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### Oxidation of 5,6-Diamino-1,3-dimethyluracil by Metal Ions: Structure of 1,3,6,8-Tetramethyl-2,4,7,9(1H,3H,6H,8H)-pyrimido[4,5-g]pteridinetetrone

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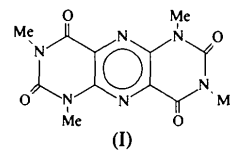
## Abstract

The structure of the title compound, C<sub>12</sub>H<sub>12</sub>N<sub>6</sub>O<sub>4</sub>, consists of independent tricyclic molecules with a central pyrazine ring and terminal pyrimidine rings. The molecular centroid coincides with a crystallographic

inversion centre, leading to a *trans* disposition of the terminal pyrimidine rings. The angle between the central pyrazine ring and the pyrimidine rings is 4.2(3)°, indicating that the molecule is almost planar.

## Comment

Previous work has shown that some *N*-oxide compounds exhibit a number of remarkable photochemical properties (Sako, Nagai & Maki, 1993). These compounds can be prepared by the oxidation of amino or nitroso uracil derivatives with a metal ion and further reaction with NaNO<sub>2</sub> (Yoneda, Sakuma, Ichiba & Shinomura, 1976). With the aim of synthesizing new *N*-oxide compounds of this type, we have investigated the influence of different metal ions on the final product of the oxidative reaction. Since enediamines are readily oxidized, especially when they are conjugated with a carbonyl group, we have studied the oxidative reaction of the enediamine 5,6-diamino-1,3-dimethyluracil with a range of metal ions. It was already known that with Cu<sup>2+</sup> the copper complex of the diamino ligand is obtained, whereas with Fe<sup>3+</sup>, 1,3,6,8-tetramethyl-2,4,5,7(1H,3H,6H,8H)-pyrimido[5,4-g]pteridinetetrone, in which the terminal pyridine rings are *cis*, is formed (Okamoto, Ogura, Kurawasa & Kinoshita, 1984). However, in boiling ethanol, the presence of one equivalent of Au<sup>3+</sup>, Hg<sub>2</sub><sup>2+</sup>, Ag<sup>+</sup> or Tl<sup>3+</sup> gives the title compound, (I), in which the terminal pyrimidine rings are *trans*. Consequently, the type of metal ion used in the reaction is not mechanistically 'innocent' and the course of the reaction depends on the redox potential of the metal ion.



A drawing of the molecule is given in Fig. 1 together with the atomic labelling scheme. Crystals of the title compound contain centrosymmetric tricyclic molecules comprising a central pyrazine ring and terminal pyrimidine rings. Bond lengths and angles in the pyrimidine and pyrazine rings are within the ranges usually found for related pyrimidine and pyrazine derivatives (Otieno, Rettig, Thompson & Trotter, 1989; Fleischer, Jeter & Florian, 1974; Suárez-Varela, Legros, Galy, Colacio, Ruiz, López-González, León & Perona, 1989). The pyrimidine and pyrazine rings are essentially planar, with maximum deviations from the calculated mean plane of 0.084(4) and 0.006(4) Å, respectively. In the pyrimidine rings there are some steric interactions involving the exocyclic groups, as shown by the short C(1)···O(2<sup>i</sup>), O(1)···C(1) and C(2)···O(1) contacts, which are 0.6 Å less than the sum of the

van der Waals radii [symmetry code: (i)  $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$ ]. Because of these steric interactions, the exocyclic groups deviate considerably from the pyrimidine mean plane. Deviations from the plane of C(5), C(6), N(1'), C(3'), N(2') and C(4') range from 0.054 (4) [O(1')] to 0.255 (4) Å [O(2)]. The dihedral angle between the pyrazine and pyrimidine rings is 4.2 (3)°, indicating that the whole molecule is almost planar. Finally, it should be noted that the shortest intermolecular contact distance of 2.880 (2) Å [C(3)( $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$ )...O(1)] indicates that only van der Waals forces are present between molecules.

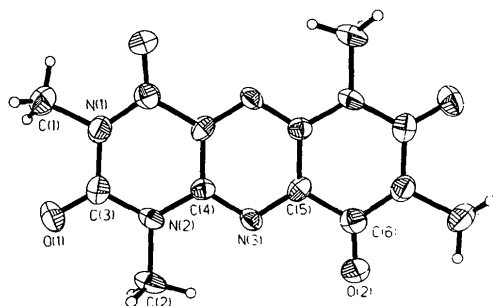


Fig. 1. Drawing of the title compound. Ellipsoids are drawn at the 50% probability level.

