

and 1.603 (4) Å are very close to values obtained for similar structures (Hamodrakas *et al.*, 1978). Pairs of molecules are probably held together by pairs of N(1)···H—N(2) hydrogen bonds [N(1)···N(2) = 2.917 (7) Å], as shown in Fig. 2 with possible hydrogen bonds indicated by dashed lines.

We wish to thank Dr C. Camoutsis for providing the material, Mr D. Akrigg for assisting us with the calculations and diagrams and the Leeds University Computing Service for the provision of computing facilities.

#### References

- CAMOUSTIS, CH. & CATSOULAKOS, P. (1976). Private communication.  
 CAMOUSTIS, CH. & CATSOULAKOS, P. (1980). *J. Heterocycl. Chem.* **17**, 1135–1136.  
 CATSOULAKOS, P. & CAMOUSTIS, CH. (1980). *J. Heterocycl. Chem.* **17**, 981–983.  
 CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.

- DECLERCQ, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* **A29**, 231–234.  
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.  
 HAMODRAKAS, S. (1974). PhD thesis, Univ. of Leeds.  
 HAMODRAKAS, S., AKRIGG, D., SHELDRIK, B. & CAMOUSTIS, C. (1978). *Acta Cryst.* **B34**, 3426–3428.  
 HAMODRAKAS, S. & FILIPPAKIS, S. E. (1977). *Cryst. Struct. Commun.* **6**, 301–306.  
 HAMODRAKAS, S., FILIPPAKIS, S. E. & SHELDRIK, B. (1977). *Cryst. Struct. Commun.* **6**, 209–214.  
 KÁLMÁN, A., DUFFIN, B. & KUCSMAN, A. (1971). *Acta Cryst.* **B27**, 586–594.  
 LOMBARDINO, J. G. & WISEMAN, E. H. (1971). *J. Med. Chem.* **14**, 973–977.  
 MOTHERWELL, W. D. S. (1978). *PLUTO* 78. Cambridge Crystallographic Data Centre, England.  
 PANAGIOTOPOULOS, N. G. & FILIPPAKIS, S. E. (1980). *Cryst. Struct. Commun.* **9**, 313–320.  
 PANAGIOTOPOULOS, N. G., FILIPPAKIS, S. E. & CATSOULAKOS, P. (1980). *Cryst. Struct. Commun.* **9**, 313–320.  
 PERDIKATIS, B., CATSOULAKOS, P. & FILIPPAKIS, S. E. (1979). *Cryst. Struct. Commun.* **8**, 213–220.  
 SHAKKED, Z. & RABINOVICH, D. (1977). Proceedings of the Fourth European Crystallographic Meeting, Oxford, pp. 142–143.  
 SHELDRIK, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.  
 SIANESI, E., REDAELLI, R., MAGISTRETTI, M. S. & MASSARANI, E. (1973). *J. Med. Chem.* **16**, 1133–1137.

*Acta Cryst.* (1983). **C39**, 745–747

## Structure of 8,5'-Anhydro-8-hydroxy-9-β-D-ribofuranosyladenine (8,5'-O-cyclo-A) Monohydrate, C<sub>10</sub>H<sub>11</sub>N<sub>5</sub>O<sub>4</sub>·H<sub>2</sub>O

BY SHIGETOSHI SUGIO, HIROSHI MIZUNO, KUNIHIRO KITAMURA, KENSAKU HAMADA, MORIO IKEHARA AND KEN-ICHI TOMITA

*Faculty of Pharmaceutical Sciences, Osaka University, Yamadaoka, Suita, Osaka 565, Japan*

(Received 8 January 1983; accepted 1 February 1983)

**Abstract.**  $M_r = 283.3$ , monoclinic,  $P2_1$ ,  $a = 32.747$  (6),  $b = 4.975$  (1),  $c = 8.485$  (1) Å,  $\beta = 121.22$  (1)°,  $V = 1182.1$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_m$  (floatation in benzene/CCl<sub>4</sub>) = 1.571 (2),  $D_x = 1.592$  Mg m<sup>-3</sup>, graphite-monochromated Cu  $K\alpha$ ,  $\lambda = 1.54173$  Å,  $\mu(\text{Cu } K\alpha) = 1.13$  mm<sup>-1</sup>,  $F(000) = 592$ , final  $R = 0.048$  for 2054 reflections (measured at 293 K). The two independent molecules in the asymmetric unit take very similar conformations: *anti* around the glycosyl bond and C(4')-endo-O(1')-exo sugar puckering. The crystal structure is stabilized by the hydrogen-bonding network.

