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1,3-Dimethylisoguanine trihydrate

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Abstract

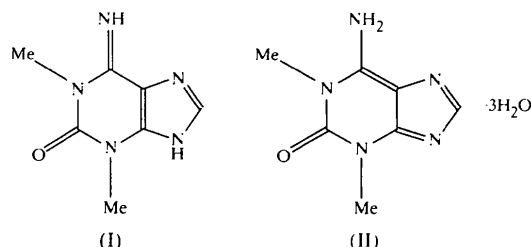
The title compound, isolated from the marine sponge *Amphimedon viridis*, crystallizes with three molecules of water, $C_7H_9N_5O \cdot 3H_2O$. The water molecules are involved in four hydrogen bonds with 1,3-dimethylisoguanine, having N...O distances 3.010 (3), 2.857 (3), 2.762 (3) and 2.810 (3) Å. The molecules are linked together through four water–water hydrogen bonds,

having O...O distances 2.812 (3), 2.739 (2), 2.784 (3) and 2.796 (3) Å.

Comment

Recently Chehade *et al.* (1997) and Mitchell *et al.* (1997) reported the isolation and the identification of a new biologically active purine, 1,3-dimethylisoguanine, (I), from the marine sponge *Amphimedon viridis*. In both communications, the structure was established by analysis of spectroscopic data, mainly NMR and mass spectrometry analysis. However, some discrepancies were observed in the 1H NMR and ^{13}C NMR data reported.

In order to confirm the structure proposed, we have achieved the recrystallization of the compound in methanol and performed the X-ray diffraction analysis. The results show that 1,3-dimethylisoguanine exists in a different tautomeric form, (II), than that previously reported (Chehade *et al.*, 1997; Mitchell *et al.*, 1997).



1,3-Dimethylisoguanine crystallizes with three molecules of water linked through four hydrogen bonds, N13...OW1 [3.010 (3) Å], N13...OW2 [2.857 (3) Å], N7...OW1 [2.762 (3) Å] and N9...OW3 [2.810 (3) Å] (Fig. 1).

The C8=N7 [1.325 (3) Å] and C4=N9 [1.336 (3) Å] bond lengths have a significant double-bond character which is consistent with the canonical form, (II). The C10—N1 [1.475 (3) Å] and C12—N3 [1.458 (3) Å] bond lengths have expected Csp^3 —N values (Allen *et al.*, 1987). The Csp^2 —N bond lengths have normal values except C6—N13 due to a π -electron delocalization. This can be inferred from a shortening of the C4—C5 [1.377 (3) Å] and C6—N13 [1.325 (3) Å] single bonds, and a lengthening of the C5=C6 [1.395 (3) Å] double bond.

The purine system is almost planar [maximum deviation 0.014 (1) Å for C2] and N13, O11, C10 and C12 lie -0.018 (3), 0.037 (2), -0.014 (3) and -0.023 (3) Å, respectively, out of the plane.

The imidazole ring is planar within experimental error and the pyrimidine ring is slightly puckered [maximum deviation 0.007 (1) Å for C2]. The dihedral angle between the planes through the two rings is 0.78 (2)°, similar to those observed in several other purine derivatives (Sletten & Jensen, 1969; Rosen & Hybl, 1971; Rasmussen & Sletten, 1973).

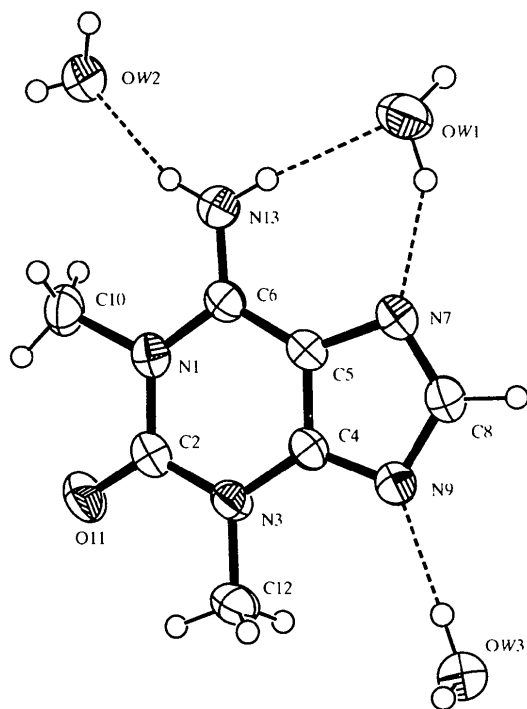


Fig. 1. The molecular structure of 1,3-dimethylisoguanine trihydrate showing 50% probability displacement ellipsoids. Hydrogen bonds are indicated by dashed lines.

