Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1054). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.
Baker, W. (1941). *J. Chem. Soc.* pp. 662–670.
Bolhuis, F. van & Kiers, C. T. (1978). *Acta Cryst.* B**34**, 1015–1016.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Davidge, H., Davies, A. G., Kenyon, J. & Mason, R. F. (1958). *J. Chem. Soc.* pp. 4569–4573.
Hayashi, S. (1954). *Kumamoto Pharm. Bull.* **1**, 93–101.
Lindberg, B. (1953). *Sven. Kem. Tidskr.* **65**, 113–118.
Mehta, G., Srikrishna, A., Veera Reddy, A. & Nair, M. S. (1981). *Tetrahedron*, **37**, 4543–4559.
Norman, R. O. C. (1978). *Principles of Organic Synthesis*, 2nd edition, pp. 396–397. London: Chapman and Hall.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Shiraishi, S., Ikeuchi, S., Seno, M. & Asahara, T. (1978). *Bull. Chem. Soc. Jpn*, **51**, 921–925.

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1,5-Anhydro-2,3-dideoxy-2-(guanin-9-yl)-D-*arabino*-hexitol

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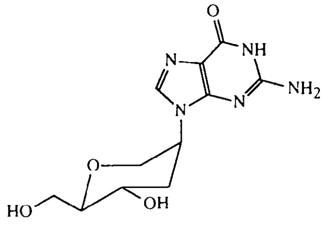
Abstract

The molecular shape of the title compound, $C_{11}H_{15}N_5O_4$, in the crystalline state is characterized by the chair conformation of the sugar moiety and the axial position of the guanine substituent.

Comment

Interest in pyranose nucleosides has grown recently because of the discovery of the interesting antiviral activity of anhydrohexitol nucleosides (Verheggen *et al.*, 1993) and because of their use as building blocks for oligonucleotides (Eschenmoser, 1993; Herdewijn *et al.*, 1994). Oligonucleotides composed of 1,5-anhydrohexitol nucleosides were shown to hybridize strongly with natural DNA and RNA and to be enzymatically stable (Van Aerschot, Verheggen, Hendrix & Herdewijn, 1995). In order to verify the influence of the incorporation of the six-membered anhydrohexitol ring on the nucleoside and oligonucleotide conformation, single-crystal structure determinations of these building units were undertaken. The structure of the title compound, (I), is reported here.



(I)

The title compound was synthesized as described previously (Verheggen *et al.*, 1993) and crystallized in the orthorhombic space group $P2_12_12_1$, containing one molecule in the asymmetric unit. The molecular structure with the labelling scheme is shown in Fig. 1.

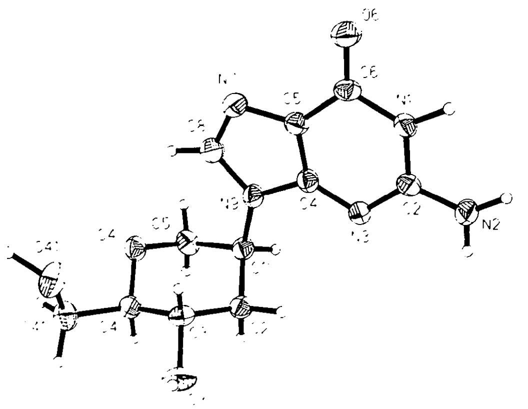


Fig. 1. View of the molecule with atomic labelling, showing 50% probability displacement ellipsoids (*SHELXTL/PC*: Sheldrick 1990). H atoms are shown as small circles of arbitrary radii.

The heterocyclic base points away from the sugar moiety (*anti* orientation), as reflected by the glycosidic torsion angle χ, C5′—C1′—N9—C4 = −167.7 (3)°, which is in the usual range for purine nucleosides (Saenger, 1984). Bond lengths and angles of the base are in the normal range for guanine derivatives (Taylor & Kennard, 1982). The best plane through the guanine ring (r.m.s. deviation 0.024 Å) makes an angle of 82.1 (1)° with the best plane through the anhydrohexitol ring (r.m.s. deviation 0.231 Å).

