (4)	0.0025 (4)	-0.0091 (4)

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S1	0.0502 (2)	0.02887 (19)	0.02849 (18)	-0.01687 (14)	0.00523 (14)	-0.00838 (13)
C1	0.0229 (5)	0.0250 (6)	0.0256 (6)	-0.0036 (4)	0.0006 (4)	-0.0076 (4)
C2	0.0294 (6)	0.0256 (6)	0.0296 (6)	-0.0077 (5)	0.0026 (5)	-0.0104 (5)
C3	0.0303 (6)	0.0249 (6)	0.0293 (6)	-0.0059 (5)	0.0021 (5)	-0.0048 (5)
C4	0.0252 (6)	0.0309 (6)	0.0242 (6)	-0.0048 (4)	0.0018 (4)	-0.0067 (5)
C5	0.0509 (8)	0.0324 (7)	0.0400 (7)	-0.0099 (6)	0.0072 (6)	-0.0188 (6)
C6	0.0388 (7)	0.0420 (7)	0.0256 (6)	-0.0044 (6)	-0.0037 (5)	-0.0050 (5)

Geometric parameters (\AA , $^\circ$)

O1—C4	1.4237 (14)	C2—C5	1.5185 (17)
O1—H1O	0.8800	C3—C4	1.5211 (17)
O2—C2	1.4223 (15)	C3—H3A	0.9700
O2—H2O	0.8800	C3—H3B	0.9700
N1—C1	1.3365 (15)	C4—C6	1.5166 (17)
N1—C2	1.4660 (15)	C5—H5A	0.9600
N1—H1N	0.9200	C5—H5B	0.9600
N2—C1	1.3359 (15)	C5—H5C	0.9600
N2—C4	1.4658 (15)	C6—H6A	0.9600
N2—H2N	0.9199	C6—H6B	0.9600
S1—C1	1.7001 (12)	C6—H6C	0.9600
C2—C3	1.5161 (17)		
C4—O1—H1O	104.7	C4—C3—H3B	109.1
C2—O2—H2O	107.2	H3A—C3—H3B	107.9
C1—N1—C2	124.46 (10)	O1—C4—N2	109.54 (10)
C1—N1—H1N	117.0	O1—C4—C6	106.20 (10)
C2—N1—H1N	118.0	N2—C4—C6	109.09 (10)
C1—N2—C4	125.07 (10)	O1—C4—C3	112.36 (10)
C1—N2—H2N	118.2	N2—C4—C3	107.21 (9)
C4—N2—H2N	116.1	C6—C4—C3	112.39 (10)
N2—C1—N1	119.07 (11)	C2—C5—H5A	109.5
N2—C1—S1	119.89 (9)	C2—C5—H5B	109.5
N1—C1—S1	121.04 (9)	H5A—C5—H5B	109.5
O2—C2—N1	109.74 (10)	C2—C5—H5C	109.5
O2—C2—C3	106.53 (10)	H5A—C5—H5C	109.5
N1—C2—C3	107.89 (9)	H5B—C5—H5C	109.5
O2—C2—C5	111.08 (10)	C4—C6—H6A	109.5
N1—C2—C5	108.47 (10)	C4—C6—H6B	109.5
C3—C2—C5	113.05 (11)	H6A—C6—H6B	109.5
C2—C3—C4	112.40 (10)	C4—C6—H6C	109.5
C2—C3—H3A	109.1	H6A—C6—H6C	109.5
C4—C3—H3A	109.1	H6B—C6—H6C	109.5
C2—C3—H3B	109.1		
C4—N2—C1—N1	-2.11 (17)	N1—C2—C3—C4	52.12 (13)
C4—N2—C1—S1	178.50 (8)	C5—C2—C3—C4	172.06 (10)
C2—N1—C1—N2	1.77 (18)	C1—N2—C4—O1	-94.88 (13)
C2—N1—C1—S1	-178.85 (9)	C1—N2—C4—C6	149.26 (11)
C1—N1—C2—O2	88.79 (13)	C1—N2—C4—C3	27.30 (15)
C1—N1—C2—C3	-26.90 (16)	C2—C3—C4—O1	68.34 (13)

C1—N1—C2—C5	-149.69 (12)	C2—C3—C4—N2	-52.07 (12)
O2—C2—C3—C4	-65.66 (12)	C2—C3—C4—C6	-171.94 (10)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1O \cdots O2	0.88	1.98	2.727 (2)	143
O2—H2O \cdots S1 ⁱ	0.88	2.37	3.249 (1)	173
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Symmetry codes: (i) $-x, -y+2, -z+1$; (ii) $-x+1, -y+2, -z+1$; (iii) $-x, -y+2, -z+2$.

Fig. 1

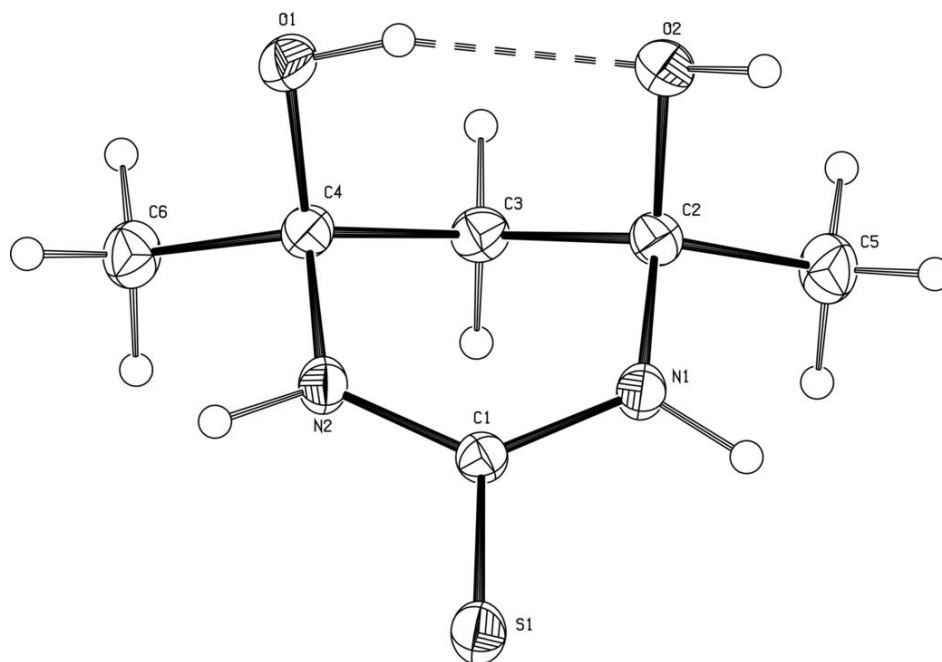


Fig. 2