The crystalline packing is stabilized by a three-dimensional network of hydrogen bonds involving the water molecules. The N13...OW2, OW2...OW3 and OW3...N9 hydrogen bonds link the molecules in a ribbon that run parallel to the *a* axis. The ribbons are linked in the [010] direction by hydrogen bonds between OW1...OW2 and OW1...OW3. A packing diagram viewed perpendicular to the *xy* plane is shown in Fig. 2. Hydrogen-bonding details are given in Table 2.

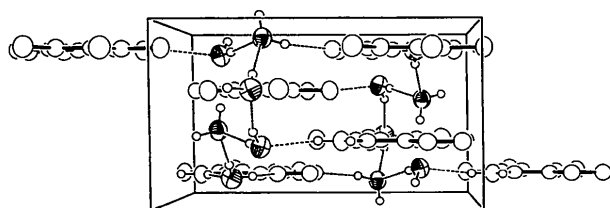


Fig. 2. Packing diagram viewed perpendicular to the *xy* plane. The shaded octants denote water molecules. H atoms not involved in hydrogen bonds are omitted.

Experimental

Suitable single crystals of the title compound were obtained by slow evaporation of a methanol solution.

Crystal data

C₇H₉N₃O·3H₂O
M_r = 233.24

Cu K α radiation
 λ = 1.54180 Å

Monoclinic

*P*2₁/*n*

a = 11.396 (1) Å

b = 6.742 (2) Å

c = 14.142 (1) Å

β = 94.58 (1)°

V = 1083.1 (3) Å³

Z = 4

D_s = 1.430 Mg m⁻³

D_m not measured

Data collection

Enraf-Nonius CAD-4

diffractometer

$\omega/2\theta$ scans

Absorption correction: none

2182 measured reflections

2083 independent reflections

1448 reflections with

I > 2 σ (*I*)

Cell parameters from 25

reflections

θ = 22–35°

μ = 1.01 mm⁻¹

T = 293 (2) K

Needle

0.25 × 0.10 × 0.10 mm

Colorless

Refinement

Refinement on *F*²

$R[F^2 > 2\sigma(F^2)] = 0.048$

wR(*F*²) = 0.161

S = 1.041

2083 reflections

173 parameters

H atoms treated by a

mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0908P)^2$

+ 0.2303*P*]

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

*R*_{int} = 0.043

θ_{max} = 75.02°

h = 0 → 14

k = 0 → 8

l = -17 → 17

2 standard reflections

frequency: 120 min

intensity decay: 1.5%

(Δ/σ)_{max} = 0.012

$\Delta\rho_{max}$ = 0.28 e Å⁻³

$\Delta\rho_{min}$ = -0.35 e Å⁻³

Extinction correction:

SHELXL97 (Sheldrick, 1997)

Extinction coefficient:

0.0022 (7)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

N1—C6	1.371 (3)	N7—C5	1.383 (2)
N1—C2	1.408 (3)	N9—C4	1.336 (3)
N1—C10	1.475 (3)	N9—C8	1.372 (3)
N3—C4	1.372 (2)	C4—C5	1.377 (3)
N3—C2	1.376 (3)	C5—C6	1.395 (3)
N7—C8	1.325 (3)		
C6—N1—C2	124.50 (17)	C2—N3—C12	118.86 (17)
C6—N1—C10	119.76 (18)	N13—C6—N1	120.43 (19)
C2—N1—C10	115.74 (17)	N13—C6—C5	123.15 (19)
C4—N3—C2	120.32 (17)	N1—C6—C5	116.42 (18)
C4—N3—C12	120.82 (18)		