According to Cremer & Pople (1975), the hexitol ring can be described by a puckering amplitude Q, a phase angle φ and a polar position θ. These values [0.566 (3) Å, 185.6 (1) and 6.1 (1)°, respectively] are close to those of an ideal cyclohexane chair. The substituents at C3′ and C4′ are placed equatorially, in contrast to the base at C1′ which is found to be in the axial position.

The conformation of the molecule is very similar to that observed for the inosine derivative (Verheggen *et al.*, 1995), except for the position of O41′. This is reflected by the orientation about the C4′—C41′ bond which is + synclinal, comparable with that of normal nucleosides given by the torsion angle γ (Saenger, 1984); γ = 49.4 (4)°. For the inosine derivative, an antiperiplanar conformation was observed about the C4′—C41′ bond. This illustrates that the position of the O41′ atom is strongly influenced by intermolecular hydrogen bonds in the crystal lattice.

The crystal packing (Fig. 2, Table 3) is dominated by the formation of Hoogsteen-like GG base pairs, linking molecules related by a screw axis in the b direction. These parallel chains further interact by hydrogen-bonding between the hexose hydroxy groups and guanine, and between the hexose atoms O41′ and O4′.

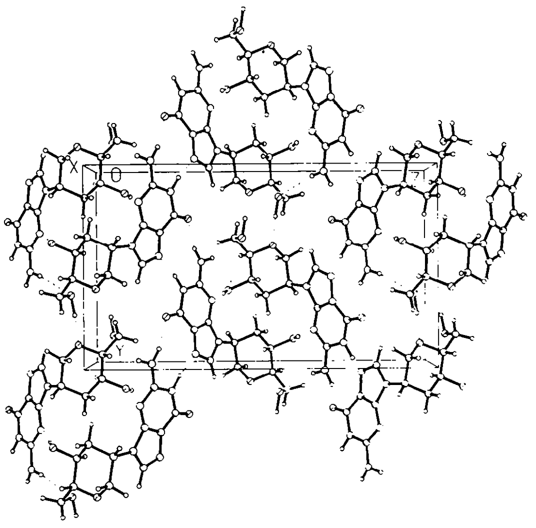


Fig. 2. Molecular packing and hydrogen bonding in the anhydrohexitol nucleoside, (I), as seen in projection down the a axis (*SHELXTL/PC*; Sheldrick, 1990). Dashed lines indicate the hydrogen bonding interactions.

A striking difference between the structures of most pyranose nucleosides and anhydrohexitol nucleosides is the axial orientation of the base moiety in the latter structures. Most pyranose nucleosides have an equatorially oriented base moiety. The axial orientation is also observed in purine and for pyrimidine bases. It is not clear at the moment if this orientation is due to steric factors or to 1,3-*syn* diaxial interactions. It would be interesting to determine if this preferential orientation is also observed in the HNA (hexitol nucleic acid) structure.

Experimental

The title compound was synthesized as described by Verheggen *et al.* (1993) and crystallized by evaporation from water.

Crystal data

$C_{11}H_{15}N_5O_4$
$M_r = 281.28$
Orthorhombic
$P2_12_12_1$
$a = 5.7600 (10)$ Å
$b = 11.043 (2)$ Å
$c = 18.9740 (10)$ Å
$V = 1206.9 (3)$ Å^3
$Z = 4$
$D_x = 1.548$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 20 reflections
$\theta = 24.8–41.4°$
$\mu = 1.021$ mm^{-1}
$T = 289 (2)$ K
Block
0.40 × 0.40 × 0.15 mm
Transparent

