

## Structure of 2',3'-*O*-Isopropylidene-guanosine Hemihydrate

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**Abstract.**  $C_{13}H_{17}N_5O_5 \cdot \frac{1}{2}H_2O$ ,  $M_r = 332.3$ , monoclinic,  $P2_1$ ,  $a = 11.595(2)$ ,  $b = 6.757(3)$ ,  $c = 19.593(4)$  Å,  $\beta = 97.65(2)^\circ$ ,  $V = 1521.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.450$ ,  $D_m = 1.489$  Mg m<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.5418$  Å,  $\mu(Cu K\alpha) = 0.89$  mm<sup>-1</sup>,  $F(000) = 700$ ,  $T = 293$  K,  $R = 0.057$ ,  $wR = 0.077$  for 1832 unique reflections with  $I > 3\sigma(I)$ . There are two crystallographically independent molecules in the asymmetric unit with one water of crystallization. The nucleoside moiety in both molecules has the same conformation: a *syn* base, C(1')-*endo* (*E*) ribose and *trans-gauche* about the C(4')–C(5') bond. The dioxolane ring however assumes different conformations, C(9)*endo*–O(3')*exo* in molecule *A* and O(2')*endo*–C(9)*exo* in molecule *B*. The crystal structure is stabilized by several hydrogen bonds with molecules *A* and *B* exhibiting base pairing. Molecules of type *A*, related by a  $2_1$  screw axis, show partial stacking of the guanine bases.

**Introduction.** The crystal structure analysis of the title compound was undertaken as part of our studies on isopropylidene derivatives of nucleosides (Katti, Seshadri & Viswamitra, 1981; Gautham, Seshadri & Viswamitra, 1983; Gautham, Seshadri, Viswamitra & Salisbury, 1983). Such structures serve as models for studying the flexibility of nucleoside conformations under external cyclic constraints (Viswamitra & Gautham, 1984).

**Experimental.** Needle-shaped crystals were grown from water/acetone solution of the compound (Sigma Chemicals) by slow evaporation. Density measured by flotation in  $CCl_4/C_6H_6$  suggested two molecules in the asymmetric unit. Unit-cell parameters were refined using 25 accurately determined reflections ( $19 \leq \theta \leq 51^\circ$ ) on a CAD-4 diffractometer. Intensity data were collected using  $Cu K\alpha$  radiation,  $\omega$ - $2\theta$  scan, from crystal of dimensions  $1.2 \times 0.06 \times 0.04$  mm to  $(\sin \theta)/\lambda$   $0.588$  Å<sup>-1</sup>. The data were corrected for Lorentz and polarization effects. Absorption corrections were not applied. 1969 reflections were measured for  $-13 \leq h \leq 13$ ,  $0 \leq k \leq 7$  and  $0 \leq l \leq 23$ , of which 1832 were uniquely observed with  $I > 3\sigma(I)$ . Two reflections,  $\bar{2}1\bar{3}$  and  $\bar{2}11$ , monitored periodically during the data collection showed negligible variation indicating instru-

mental and crystal stability. The structure was solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All atoms of molecule *A* were located directly from an *E* map computed with the best set of phases (CFOM = 2.25). Molecule *B* was located using weighted Fourier syntheses. Full-matrix refinement on *F* with anisotropic temperature factors reduced *R* to 0.096. H atoms were fixed from geometric considerations wherever possible and refined isotropically. The refinement of the structure converged at  $R = 0.057$  and  $wR = 0.077$ . The function minimized in the final cycles of refinement was  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1/\sigma^2(F)$ . Maximum  $\Delta/\sigma$  for non-hydrogen atoms = 1.0; residual electron density in the final difference Fourier map within  $\pm 0.34$  e Å<sup>-3</sup>. All calculations were performed using Enraf-Nonius (1983) *Structure Determination Package* on a PDP 11/44 computer.

**Discussion.** The final positional parameters of the non-hydrogen atoms are given in Table 1,\* bond

\* Lists of structure factors, anisotropic thermal parameters, torsion angles, least-squares-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51238 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

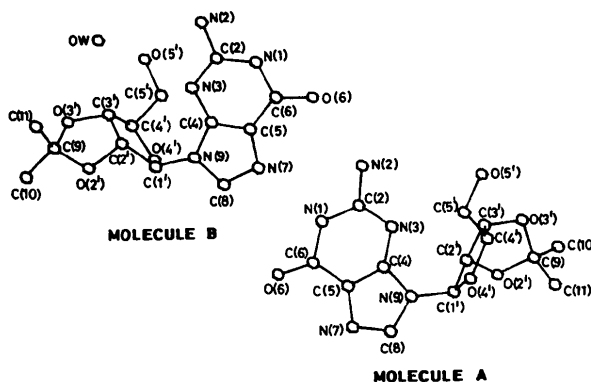


Fig. 1. Structure of molecules *A* and *B*.

