

9-(1,3-Anhydro- $\beta$ -D-psicofuranosyl)-  
adenineJarkko Roivainen,<sup>a</sup> Igor Mikhailopulo,<sup>a</sup> Hans Reuter<sup>b\*</sup> and  
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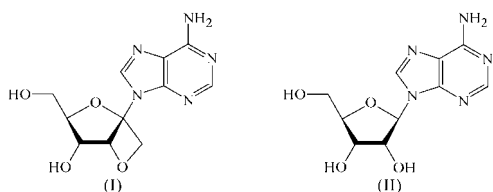
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In the structure of the title compound, C<sub>11</sub>H<sub>13</sub>N<sub>5</sub>O<sub>4</sub>, the glycosidic torsion angle,  $\chi$ , is  $-107.1(2)^\circ$  [nucleic acid nomenclature used throughout the manuscript; IUPAC–IUB Joint Commission on Biochemical Nomenclature (1983). *Eur. J. Biochem.* **131**, 9–15], indicating the *anti* conformation. The furanosyl ring adopts an N-type sugar pucker with the following pseudorotational parameters:  $P_N = 50.5(2)^\circ$  and  $\nu_{\max} = 34.9(1)^\circ$ . The conformation around the C5'–C6' bond is *ap* (*gauche,trans*; *gt*;  $-g$ ), with a torsion angle  $\gamma$  of  $176.28(19)^\circ$ . The 1',2'-oxetane ring is not planar but folded along C3'...C1', with an angle of  $9.6(1)^\circ$ .

## Comment

In recent years, conformationally rigid 1,3-anhydro- $\beta$ -D-psicofuranosyl nucleosides have attracted much attention as constituents of oligonucleotides, the exciting biochemical and biophysical properties of which have been investigated in detail by Chattopadhyaya and co-workers (Bogucka *et al.*, 2005, and references therein); however, structural data have not heretofore been published. Recently, we described the synthesis of the anhydro nucleoside (I) (Roivainen *et al.*, 2002), and deduced its structure from UV and NMR spectroscopic data to be consistent with that shown in the scheme below. Its single-crystal X-ray structure (Fig. 1) was determined in order to confirm this assignment.



As might be expected, the structures of the adenine bases of (I) and adenosine (II) (Lai & Marsh, 1972), which represents the conformationally unrigid counterpart to (I), are very similar. The orientation of the almost planar adenine base of (I) relative to the sugar ring is *anti*, with a glycosyl torsion

angle  $\chi$  (C4–N9–C2'–O5') (IUPAC–IUB Joint Commission on Biochemical Nomenclature, 1983) of  $-107.1(2)^\circ$ , which differs substantially from that of  $-170.1^\circ$  found for adenosine. The furanosyl ring of (I) in the solid state adopts the N-type sugar pucker with the following pseudorotational parameters:  $P_N = 50.5(2)^\circ$  (C5'-*exo*) and  $\nu_{\max} = 34.9(1)^\circ$ . The N conformation was also found in the crystal structure of adenosine, although through somewhat different pseudorotational parameters, *viz.*  $P_N = 7.2^\circ$  (C2'-*exo*/C3'-*endo*;  $^3T_2$ ) and  $\nu_{\max} = 36.0^\circ$  (Lai & Marsh, 1972). It is noteworthy that the insertion of the 1',2'-oxetane ring into adenosine did not lead to an essential change of bond distances within the furanose ring (the deviations are  $\pm 0.007 \text{ \AA}$  for all bonds, but the C5'–C4' bond was shorter by  $0.014 \text{ \AA}$  than the relevant C3'–C4' bond of adenosine). Thus, the C5'–O5' bond is longer than O5'–C2', in accordance with an analogous correlation in most purine nucleosides (Seela *et al.*, 1999). The 1',2'-oxetane ring itself is not planar but folded along C3'...C1', with an angle of  $9.6(1)^\circ$ .

The glycosidic bond length of (I) [C2'–N9 =  $1.438(2) \text{ \AA}$ ] is shorter than that of adenosine by  $0.028 \text{ \AA}$  (Lai & Marsh, 1972). The conformations around the exocyclic C5'–C6' bond in the solid state of (I) and the corresponding C4'–C5' bond of adenosine are similar, *viz.* *ap* (*gauche,trans*; *gt*;  $-g$ ), with torsion angles of  $176.28(19)$  and  $177.0^\circ$ , respectively.

In the extended structure, all molecules are linked together *via* a three-dimensional network of hydrogen bonds. The main intermolecular feature, an eight-membered ring (Fig. 2), consists of hydroxy groups O6' and O4' of two different molecules, and amino group N6 and atom N1 of a third molecule. Whereas the hydroxy groups function as both donors and acceptors of hydrogen bonds, atom N1 serves only as an acceptor and the NH<sub>2</sub>– group as a donor. Three of the four intermolecular hydrogen bonds are found within this ring system. The fourth connects a fourth, exocyclic, molecule with the NH<sub>2</sub> groups inside the eight-membered supramolecular ring. The geometric details of all four hydrogen bonds are given in Table 2. As can be seen from the donor–acceptor distances, which are in the range  $2.633(3)$ – $3.043(2) \text{ \AA}$ , only the hydrogen bond between the hydroxy groups is relatively strong, whereas the other three are weaker.