Data collection

Siemens *P4-PC* diffractometer
$2\theta/\omega$ scans
Absorption correction: none
1368 measured reflections
1169 independent reflections
1140 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0501$
$\theta_{\rm max} = 54.76°$
$h = -1 \rightarrow 6$
$k = -1 \rightarrow 11$
$l = -1 \rightarrow 20$
3 standard reflections monitored every 97 reflections
intensity decay: 6.86%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0359$
$wR(F^2) = 0.0968$
$S = 1.086$
1169 reflections
242 parameters
H atoms refined with $U_{\rm iso}$
$w = 1/[\sigma^2(F_o^2) + (0.0756P)^2 + 0.0866P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.207$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.179$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0068 (14)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = 0.22 (38)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N1	−0.1440 (4)	0.8792 (2)	0.73440 (11)	0.0269 (6)
C2	−0.3218 (5)	0.9057 (3)	0.68976 (13)	0.0254 (7)
N2	−0.3811 (5)	1.0232 (2)	0.68508 (15)	0.0336 (7)
N3	- 0.4390 (5)	0.8231 (2)	0.65305 (12)	0.0271 (6)
C4	−0.3555 (6)	0.7107 (3)	0.66323 (14)	0.0252 (7)
C5	−0.1676 (6)	0.6761 (3)	0.7040 (2)	0.0271 (7)
C6	−0.0456 (6)	0.7652 (3)	0.74280 (14)	0.0274 (7)
O6	0.1265 (5)	0.7503 (2)	0.78044 (11)	0.0403 (6)

N7	−0.1314 (5)	0.5527 (2)	0.69979 (12)	0.0325 (7)
C8	−0.2937 (6)	0.5135 (3)	0.6576 (2)	0.0322 (8)
N9	−0.4367 (5)	0.6041 (2)	0.63339 (11)	0.0273 (6)
C1′	−0.6362 (6)	0.5932 (3)	0.58475 (15)	0.0271 (7)
C2′	−0.5775 (6)	0.6472 (3)	0.51328 (15)	0.0268 (7)
C3′	−0.4109 (6)	0.5695 (3)	0.47173 (14)	0.0271 (7)
O3′	−0.3880 (5)	0.6204 (2)	0.40286 (11)	0.0391 (6)
C4′	−0.5090 (5)	0.4421 (3)	0.46598 (14)	0.0279 (7)
C41′	−0.3616 (6)	0.3559 (3)	0.4239 (2)	0.0356 (8)
O41′	−0.1237 (4)	0.3582 (2)	0.44553 (13)	0.0439 (6)
O4′	−0.5425 (4)	0.3936 (2)	0.53593 (10)	0.0312 (6)
C5′	−0.7075 (6)	0.4624 (3)	0.5752 (2)	0.0314 (8)