Table 1. Final positional parameters and equivalent isotropic thermal parameters

	x	y	z	$B_{eq}(\text{\AA}^2)$
N(1)A	0.6159 (7)	0.499	0.0031 (4)	2.0 (2)
C(2)A	0.6583 (9)	0.484 (2)	0.0707 (5)	2.0 (2)
N(2)A	0.7742 (7)	0.487 (2)	0.0870 (5)	2.7 (2)
N(3)A	0.5934 (7)	0.469 (2)	0.1212 (4)	2.0 (2)
C(4)A	0.4769 (9)	0.473 (2)	0.0963 (5)	1.8 (2)
C(5)A	0.4260 (8)	0.494 (2)	0.0299 (5)	1.9 (2)
C(6)A	0.4970 (9)	0.501 (2)	-0.0234 (5)	1.9 (2)
O(6)A	0.4674 (7)	0.508 (1)	-0.0865 (4)	2.9 (2)
N(7)A	0.3053 (7)	0.495 (2)	0.0268 (4)	2.4 (2)
C(8)A	0.2886 (9)	0.478 (2)	0.0910 (6)	2.2 (2)
N(9)A	0.3896 (7)	0.462 (2)	0.1361 (4)	1.9 (2)
C(1')A	0.3982 (9)	0.443 (2)	0.2096 (5)	2.2 (2)
C(2')A	0.4882 (9)	0.282 (2)	0.2403 (5)	2.4 (2)
O(2')A	0.4424 (7)	0.1597	0.2892 (4)	2.7 (2)
C(3')A	0.5878 (9)	0.396 (2)	0.2803 (6)	1.9 (2)
O(3')A	0.5992 (7)	0.312 (1)	0.3476 (4)	2.6 (2)
C(4')A	0.5488 (9)	0.617 (2)	0.2815 (6)	2.3 (2)
O(4')A	0.4340 (6)	0.626 (1)	0.2417 (4)	2.6 (2)
C(5')A	0.628 (1)	0.762 (2)	0.2491 (7)	3.1 (3)
O(5')A	0.7376 (7)	0.775 (2)	0.2898 (5)	4.3 (2)
C(9)A	0.488 (1)	0.223 (2)	0.3571 (6)	2.9 (3)
C(10)A	0.518 (1)	0.034 (2)	0.4022 (7)	3.8 (3)
C(11)A	0.408 (1)	0.363 (2)	0.3859 (7)	3.9 (3)
N(1)B	1.0962 (7)	0.531 (2)	-0.0669 (4)	2.1 (2)
C(2)B	1.1117 (9)	0.506 (2)	-0.1335 (5)	2.2 (2)
N(2)B	1.2197 (7)	0.515 (2)	-0.1495 (5)	2.9 (2)
N(3)B	1.0255 (7)	0.474 (2)	-0.1835 (4)	2.4 (2)
C(4)B	0.9210 (8)	0.470 (2)	-0.1599 (5)	1.8 (2)
C(5)B	0.8964 (8)	0.503 (2)	-0.0953 (5)	1.8 (2)
C(6)B	0.9893 (9)	0.531 (2)	-0.0420 (5)	2.0 (2)
O(6)B	0.9854 (7)	0.549 (1)	0.0211 (4)	3.2 (2)
N(7)B	0.7783 (7)	0.487 (2)	-0.0926 (4)	2.3 (2)
C(8)B	0.7341 (9)	0.441 (2)	-0.1555 (6)	2.1 (2)
N(9)B	0.8163 (7)	0.429 (1)	-0.1992 (4)	1.9 (2)
C(1')B	0.7924 (9)	0.351 (2)	-0.2689 (6)	2.1 (2)
C(2')B	0.8658 (9)	0.433 (2)	-0.3195 (6)	2.3 (2)
O(2')B	0.7932 (7)	0.454 (2)	-0.3830 (4)	3.8 (2)
C(3')B	0.954 (1)	0.277 (3)	-0.3341 (6)	3.4 (3)
O(3')B	0.935 (1)	0.250 (2)	-0.4060 (5)	6.3 (3)
C(4')B	0.919 (1)	0.088 (2)	-0.2973 (7)	3.3 (3)
O(4')B	0.8137 (7)	0.134 (1)	-0.2683 (4)	3.3 (2)
C(5')B	1.006 (1)	0.014 (2)	-0.2388 (8)	4.5 (3)
O(5')B	1.1155 (7)	-0.026 (2)	-0.2573 (6)	5.6 (3)
C(9)B	0.856 (1)	0.397 (3)	-0.4368 (6)	4.4 (4)
C(10)B	0.772 (2)	0.303 (5)	-0.4925 (9)	9.5 (8)
C(11)B	0.925 (2)	0.560 (4)	-0.4616 (9)	8.2 (6)
OW	1.1755 (9)	0.644 (2)	-0.3318 (6)	5.8 (3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $\frac{1}{3}(a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3))$ .