**Introduction.** The glycosyl torsion angle in cyclonucleosides and cyclonucleotides is determined by a covalent bond between the base and the furanose ring. Such an imposed restriction about the particular bond is suitable for comparison of the molecular conformation in the crystal with that in solution. To this aim, crystal

structures of 8,5'-cyclonucleosides have been solved by X-ray analysis. However, these molecules possessed either an isopropylidene or an ethoxymethylidene group in the sugar moiety. In the present molecule, which was synthesized, such an additional group is not involved and the net effect imposed by the fused C(8)–O(5') linkage could be estimated.

**Experimental.** Colorless prismatic crystals from aqueous solution by slow evaporation at room temperature; cell dimensions by a least-squares refinement of the  $2\theta$  values of 25 reflections with  $2\theta = 27$ –47°; crystal 0.08 × 0.08 × 0.4 mm, Rigaku–Denki AFC-5 automated diffractometer,  $2\theta_{\text{max}} = 128^\circ$ ,  $\theta$ – $2\theta$  scan technique; of 2216 unique reflections,  $-38 \leq h \leq 32$ ,  $0 \leq k \leq 5$  and  $0 \leq l \leq 9$ , 2059 had  $|F_o| > 3\sigma(F_o)$ ; three standard reflections, 10,0,0, 020 and 002, monitored after every 100 reflections, showed less than 2 (1)% intensity fluctuation throughout data collection;

intensities corrected for Lorentz and polarization factors but not for absorption; direct methods [*MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978)]; positional and anisotropic thermal parameters for all non-H atoms were refined by block-diagonal least squares (*HBL5 V*: Ashida, 1979),  $\sum w(|F_o| - k|F_c|)^2$  minimized with  $w = [\sigma^2(F_o) + 0.04124|F_o| + 0.0014|F_o|^2]^{-1}$ ; all H atoms except for those of the water molecules were located on a difference Fourier map; their positional and isotropic thermal parameters (fixed to  $3.0 \text{ \AA}^2$ ) were not included in the refinement; five intense low-angle reflections, 303, 001, 002, 201 and 301, were affected by secondary extinction and excluded; final *R* and *wR* for 2054 reflections = 0.048 and 0.068, respectively, *S* for 362 parameters (nine for each non-H atom and two for overall scale and thermal parameters) = 0.952; the mean and the maximum values of the ratios of least-squares shift to error in the final refinement cycle were 0.006 and 0.026; maximum and minimum heights on final difference Fourier maps were 0.23 and  $-0.30 \text{ e \AA}^{-3}$  and no other significant features were observed; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); ACOS 700 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Table 1. Final positional and equivalent isotropic thermal parameters for the non-H atoms with their estimated standard deviations in parentheses