Table 2. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N13—H131...OW1	0.83 (3)	2.18 (3)	3.010 (3)	173 (2)
N13—H132...OW2	0.85 (3)	2.04 (3)	2.857 (3)	162 (2)
OW1—H11...N7	0.91 (2)	1.93 (3)	2.762 (3)	152 (3)
OW1—H12...OW3 ⁱ	0.90 (2)	1.93 (2)	2.812 (3)	167 (3)
OW2—H21...OW3 ⁱⁱ	0.76 (2)	1.98 (2)	2.739 (2)	176 (3)
OW2—H22...OW1 ⁱⁱⁱ	0.88 (2)	1.98 (2)	2.784 (3)	153 (3)
OW3—H31...N9	0.90 (2)	1.91 (2)	2.810 (3)	171 (2)
OW3—H32...OW2 ^{iv}	0.89 (2)	1.93 (2)	2.796 (3)	165 (2)

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

The methyl H atoms were included in calculated positions and refined as riding with C—H distance 0.96 Å and *U*_{iso} 1.5 times the *U*_{eq} of the C atom. The remaining H atoms were located by difference synthesis and refined with *U*_{iso} set at 1.2 times the *U*_{eq} of the parent atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (Fair, 1990). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1180). Services for accessing these data are described at the back of the journal.

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(+)-(2*S*,7*R*,9*R*,10*S*)-2-Ethenyl-4,4,7-trimethyl-3-(toluene-4-sulfonyl)-3,4,4*a*,5,6,7,8,8*a*-octahydro-2*H*-1,3-benzoxazine

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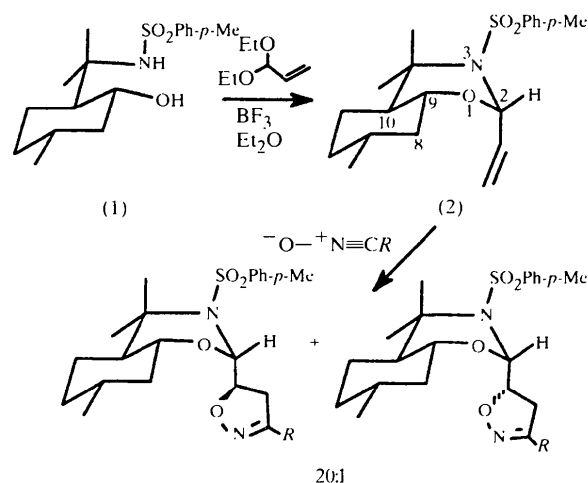
Abstract

The title compound, C₂₀H₂₉NO₃S, was studied in order to determine its absolute configuration, which could not

be determined unambiguously by NMR techniques. The results have shown a boat conformation for the oxazine moiety, with *S* stereochemistry at the stereocentre bearing the alkene function.

Comment

As part of a study aimed at the development of methods for the asymmetric synthesis of 2-isoxazolines, we have been involved in using conformationally rigid *trans*-decaline systems. To this end, we have prepared the title compound, (2), from the condensation of acrolein diethylacetal and (–)-8-tosylaminomenthol, (1), obtained from pulegone (He & Eliel, 1987).



Of some significance was the high level of asymmetric induction observed for the cycloaddition of this compound with nitrile oxides (Lacoste *et al.*, 1998). This finding heightened our interest in understanding the stereochemical bias which leads to olefin facial discrimination. We have carried out extensive NMR experiments but some of the evidence obtained from NOE (nuclear Overhauser effect) experiments was weak. The results were nonetheless inconsistent with the anticipated all-chair *trans* benzoxazine ring system. Also, our NOE results supported a *cis*, but distant, relationship between atoms H9 and H2 and, surprisingly, a possible spatial proximity between the alkene function and protons H10 and H8_{ax}. These results point to a half-chair or a boat conformation for the oxazine ring. Since there were striking structural differences between the *N*-benzyl derivative (Soucy *et al.*, 1998), and compound (2), we felt that the absolute configuration required confirmation by X-ray diffraction analysis.

The crystal structure of (2) belongs to the chiral *P*2₁2₁2₁ space group. A labelled diagram of the molecule is shown in Fig. 1 and selected bond distances and angles are listed in Table 1.

The crystallographic results have shown a boat conformation for the oxazine moiety, with *S* stereochemistry at the C2 stereocentre bearing the alkene function,