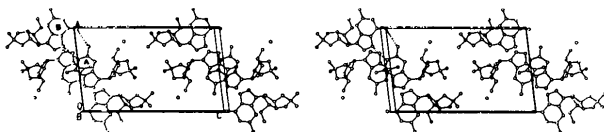


Fig. 2. Stereoview of the crystal structure down the  $b$  axis. Molecules  $A$  and  $B$  show base pairing.  $2_1$  screw-related  $A$  molecules show partial base stacking.

lengths and valence angles are listed in Table 2. Fig. 1 shows a perspective view of the two molecules and a stereoview of the crystal structure is given in Fig. 2.

The guanosine base is essentially planar in molecule  $A$ . The exocyclic  $O(6)$  atom deviates from the ring plane by  $0.09(1)\text{\AA}$ . In the crystallographically independent molecule  $B$ ,  $C(8)$  and  $N(9)$  are displaced from the mean ring plane by  $-0.10(1)\text{\AA}$ . The conformation

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

	Molecule A	Molecule B	Molecule A	Molecule B
N(1)—C(2)	1.35 (1)	1.35 (1)	C(1')—C(2')	1.57 (2)
N(1)—C(6)	1.41 (1)	1.40 (1)	C(1')—O(4')	1.43 (2)
C(2)—N(2)	1.34 (1)	1.33 (1)	C(2')—O(2')	1.42 (1)
C(2)—N(3)	1.32 (1)	1.32 (1)	C(2')—C(3')	1.52 (2)
N(3)—C(4)	1.37 (1)	1.35 (1)	O(2')—C(9)	1.44 (1)
C(4)—C(5)	1.36 (1)	1.35 (1)	C(3')—O(3')	1.43 (1)
C(4)—N(9)	1.37 (1)	1.38 (1)	C(3')—C(4')	1.56 (2)
C(5)—C(6)	1.42 (1)	1.42 (1)	O(3')—C(9)	1.45 (2)
C(5)—N(7)	1.39 (1)	1.38 (1)	C(4')—O(4')	1.45 (1)
C(6)—O(6)	1.24 (1)	1.25 (1)	C(4')—C(5')	1.54 (2)
N(7)—C(8)	1.30 (1)	1.31 (1)	C(5')—O(5')	1.41 (1)
C(8)—N(9)	1.37 (1)	1.37 (1)	C(9)—C(10)	1.56 (2)
N(9)—C(1')	1.44 (1)	1.46 (1)	C(9)—C(11)	1.49 (2)
C(2)A—N(1)A—C(6)A	124.9 (9)		C(2)B—N(1)B—C(6)B	125.4 (8)
N(1)A—C(2)A—N(2)A	117.0 (9)		N(1)B—C(2)B—N(2)B	118.2 (9)
N(1)A—C(2)A—N(3)A	124.6 (9)		N(1)B—C(2)B—N(3)B	123 (1)
N(2)A—C(2)A—N(3)A	118.4 (9)		N(2)B—C(2)B—N(3)B	118.3 (9)
C(2)A—N(3)A—C(4)A	111.3 (9)		C(2)B—N(3)B—C(4)B	111.9 (9)
N(3)A—C(4)A—C(5)A	128 (1)		N(3)B—C(4)B—C(5)B	128.7 (9)
N(3)A—C(4)A—N(9)A	124.6 (9)		N(3)B—C(4)B—N(9)B	125 (1)
C(5)A—C(4)A—N(9)A	106.9 (8)		C(5)B—C(4)B—N(9)B	106.0 (8)
C(4)A—C(5)A—C(6)A	119.2 (9)		C(4)B—C(5)B—C(6)B	118.7 (9)
C(4)A—C(5)A—N(7)A	110 (1)		C(4')B—C(5')B—O(5')B	114 (1)
C(6)A—C(5)A—N(7)A	130.4 (9)		O(2')B—C(9)B—O(3')B	104 (1)
N(1)A—C(6)A—C(5)A	111.4 (8)		O(2')B—C(9)B—C(10)B	108 (1)