3680 measured reflections  
3468 independent reflections  
794 observed reflections  
[ $F > 6.0\sigma(F)$ ]

#### Refinement

Refinement on  $F$   
 $R = 0.0482$   
 $wR = 0.0526$   
 $S = 2.3091$   
794 reflections  
112 parameters  
Only H-atom  $U$ 's refined  
Unit weights applied  
 $(\Delta/\sigma)_{\max} = 0.324$

3 standard reflections  
frequency: 90 min  
intensity decay: 2%

$\Delta\rho_{\max} = 0.37 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.36 \text{ e } \text{Å}^{-3}$   
Extinction correction: none  
Atomic scattering factors  
from *International Tables*  
for *X-ray Crystallography*  
(1974, Vol. IV, Tables  
2.2B and 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
N(3)	0.3338 (3)	0.1541 (8)	0.5171 (3)	0.031 (2)
N(2)	0.2922 (3)	-0.1200 (9)	0.6121 (3)	0.033 (2)
C(5)	0.3107 (4)	0.3342 (11)	0.4607 (4)	0.037 (2)
N(1)	0.1455 (3)	-0.1373 (10)	0.6247 (4)	0.037 (2)
C(4)	0.2723 (4)	0.0680 (11)	0.5553 (4)	0.028 (2)
O(1)	0.2481 (3)	-0.3981 (7)	0.6969 (3)	0.050 (2)
O(2)	0.4457 (3)	0.3441 (8)	0.4155 (3)	0.050 (2)
C(3)	0.2300 (5)	-0.2290 (11)	0.6485 (4)	0.034 (3)
C(6)	0.3767 (4)	0.4326 (13)	0.4155 (4)	0.037 (3)
C(2)	0.3828 (4)	-0.2098 (13)	0.6389 (6)	0.048 (3)
C(1)	0.0802 (5)	-0.2598 (17)	0.6627 (7)	0.061 (4)

Table 2. Selected geometric parameters (Å, °)

N(3)—C(5)	1.337 (8)	C(5)—C(4')	1.398 (9)
N(3)—C(4)	1.330 (9)	N(1)—C(3)	1.398 (9)
N(2)—C(4)	1.375 (8)	N(1)—C(1)	1.477 (11)
N(2)—C(3)	1.387 (9)	N(1)—C(6')	1.372 (9)
N(2)—C(2)	1.476 (8)	O(1)—C(3)	1.219 (8)
C(5)—C(6)	1.476 (10)	O(2)—C(6)	1.215 (8)
C(5)—N(3)—C(4)	116.2 (5)	N(3)—C(4)—N(2)	118.4 (5)
C(4)—N(2)—C(3)	122.1 (5)	N(3)—C(4)—C(5')	121.3 (6)
C(4)—N(2)—C(2)	120.4 (6)	N(2)—C(4)—C(5')	120.3 (6)
C(3)—N(2)—C(2)	117.5 (5)	N(2)—C(3)—N(1)	116.4 (6)
N(3)—C(5)—C(6)	117.9 (6)	N(2)—C(3)—O(1)	121.4 (6)
N(3)—C(5)—C(4')	122.4 (6)	N(1)—C(3)—O(1)	122.1 (7)
C(6)—C(5)—C(4')	119.7 (6)	C(5)—C(6)—O(2)	123.5 (7)
C(3)—N(1)—C(1)	115.1 (6)	C(5)—C(6)—N(1')	114.2 (6)
C(3)—N(1)—C(6')	125.4 (6)	O(2)—C(6)—N(1')	122.3 (7)
C(1)—N(1)—C(6')	118.6 (6)		

Symmetry code: (i)  $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$ .

Data collection: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: MU1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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#### Experimental

5,6-Diamino-1,3-dimethyluracil (0.1 g, 0.59 mmol) and Na[AuCl<sub>4</sub>].*n*H<sub>2</sub>O (0.33 mmol) were suspended in 10 ml of ethanol and the mixture heated at reflux for 1 h. After filtration of metallic gold, the solution was concentrated to 5 ml and allowed to stand at room temperature for one day, whereupon pale yellow crystals formed. Analysis: found C 46.69, H 3.71, N 27.32%; calculated for C<sub>12</sub>H<sub>12</sub>N<sub>6</sub>O<sub>4</sub> C 47.37, H 3.98, N 27.62%. The crystal used for the diffraction analysis was obtained from a dimethylformamide solution kept at 277 K.