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
N(1) <i>A</i>	0.2266 (1)	-0.1143 (9)	0.2671 (5)	2.82 (3)
C(2) <i>A</i>	0.1954 (1)	0.0729 (11)	0.1655 (6)	3.12 (4)
N(3) <i>A</i>	0.1609 (1)	0.1863 (8)	0.1856 (5)	2.87 (4)
C(4) <i>A</i>	0.1629 (1)	0.0898 (9)	0.3379 (5)	2.24 (4)
C(5) <i>A</i>	0.1947 (1)	-0.0945 (9)	0.4608 (5)	2.06 (3)
C(6) <i>A</i>	0.2277 (1)	-0.2070 (9)	0.4190 (5)	2.39 (4)
N(7) <i>A</i>	0.1862 (1)	-0.1447 (8)	0.6028 (4)	2.27 (3)
C(8) <i>A</i>	0.1487 (1)	0.0043 (9)	0.5565 (5)	2.11 (4)
N(9) <i>A</i>	0.1328 (1)	0.1532 (8)	0.4015 (4)	2.34 (3)
N(6) <i>A</i>	0.2592 (1)	-0.3958 (10)	0.5202 (5)	3.12 (4)
O(1') <i>A</i>	0.0860 (1)	0.5111 (6)	0.4044 (4)	2.54 (3)
C(1') <i>A</i>	0.0870 (1)	0.2969 (9)	0.2982 (5)	2.12 (4)
C(2') <i>A</i>	0.0452 (1)	0.1118 (9)	0.2577 (5)	2.32 (4)
C(3') <i>A</i>	0.0302 (1)	0.2104 (10)	0.3943 (5)	2.78 (4)
C(4') <i>A</i>	0.0705 (1)	0.3960 (10)	0.5202 (5)	2.62 (4)
C(5') <i>A</i>	0.1115 (2)	0.2642 (10)	0.6878 (6)	3.13 (5)
O(2') <i>A</i>	0.0071 (1)	0.1458 (7)	0.0715 (4)	3.14 (3)
O(3') <i>A</i>	-0.0125 (1)	0.3652 (10)	0.3026 (5)	4.53 (4)
O(5') <i>A</i>	0.1260 (1)	0.0042 (6)	0.6510 (4)	2.57 (3)
N(1) <i>B</i>	0.2732 (1)	0.3161 (9)	-0.1408 (4)	2.94 (4)
C(2) <i>B</i>	0.3053 (1)	0.1244 (11)	-0.1137 (5)	2.92 (4)
N(3) <i>B</i>	0.3388 (1)	0.0153 (9)	0.0411 (4)	2.76 (3)
C(4) <i>B</i>	0.3371 (1)	0.1103 (8)	0.1860 (5)	2.15 (4)
C(5) <i>B</i>	0.3054 (1)	0.2968 (9)	0.1813 (5)	2.24 (4)
C(6) <i>B</i>	0.2726 (1)	0.4075 (10)	0.0104 (5)	2.49 (4)
N(7) <i>B</i>	0.3145 (1)	0.3470 (8)	0.3590 (4)	2.33 (3)
C(8) <i>B</i>	0.3512 (1)	0.2002 (8)	0.4634 (5)	1.97 (3)
N(9) <i>B</i>	0.3673 (1)	0.0478 (8)	0.3692 (4)	2.22 (3)
N(6) <i>B</i>	0.2406 (1)	0.5978 (9)	-0.0179 (4)	2.94 (4)
O(1') <i>B</i>	0.4140 (1)	-0.3095 (6)	0.5597 (4)	2.65 (3)
C(1') <i>B</i>	0.4132 (1)	-0.0943 (9)	0.4507 (5)	2.26 (4)
C(2') <i>B</i>	0.4552 (1)	0.0901 (9)	0.5785 (6)	2.37 (4)
C(3') <i>B</i>	0.4703 (1)	-0.0091 (10)	0.7728 (5)	2.76 (4)
C(4') <i>B</i>	0.4297 (1)	-0.1937 (9)	0.7389 (5)	2.52 (4)
C(5') <i>B</i>	0.3890 (1)	-0.0574 (11)	0.7434 (6)	3.02 (4)
O(2') <i>B</i>	0.4931 (1)	0.0554 (7)	0.5437 (4)	3.12 (4)
O(3') <i>B</i>	0.5124 (1)	-0.1661 (10)	0.8523 (4)	4.61 (5)
O(5') <i>B</i>	0.3739 (1)	0.1991 (6)	0.6467 (3)	2.56 (3)
O <sub>W1</sub>	0.1036 (1)	0.6485 (10)	-0.0242 (6)	5.44 (5)
O <sub>W2</sub>	0.3962 (1)	-0.4492 (10)	0.0598 (6)	5.37 (6)

**Discussion.** The final atomic coordinates with their estimated standard deviations are given in Table 1.\* All the bond distances and angles shown in Table 2 are in good agreement with those of related cyclonucleosides. In spite of the fused C(8)—O(5') linkage, C(8)—N(9)—C(1') and C(4)—N(9)—C(1') are not so different from those of adenosine (Lai & Marsh, 1972).

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38376 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) for the non-H atoms