N(1)A—C(6)A—O(6)A	119.8 (9)		O(2')B—C(9)B—C(11)B	113 (1)
C(5)A—C(6)A—O(6)A	129 (1)		O(3')B—C(9)B—C(10)B	110 (2)
C(5)A—N(7)A—C(8)A	103.6 (8)		O(3')B—C(9)B—C(11)B	109 (1)
N(7)A—C(8)A—N(9)A	114 (1)		C(4)B—C(5)B—N(7)B	110.9 (8)
C(4)A—N(9)A—C(8)A	105.2 (9)		C(6)B—C(5)B—N(7)B	130 (1)
C(4)A—N(9)A—C(1')A	128.5 (8)		N(1)B—C(6)B—C(5)B	112 (1)
C(8)A—N(9)A—C(1')A	126.3 (9)		N(1)B—C(6)B—O(6)B	119.9 (9)
N(9)A—C(1')A—C(2')A	113.5 (9)		C(5)B—C(6)B—O(6)B	128 (2)
N(9)A—C(1')A—O(4')A	110 (1)		C(5)B—N(7)B—C(8)B	104.4 (9)
C(1')A—C(2')A—O(2')A	107.0 (8)		N(7)B—C(8)B—N(9)B	112.6 (9)
C(1')A—C(2')A—O(2')A	111.9 (8)		C(4)B—N(9)B—C(8)B	106.0 (8)
O(2')A—C(2')A—C(3')A	105 (2)		C(4)B—N(9)B—C(1')B	129.8 (9)
O(2')A—C(2')A—C(3')A	106.0 (8)		C(8)B—N(9)B—C(1')B	123.2 (8)
C(2')A—O(2')A—C(9)A	109.0 (8)		N(9)B—C(1')B—C(2')B	115.8 (9)
C(2')A—C(3')A—O(3')A	104.2 (9)		N(9)B—C(1')B—O(4')B	109.8 (9)
C(2')A—C(3')A—C(4')A	106.9 (9)		C(2')B—C(1')B—O(4')B	105.1 (9)
O(3')A—C(3')A—C(4')A	111 (1)		C(1')B—C(2')B—O(2')B	107.3 (8)
C(3')A—O(3')A—C(9)A	108.0 (8)		C(1')B—C(2')B—C(3')B	110 (2)
C(3')A—C(4')A—O(4')A	106.3 (9)		O(2')B—C(2')B—C(3')B	104.1 (9)
C(3')A—C(4')A—C(5')A	115 (1)		C(2')B—O(2')B—C(9)B	108.8 (9)
O(4')A—C(4')A—C(5')A	108 (1)		C(2')B—C(3')B—O(3')B	105 (2)
C(1')A—O(4')A—C(4')A	113.2 (9)		C(2')B—C(3')B—C(4')B	105 (2)
C(4')A—C(5')A—O(5')A	110 (2)		O(3')B—C(3')B—C(4')B	111 (1)
O(2')A—C(9)A—O(3')A	103.4 (9)		C(3')B—O(3')B—C(9)B	110 (1)
O(2')A—C(9)A—C(10)A	109 (2)		C(3')B—C(4')B—O(4')B	107 (2)
O(2')A—C(9)A—C(11)A	111.5 (9)		C(3')B—C(4')B—C(5')B	115 (2)
C(1')A—C(9)A—C(10)A	106 (1)		O(4')B—C(4')B—C(5')B	107 (2)
O(3')A—C(9)A—C(11)A	113 (1)		C(1')B—O(4')B—C(4')B	111.1 (9)
C(10)A—C(9)A—C(11)A	114 (2)		C(10)B—C(9)B—C(11)B	114 (1)

of the base with respect to the sugar ring is *syn* in both molecules with glycosidic torsion  $\chi(O(4')-C(1')-N(9)-C(4))$  (IUPAC-IUB Joint Commission on Biochemical Nomenclature, 1983) =  $74.1(14)$  and  $77.5(14)^\circ$  respectively. The *syn* conformation has been observed previously in the crystal structure of 2',3'-*O*-isopropylidene-5'-*O*-tosyluridine (Gautham, Seshadri, Viswamitra & Salisbury, 1983).