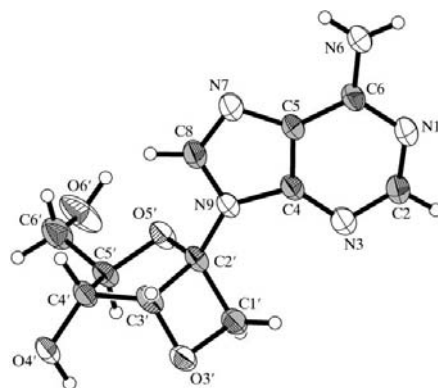
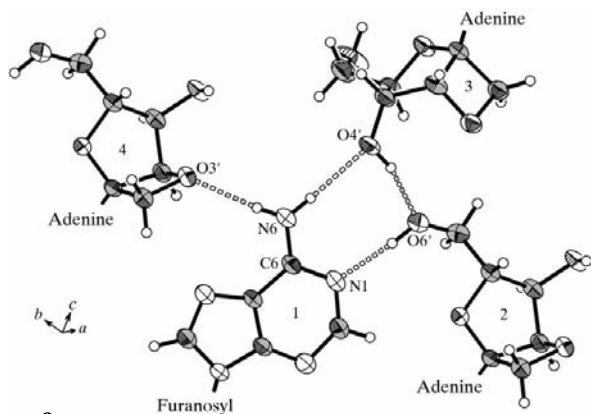


Figure 1

A perspective view of nucleoside (I), showing the atom-numbering scheme, displacement ellipsoids at the 50% probability level for non-H atoms and H atoms as spheres of small arbitrary size.



**Figure 2**  
Part of the crystal structure of nucleoside (I), showing the main structural features of the hydrogen-bonding scheme. [Symmetry codes for the generation of the different molecules are as follows: (1)  $x, y, z$ ; (2)  $2 - x, -\frac{1}{2} + y, 1 - z$ ; (3)  $1 + x, y, 1 + z$ ; (4)  $1 - x, \frac{1}{2} + y, 1 - z$ .]

## Experimental

The synthesis of compound (I) has been described previously (Roivainen *et al.*, 2002). Samples for X-ray analyses were crystallized from a mixture of methanol and 2-propanol. Single crystals suitable for X-ray diffraction were selected directly from the sample as prepared.

### Crystal data

$C_{11}H_{13}N_5O_4$	$Z = 2$
$M_r = 279.26$	$D_x = 1.518 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 5.4154 (5) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$b = 9.8941 (8) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 11.4431 (12) \text{ \AA}$	Plate, colourless
$\beta = 94.970 (14)^\circ$	$0.35 \times 0.22 \times 0.08 \text{ mm}$
$V = 610.82 (10) \text{ \AA}^3$	

### Data collection

Bruker P4 diffractometer	1686 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.023$
2053 measured reflections	$\theta_{\text{max}} = 30.0^\circ$
1878 independent reflections	

### Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
$wR(F^2) = 0.109$	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
$S = 1.04$	Extinction correction: <i>SHELXTL</i>
1878 reflections	Extinction coefficient: 0.037 (8)
186 parameters	Absolute structure: based on known absolute configuration of the chemical entity
H atoms treated by a mixture of independent and constrained refinement	Flack parameter: $-0.7 (13)$
$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 0.0578P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

In the absence of suitable anomalous scattering atoms, refinement of the Flack (1983) parameter led to an inconclusive result. All H atoms were initially found in a difference Fourier synthesis. In order to maximize the data/parameter ratio, H atoms bonded to C atoms were placed in geometrically idealized positions ( $C-H = 0.93-0.98 \text{ \AA}$ ) and constrained to ride on their parent atoms. In order to describe the hydrogen-bonding scheme as well as possible, the positions of the H atoms of the OH and  $NH_2$  groups were first allowed to refine restrained to common O-H and N-H bond lengths (DFIX).

**Table 1**

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

N9—C2'	1.438 (2)	C2'—O5'	1.418 (2)
C1'—O3'	1.463 (3)	C2'—C3'	1.533 (3)
C1'—C2'	1.535 (3)	C3'—O3'	1.451 (3)
O4'—C4'	1.409 (2)	C5'—O5'	1.450 (2)
C8—N9—C2'	122.95 (17)	O3'—C3'—C4'	111.13 (16)
O5'—C2'—N9	106.95 (17)	O3'—C3'—C2'	90.96 (15)
N9—C2'—C3'	119.45 (16)	C3'—O3'—C1'	91.80 (15)
O5'—C2'—C1'	116.03 (16)	O5'—C5'—C4'	104.89 (16)
N9—C2'—C1'	119.60 (17)	C3'—C4'—C5'	102.24 (15)
C3'—C2'—C1'	86.02 (16)	C2'—O5'—C5'	108.25 (15)
C2—N3—C4—N9	$-176.7 (2)$	C3'—C2'—O5'—C5'	$-18.9 (2)$
N7—C5—C6—N6	$-2.2 (4)$	C1'—C2'—O5'—C5'	$75.3 (2)$
N3—C4—N9—C8	$-179.9 (2)$	C6'—C5'—O5'—C2'	$155.3 (2)$
C4—N9—C2'—O5'	$-107.1 (2)$	C4'—C5'—O5'—C2'	$33.1 (2)$
N9—C2'—O5'—C5'	$-148.35 (16)$	C4'—C5'—C6'—O6'	$176.28 (19)$

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N6—H61 $\cdots$ O3' <sup>i</sup>	0.87	2.09	2.932 (3)	166
N6—H62 $\cdots$ O4' <sup>iii</sup>	0.87	2.22	3.043 (2)	159
O4'—H4'O $\cdots$ O6' <sup>iii</sup>	0.91	1.75	2.633 (3)	162
O6'—H6'O $\cdots$ N1' <sup>iv</sup>	0.91	1.87	2.782 (3)	175

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

After refinement, the positions of these H atoms were also constrained (AFIX 3) to ride on their parent atoms.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS* (Siemens, 1996); data reduction, structure solution and refinement, molecular graphics and preparation of publication material: *SHELXTL* (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3039). Services for accessing these data are described at the back of the journal.

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