	Molecule <i>A</i>	Molecule <i>B</i>
N(1)—C(2)	1.320 (7)	1.348 (7)
N(1)—C(6)	1.352 (7)	1.371 (7)
C(2)—N(3)	1.351 (7)	1.316 (7)
N(3)—C(4)	1.348 (6)	1.346 (6)
C(4)—C(5)	1.374 (7)	1.376 (7)
C(4)—N(9)	1.383 (6)	1.378 (6)
C(5)—C(6)	1.417 (7)	1.395 (7)
C(5)—N(7)	1.391 (6)	1.400 (6)
C(6)—N(6)	1.328 (7)	1.338 (7)
N(7)—C(8)	1.308 (6)	1.288 (6)
C(8)—N(9)	1.357 (6)	1.388 (6)
C(8)—O(5')	1.347 (6)	1.332 (5)
N(9)—C(1')	1.471 (6)	1.471 (6)
O(1')—C(1')	1.406 (6)	1.406 (6)
O(1')—C(4')	1.439 (6)	1.439 (6)
C(1')—C(2')	1.535 (6)	1.537 (7)
C(2')—C(3')	1.554 (7)	1.554 (7)
C(2')—O(2')	1.427 (6)	1.427 (6)
C(3')—C(4')	1.508 (7)	1.517 (7)
C(3')—O(3')	1.423 (7)	1.415 (7)
C(4')—C(5')	1.509 (7)	1.511 (7)
C(5')—O(5')	1.466 (6)	1.458 (7)
C(2)—N(1)—C(6)	119.5 (5)	117.6 (5)
N(1)—C(2)—N(3)	128.9 (5)	129.5 (5)
C(2)—N(3)—C(4)	110.2 (4)	111.0 (4)
N(3)—C(4)—C(5)	127.3 (4)	126.8 (4)
N(3)—C(4)—N(9)	127.1 (4)	127.3 (4)
C(5)—C(4)—N(9)	105.6 (4)	105.9 (4)
C(4)—C(5)—C(6)	116.8 (4)	117.3 (4)
C(4)—C(5)—N(7)	111.4 (4)	110.7 (4)
C(6)—C(5)—N(7)	131.8 (4)	132.0 (5)
N(1)—C(6)—C(5)	117.2 (4)	117.7 (5)
N(1)—C(6)—N(9)	119.0 (5)	117.1 (5)
C(5)—C(6)—N(9)	123.7 (5)	125.2 (5)
C(5)—N(7)—C(8)	102.4 (4)	104.0 (4)
N(7)—C(8)—N(9)	115.5 (4)	114.3 (4)
N(7)—C(8)—O(5')	122.9 (4)	124.2 (4)
N(9)—C(8)—O(5')	121.6 (4)	121.5 (4)
C(4)—N(9)—C(8)	105.1 (4)	105.2 (4)
C(4)—N(9)—C(1')	126.2 (4)	126.9 (4)
C(8)—N(9)—C(1')	127.2 (4)	126.3 (4)
C(1')—O(1')—C(4')	105.6 (3)	105.3 (3)
N(9)—C(1')—O(1')	110.0 (3)	109.9 (4)
N(9)—C(1')—C(2')	111.0 (3)	111.6 (4)
O(1')—C(1')—C(2')	106.5 (4)	106.6 (4)
C(1')—C(2')—C(3')	103.5 (4)	103.8 (4)
C(1')—C(2')—O(2')	110.1 (4)	109.7 (4)
C(3')—C(2')—O(2')	110.9 (4)	110.6 (4)
C(2')—C(3')—C(4')	102.9 (4)	103.2 (4)
C(2')—C(3')—O(3')	111.3 (4)	112.4 (4)
C(4')—C(3')—O(3')	107.9 (4)	107.4 (4)
O(1')—C(4')—C(3')	104.4 (4)	103.8 (4)
O(1')—C(4')—C(5')	111.1 (4)	111.6 (4)
C(3')—C(4')—C(5')	115.2 (4)	114.9 (4)
C(4')—C(5')—O(5')	114.3 (4)	115.2 (4)
C(8)—O(5')—C(5')	117.8 (4)	118.8 (4)

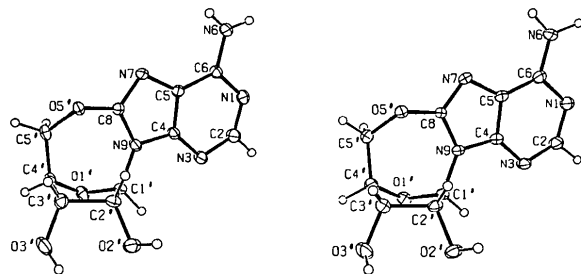


Fig. 1. ORTEP drawings (Johnson, 1976) of molecules *A* and *B*.

Molecules *A* and *B* in an asymmetric unit possess quite similar conformations as shown in Fig. 1. The glycosyl torsion angle corresponds to the *anti* conformation  $\{\chi_{CN} = 67.4 (6)^\circ [68.2 (6)^\circ]$ ; hereinafter, values shown in brackets are for molecule *B*, and is slightly larger than that found in other 8,5'-cyclonucleosides ( $51$ – $64^\circ$ ).

In all 8,5'-cyclonucleosides, the O(5') or S atom is located over the center of the furanose ring, the so-called *endo* form, and the extra seven-membered ring formed by cyclization takes the chair conformation. This feature is also observed in 6,5'- and 2,5'-cyclopyrimidine nucleosides (Yamagata, Fukumoto, Fujii, Tomita, Maruyama & Honjo, 1983).