#### Crystal data

C<sub>12</sub>H<sub>12</sub>N<sub>6</sub>O<sub>4</sub>  
 $M_r = 304.3$   
Monoclinic  
*C*2/*c*  
 $a = 15.750 (3) \text{ Å}$   
 $b = 6.112 (2) \text{ Å}$   
 $c = 13.704 (3) \text{ Å}$   
 $\beta = 105.98 (3)^\circ$   
 $V = 1268.2 (6) \text{ Å}^3$   
 $Z = 4$   
 $D_x = 1.594 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069 \text{ Å}$   
Cell parameters from 25 reflections  
 $\theta = 12.5\text{--}17.5^\circ$   
 $\mu = 0.12 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
Prism  
 $0.5 \times 0.2 \times 0.15 \text{ mm}$   
Pale yellow

#### Data collection

Stoe Siemens AED 2 diffractometer  
 $\omega/2\theta$  scans  
Absorption correction: none

$R_{\text{int}} = 0.0601$   
 $\theta_{\text{max}} = 32.5^\circ$   
 $h = -2 \rightarrow 23$   
 $k = -2 \rightarrow 9$   
 $l = -20 \rightarrow 20$

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### $\alpha,\alpha$ -allo-Trehalose Trihydrate†

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#### Abstract

The low-temperature X-ray structure of  $\alpha,\alpha$ -allo-trehalose trihydrate ( $\alpha$ -D-allopyranosyl  $\alpha$ -D-allopyranoside trihydrate,  $C_{12}H_{22}O_{11} \cdot 3H_2O$ ) is reported. There are two conformationally similar, but symmetry-independent sugar molecules plus six water molecules in the asymmetric unit. The sugar molecules lack internal crystallographic symmetry because of the relative conformations of the hydroxymethyl substituents and the torsion angles about the glycosidic linkage. The pyranose rings have slightly distorted  ${}^4C_1$  conformations. The sugar and water molecules are linked by many hydrogen bonds to form a complex three-dimensional network. The intramolecular O...O contact distances are larger than those reported in a calcium complex of  $\alpha,\alpha$ -allo-trehalose.

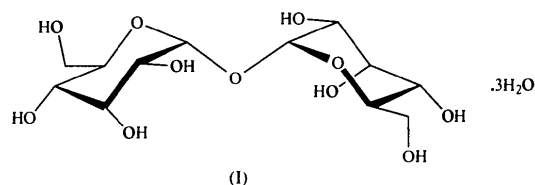
#### Comment

Studies (Birch, Cowell & Eyton, 1970; Lee & Birch, 1975) have shown that isomolar solutions of  $\alpha,\alpha$ -

† Crystal Structures of Trehalose Derivatives, Part 10. For Part 9, see Linden & Lee (1995).

trehalose, its derivatives and the corresponding methyl  $\alpha$ -D-glycopyranoside analogues are equisweet, suggesting that only one half of the disaccharide molecule is actually involved in the interaction with the taste-receptor site. In pyranose structures, the C(4) and C(3) hydroxy groups have been shown (Birch & Lee, 1974; Lindley & Birch, 1975) to be the Shallenberger AH,B glucophore (Shallenberger & Acree, 1967). However, the sweetness of D-galactose (Shallenberger & Acree, 1971),  $\alpha,\alpha$ -galacto-trehalose (Lee & Birch, 1975), D-allose and  $\alpha,\alpha$ -allo-trehalose (Lee, 1994) is only about half that of D-glucose, even though in each of these sugars the group C(4)—OH,C(3)—O acts as the AH,B glucophore. For this reason, we are interested in the three-dimensional molecular structure of these analogues of trehalose.

Furthermore, pyranose sugars and cyclohexitols are known to form strong complexes with cations if the six-membered ring contains an axial-equatorial-axial sequence of hydroxy groups (Angyal, 1974).  $\alpha,\alpha$ -allo-Trehalose has such an arrangement of hydroxy groups in each of its sugar rings. In fact, being a 1,1-linked disaccharide,  $\alpha,\alpha$ -allo-trehalose actually has an axial-equatorial-axial-equatorial-axial sequence of five O atoms and it has been found to complex with  $CaCl_2$  to form the pentadentate complex,  $\alpha,\alpha$ -allo-trehalose. $CaCl_2 \cdot 5H_2O$ , where the cation has an unusual ninefold coordination mode with five O atoms of the sugar and four water molecules (Ollis, James, Angyal & Pojer, 1978). It might be expected that the geometrical constraints induced by the coordination would cause conformational changes in the sugar molecule and it is of interest to compare the conformations of the free and coordinated sugars. Therefore, we now report the X-ray structure of  $\alpha,\alpha$ -allo-trehalose trihydrate, (I).



The asymmetric unit of (I) contains two independent molecules of  $\alpha,\alpha$ -allo-trehalose (molecules A and B) plus six independent water molecules. A comparison of the atomic coordinates of the eight residues in the asymmetric unit, by using the *MISSYM* routine (Le Page, 1987, 1988) of the program *PLATON* (Spek, 1990), confirmed that the molecules were unrelated by any crystallographic symmetry from a space group of higher symmetry. Molecules A and B, with their atomic numbering, are shown in Fig. 1. For comparison purposes, the atomic numbering for molecule B was obtained by adding 20 to the atom numbers of the corresponding atoms in molecule A. Fig. 1 also depicts the correct absolute configuration of the molecules as established by the synthesis of the compound. The two