Table 2. *Selected geometric parameters (Å, °)*

N1—C2	1.361 (4)	C8—N9	1.375 (4)
N1—C6	1.389 (4)	N9—C1′	1.479 (4)
C2—N3	1.331 (4)	C1′—C5′	1.513 (5)
C2—N2	1.346 (4)	C1′—C2′	1.519 (4)
N3—C4	1.345 (4)	C2′—C3′	1.509 (5)
C4—C5	1.383 (4)	C3′—O3′	1.429 (4)
C4—N9	1.387 (4)	C3′—C4′	1.521 (4)
C5—N7	1.381 (4)	C4′—O4′	1.444 (4)
C5—C6	1.416 (4)	C4′—C41′	1.505 (5)
C6—O6	1.232 (4)	C41′—O41′	1.431 (5)
N7—C8	1.304 (4)	O4′—C5′	1.427 (4)
C2—N1—C6	125.0 (2)	C8—N9—C4	106.2 (2)
N3—C2—N2	119.8 (3)	C8—N9—C1′	127.9 (2)
N3—C2—N1	124.1 (3)	C4—N9—C1′	125.9 (2)
N2—C2—N1	116.1 (3)	N9—C1′—C5′	111.3 (2)
C2—N3—C4	112.1 (2)	N9—C1′—C2′	110.6 (2)
N3—C4—C5	127.9 (3)	C5′—C1′—C2′	109.2 (2)
N3—C4—N9	127.1 (3)	C3′—C2′—C1′	112.7 (2)
C5—C4—N9	105.0 (3)	O3′—C3′—C2′	108.3 (2)
N7—C5—C4	111.0 (3)	O3′—C3′—C4′	109.5 (2)
N7—C5—C6	129.8 (3)	C2′—C3′—C4′	109.1 (2)
C4—C5—C6	119.2 (3)	O4′—C4′—C41′	109.2 (3)
O6—C6—N1	121.0 (3)	O4′—C4′—C3′	109.1 (2)
O6—C6—C5	127.5 (3)	C41′—C4′—C3′	114.4 (3)
N1—C6—C5	111.5 (3)	O41′—C41′—C4′	112.1 (3)
C8—N7—C5	104.8 (3)	C5′—O4′—C4′	111.8 (2)
N7—C8—N9	113.1 (3)	O4′—C5′—C1′	113.0 (3)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N7^{i}	0.99 (4)	1.83 (4)	2.784 (3)	160 (3)
N2—H2*A*···O6^{i}	1.02 (4)	1.98 (4)	2.978 (4)	164 (3)
N2—H2*B*···O41′^{ii}	0.85 (4)	2.31 (4)	3.132 (4)	161 (3)
O3′—H3′2···N3^{iii}	0.77 (6)	2.10 (6)	2.864 (4)	176 (3)
O41′—H41′···O4′^{iv}	1.12 (4)	1.72 (4)	2.841 (3)	175 (3)

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.

Scattering factors, dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography*, (1992, Vol. C, Tables 6.1.1.4, 4.2.6.8 and 4.2.4.2).

Data collection and data reduction: *XSCANS* (Siemens, 1994). Program used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program used to refine structure and to prepare material for publication: *SHELXL*93 (Sheldrick, 1993) and *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1015). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Eschenmoser, A. (1993). *Proceedings of the R. A. Welch Foundation 37th Conference on Chemical Research: 40 Years of the DNA Double Helix*, October 25–26, Houston, Texas.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Herdewijn, P., De Winter, H., Doboszewski, B., Verheggen, I., Augustyns, A., Hendrix, C., Saison-Behmoaras, T., De Ranter, C. & Van Aerschot, A. (1994). *Carbohydrate Modifications in Antisense Research, Hexopyronosyl-like Oligonucleotides, ACS Symposium Series*, No. 580, pp. 80–99.
Saenger, W. (1984). *Principles of Nucleic Acid Structure*. New York: Springer.
Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1994). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 3209–3212.
Van Aerschot, A., Verheggen, I., Hendrix, C. & Herdewijn, P. (1995). *Angew. Chem.* **107**, 1483–1485.
Verheggen, I., Van Aerschot, A., Toppet, S., Snoeck, R., Janssen, G., Balzarini, J., De Clercq, E. & Herdewijn, P. (1993). *J. Med. Chem.* **36**, 2033–2040.
Verheggen, I., Van Aerschot, A., Van Meervelt, L., Rozenski, J., Wiebe, L., Snoeck, R., Andrei, G., Balzarini, J., Claes, P., De Clercq, E. & Herdewijn, P. (1995). *J. Med. Chem.* **38**, 826–835.

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First Example of a Crystalline Urazole Nucleoside: (1*R*,2*R*)-Urazole-α-D-pyranosyl-2-deoxyriboside

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Abstract

The first example of a crystalline urazole nucleoside has been synthesized from the reaction of D-deoxyribose with urazole and characterized by X-ray crystallography as a single α-pyranoside diastereomer [IUPAC name: 1-(2-deoxy-α-D-*erythro*-pentopyranosyl)-1(*R*),2(*R*),4-triazolidine-3,5-dione, $C_7H_{11}N_3O_5$]. The pyranosyl group and H atom on the two pyramidal hydrazidic N atoms have an *R,R-trans* configuration, and the H atom on the trigonal imidic N atom is coplanar with the ring. Intermolecular hydrogen bonding is