The furanose ring is in the typical twist conformation C(4')-*endo*-O(1')-*exo* with  $P = 255^\circ [254^\circ]$  and  $\tau_m = 42^\circ [42^\circ]$  as defined by Altona & Sundaralingam (1972). This puckering mode is similar but not identical to those of other related compounds because of the small distortions caused by the additional ring fusion in the sugar moiety or of relaxations caused by replacement of the O atom by S. For instance, markedly smaller  $\tau_m$  values, 35 and  $32^\circ$ , are observed for 8,5'-*S*-cyclo(2',3'-ethoxymethylidene)adenosine (Tanaka, 1981) and for 8,5'-*S*-cyclo(2',3'-isopropylidene)adenosine (Tomita, Nishida, Fujiwara & Ikehara, 1970; Tanaka, 1981) and somewhat larger  $P$  values, 264 and  $259^\circ$ , are observed for 8,5'-*O*-cyclo-7-bromo(2',3'-isopropylidene)tubercidin (Asai, Anzai, Suzuki & Iwasaki, 1973) indicating the O(1')-*exo* character due to the effect of the isopropylidene group.

The crystal structure is stabilized by the extensive hydrogen-bonding network as shown in Fig. 2. All four H atoms attached to O and N atoms in each molecule are involved in intermolecular hydrogen bonding. The interbase reverse-Hoogsteen-type hydrogen bonding forms infinite chains which are commonly observed, for example, in deoxyadenosine (Watson, Sutor & Tollin, 1965), 9-methyladenosine (Stewart & Jensen, 1964),

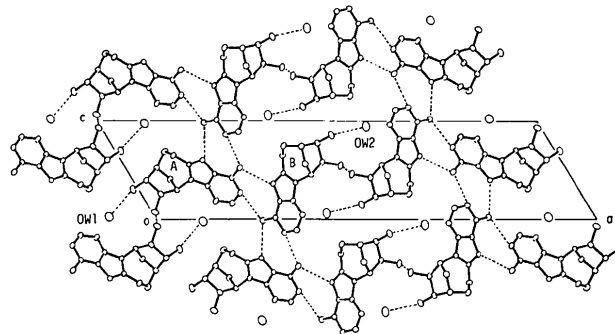


Fig. 2. Molecular packing viewed down the *b* axis. Dashed lines indicate the hydrogen bonding.

2'-*O*-methyladenosine (Prusiner & Sundaralingam, 1976) and 8,2'-cycloadenosine (Neidle, Taylor & Cowling, 1979). The hydrogen-bonding distances observed are N(6)-H...N(1) {3.028 (7) Å [3.043 (7) Å]}, N(6)-H...N(7) {3.059 (6) Å [3.038 (6) Å]}, O(2')-H...O(2') {2.700 (5) Å [2.700 (6) Å]} and O(3')-H...OW {2.888 (7) Å [2.893 (8) Å]}. Each water molecule participates as a hydrogen-bond acceptor but not as a donor.

#### References

- ALTONA, C. & SUNDARALINGAM, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.
- ASAI, K., ANZAI, K., SUZUKI, S. & IWASAKI, H. (1973). *Chem. Lett.* pp. 1197–2000.
- ASHIDA, T. (1979). *HBL5 V, The Universal Crystallographic Computing System—Osaka*, Library of Programs, Computing Center of Osaka Univ.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–73. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- LAI, T. F. & MARSH, R. E. (1972). *Acta Cryst.* **B28**, 1982–1989.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J. P. & WOOLFSON, M. M. (1978). *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs of York, England, and Louvain, Belgium.
- NEIDLE, S., TAYLOR, G. L. & COWLING, P. C. (1979). *Acta Cryst.* **B35**, 708–712.
- PRUSINER, P. & SUNDARALINGAM, M. (1976). *Acta Cryst.* **B32**, 161–169.
- STEWART, R. F. & JENSEN, L. H. (1964). *J. Chem. Phys.* **40**, 2071–2075.
- TANAKA, K. (1981). DPhil. Thesis, Osaka Univ.
- TOMITA, K., NISHIDA, T., FUJIWARA, T. & IKEHARA, M. (1970). *Biochem. Biophys. Res. Commun.* **41**, 1043–1047.
- WATSON, D. G., SUTOR, D. J. & TOLLIN, P. (1965). *Acta Cryst.* **19**, 111–124.
- YAMAGATA, Y., FUKUMOTO, S., FUJII, S., TOMITA, K., MARUYAMA, T. & HONJO, M. (1983). *Acta Cryst.* **C39**, 407–409.