The furanose ring is  $C(1')$ -*endo* in both molecules. This is an unusual conformation and could be due to the constraint imposed on the ribose by cyclization of its two hydroxyl groups. The displacement of  $C(1')$  from the least-squares plane containing the remaining four atoms is  $0.16(1)[A]$  and  $0.25(1)^\circ[B]$ . The pseudorotation parameters,  $P$  and  $\tau_{m,max}$  are  $-46.0$  and  $11.3^\circ[A]$  and  $-65.2$  and  $17.9^\circ[B]$ . The conformation about the  $C(4')-C(5')$  bond is *trans-gauche* with

$\varphi_{00} = 173.9 (10)^\circ$  and  $\varphi_{0c} = -68.1 (13)^\circ$  for molecule *A* and  $\varphi_{00} = -176.3 (11)^\circ$  and  $\varphi_{0c} = -57.0 (17)^\circ$  for molecule *B*.

In molecule *A* the dioxolane ring pucker is C(9)-*endo*-O(3')-*exo* with  $P_\lambda = -78.15^\circ$  and  $\lambda_{m,max} = 31.46^\circ$ . C(9) and O(3') deviate with respect to the three-atom plane by  $-0.31 (1)$  and  $0.16 (1)$  Å respectively. In molecule *B* the ring assumes O(2')-*endo*-C(9)-*exo* conformation with  $P_\lambda = 71.3^\circ$ ,  $\lambda_{m,max} = 29.9^\circ$  and O(2') and C(9) displaced by  $-0.22 (1)$  and  $0.21 (2)$  Å respectively.

We have earlier reported the structure of the orthorhombic form of the title compound which was grown from Me<sub>2</sub>SO (Mande, Seshadri & Viswamitra, 1988). The conformation of the nucleoside moiety in this structure was *anti*, C(3')-*exo* and *gauche-gauche*, significantly different from that observed here, namely *syn*, C(1')-*endo* and *trans-gauche*.

The two crystallographically independent molecules in the asymmetric unit exhibit base pairing with hydrogen bonds, N(7)A...H(1)-N(1)B (2.85 Å and  $170.87^\circ$ ) and O(6)A...H(12)-N(2)B (2.97 Å and  $150.34^\circ$ ). A similar hydrogen-bonding scheme has been observed in the crystal structure of 9-ethylguanine (Destro, Kistenmacher & Marsh, 1974). The crystal structure is also stabilized by base stacking and three other hydrogen bonds. Screw-related *A* molecules show partial base stacking as shown in Fig. 2 with C(6) and O(6) at a distance of 3.5 Å from the guanine ring plane.

Molecule *B* does not show any base stacking. The bases form sheets parallel to the *ac* plane. Other hydrogen bonds contributing to the stability of the structure are N(2)A-H(12)A...O(6)B (2.95 Å,  $143.83^\circ$ ), N(1)A-H(1)A...N(7)B (2.83 Å,  $164.79^\circ$ ) and OW-H(2)W...O(3')A (2.90 Å,  $154.81^\circ$ ).

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## Structure of 2,5a,9-Trimethyl-5a,6-dihydrotriphenodioxazine

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**Abstract.** C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>,  $M_r = 330.39$ , monoclinic,  $P2_1/c$ ,  $a = 6.690 (1)$ ,  $b = 13.611 (2)$ ,  $c = 19.571 (4)$  Å,  $\beta = 113.53 (2)^\circ$ ,  $V = 1634 (1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.34$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.5418$  Å,  $\mu = 66.0$  mm<sup>-1</sup>,  $F(000) = 696$ , room temperature, final  $R = 0.066$  for 1059 independent reflections and 226 parameters. In spite of the presence of an atomic group in the molecule which exerts a perturbing action, most atoms are in a *quasiplanar* disposition, which allows extended  $\pi$ -electron-charge delocalization.

**Introduction.** In the biosynthesis of ommochromes the reactivity of *o*-aminophenols plays a role of particular importance. Ommochromes are natural pigments widespread through all classes of insects, crustaceans and cephalopods (Butenandt & Schäfer, 1962). Their high photoreactivity under visible light puts these pigments in a crucial position on the scale of photoinduced excitation response. Present knowledge about the role of auxiliary pigments in the primary processes of vision suggests that ommochromes could act as screening or