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Structural Studies of Pyrimidine Cyclonucleoside Derivatives. X.* Structure of 5′-*O*-Acetyl-6,3′-anhydro-2′-deoxy-6-methyl-1-β-D-xylofuranosyluracil

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Abstract. $C_{12}H_{14}N_2O_5$, $M_r = 266{\cdot}3$, monoclinic, $P2_1$, $a = 8{\cdot}312\,(1)$, $b = 5{\cdot}559\,(1)$, $c = 13{\cdot}048\,(2)$ Å, $\beta = 98{\cdot}50\,(2)^\circ$, $V = 596{\cdot}2\,(2)$ Å^3, $Z = 2$, $D_m = 1{\cdot}480\,(1)$, $D_x = 1{\cdot}483$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}68$ mm^{-1}, $F(000) = 280$, $T = 293$ K, $R = 0{\cdot}049$ for 1055 independent observed reflections. The glycosidic torsion angle, $\chi_{\text{CN}}[\text{O}(4')\text{—C}(1')\text{—N}(1)\text{—C}(2)] = 265{\cdot}3\,(5)^\circ$, is in the *anti* range, and the furanose conformation is E_2. The orientation of O(5′) is *trans–gauche* (*gauche* ≡ –synclinal). No base stacking is observed. The molecules form infinite columns along the *b* axis by N(3)—H···O(4) hydrogen bonds between adjacent molecules related by twofold screw symmetry.

Introduction. As described in the preceding paper (Yamagata, Okabe, Tomita, Shuto, Inoue & Ueda, 1985), C-bridged cyclonucleosides provide important information about the relationship between glycosidic torsion angles and CD spectra (Ueda, Shuto, Sano, Usui & Inoue, 1982; Ueda; Usui, Shuto & Inoue, 1984; Ueda & Shuto, 1984). In this paper we deal with the structure determination of the title compound abbreviated as 6,3′-*C*-cyclo-U, as the second member of a series of C-bridged pyrimidine cyclonucleosides. 6,3′-*C*-Cyclo-U is the first example of a pyrimidine cyclonucleoside with a covalent bond between C(3′) in the sugar ring and C(6) in the normal pyrimidine base determined by X-ray diffraction.

Experimental. Title compound synthesized as described in a previous paper (Ueda & Shuto, 1984) and crystallized from methanol solution as colorless prisms; density by flotation in C_6H_6–CCl_4 mixture; crystal 0·15 × 0·25 × 0·6 mm, Rigaku automatic four-circle diffractometer, ω–2θ scanning technique, $2\theta_{\max} = 125^\circ$, graphite-monochromatized Cu $K\alpha$ radiation; unit-cell dimensions by least-squares procedure based on 2θ values ($20 < 2\theta < 47^\circ$) of 24 reflections; intensity fluctuation monitored periodically by three reflections ($\bar{5}00$, 020, 008): <2%; 1061 independent reflections ($-9 \le h \le 9$, $0 \le k \le 6$, $0 \le l \le 14$), 1055 observed with $F_o \ne 0$; Lorentz and polarization corrections; structure solved by direct interpretation of Patterson function: peaks around origin indicated orientation of uracil and cyclic six-membered rings, atomic positions determined by packing consideration; full-matrix least-squares method with anisotropic temperature factors for all non-H atoms; all H atoms located on difference Fourier map; final refinement including H atoms with isotropic temperature factors reduced R to 0·049 ($wR = 0{\cdot}053$, $S = 7{\cdot}59$);† function minimized $\sum w(|F_o| - k|F_c|)^2$, where $w = 1/\sigma^2(F_o)$ and k is the scale factor; largest peaks in final difference Fourier map: 0·22 e Å^{-3}; $(\Delta/\sigma)_{\text{av}} = 0{\cdot}02$ and $(\Delta/\sigma)_{\max} = 0{\cdot}08$, for non-H atoms; scattering factors from *International Tables for X-ray Crystallography* (1974); program system *UNICS* (1979) on an ACOS 900 computer of the Crystallographic Research Center, Institute for Protein Research, Osaka University.

^{1}H NMR spectra in $CDCl_3$ solution measured by a JEOL FX-200FT NMR spectrometer with Me_4Si as an internal reference.

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* Part IX: Yamagata, Okabe, Tomita, Shuto, Inoue & Ueda (1985).

† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42368 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates of non-*H *atoms and equivalent isotropic thermal parameters with their e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
N(1)	0·3751 (4)	0·9828 (8)	0·8491 (3)	1·7 (1)
C(2)	0·3394 (5)	1·1597 (10)	0·9175 (3)	2·0 (1)
N(3)	0·1840 (4)	1·1493 (9)	0·9431 (3)	2·4 (1)
C(4)	0·0641 (5)	0·9901 (11)	0·9037 (3)	2·4 (1)
C(5)	0·1078 (5)	0·8198 (11)	0·8310 (3)	2·4 (1)
C(6)	0·2582 (5)	0·8210 (10)	0·8040 (3)	1·8 (1)
O(2)	0·4344 (3)	1·3183 (7)	0·9497 (2)	2·5 (1)
O(4)	−0·0728 (4)	1·0092 (8)	0·9304 (3)	3·3 (1)
C(1′)	0·5384 (5)	0·9912 (9)	0·8174 (3)	1·8 (1)
C(2′)	0·5904 (5)	0·7438 (10)	0·7907 (3)	2·3 (1)
C(3′)	0·4703 (5)	0·7065 (10)	0·6904 (3)	2·1 (1)
C(4′)	0·4818 (5)	0·9496 (10)	0·6383 (3)	2·1 (1)
C(5′)	0·3259 (6)	1·0488 (11)	0·5734 (3)	2·6 (1)
C(6′)	0·3051 (5)	0·6500 (10)	0·7231 (3)	2·1 (1)
C(7′)	0·1485 (6)	0·9403 (11)	0·4213 (3)	2·8 (1)
C(8′)	0·1090 (6)	0·7490 (13)	0·3423 (4)	3·8 (2)
O(4′)	0·5247 (4)	1·1234	0·7204 (2)	2·2 (1)
O(5′)	0·2833 (4)	0·8803 (8)	0·4904 (2)	2·6 (1)
O(7′)	0·0799 (5)	1·1275 (9)	0·4285 (3)	5·2 (1)

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

N(1)–C(2)	1·389 (6)	C(1′)–O(4′)	1·454 (5)
N(1)–C(6)	1·389 (6)	C(2′)–C(3′)	1·539 (7)
N(1)–C(1′)	1·476 (6)	C(3′)–C(4′)	1·522 (7)
C(2)–N(3)	1·382 (6)	C(3′)–C(6′)	1·530 (7)
C(2)–O(2)	1·217 (6)	C(4′) C(5′)	1·542 (7)
N(3)–C(4)	1·374 (6)	C(4′)–O(4′)	1·448 (5)
C(4)–C(5)	1·425 (7)	C(5′)–O(5′)	1·435 (6)
C(4)–O(4)	1·243 (6)	O(5′)–C(7′)	1·372 (6)
C(5)–C(6)	1·348 (7)	C(7′)–C(8′)	1·484 (8)
C(6)–C(6′)	1·514 (7)	C(7′)–O(7′)	1·197 (7)
C(1′)–C(2′)	1·498 (7)		
C(2)–N(1)–C(6)	121·9 (4)	O(4′)–C(1′)–C(2′)	104·4 (3)
C(2)–N(1)–C(1′)	116·7 (4)	C(1′)–C(2′)–C(3′)	98·5 (4)
C(6)–N(1)–C(1′)	121·1 (4)	C(2′)–C(3′)–C(4′)	100·7 (4)
N(1)–C(2)–N(3)	114·9 (4)	C(2′)–C(3′)–C(6′)	106·6 (4)
N(1)–C(2)–O(2)	123·0 (4)	C(4′)–C(3′)–C(6′)	115·2 (4)
N(3)–C(2)–O(2)	121·9 (4)	C(3′)–C(4′)–C(5′)	117·3 (4)
C(2)–N(3)–C(4)	126·1 (4)	C(3′)–C(4′)–O(4′)	106·6 (4)
N(3)–C(4)–C(5)	115·8 (4)	C(5′)–C(4′)–O(4′)	105·2 (4)
N(3)–C(4)–O(4)	118·9 (4)	C(4′)–C(5′)–O(5′)	105·9 (4)
C(5)–C(4)–O(4)	125·3 (5)	C(6)–C(6′)–C(3′)	113·6 (4)
C(4)–C(5)–C(6)	120·5 (5)	C(8′)–C(7′)–O(5′)	111·0 (4)
N(1)–C(6)–C(5)	120·7 (4)	C(8′)–C(7′)–O(7′)	128·2 (5)
N(1)–C(6)–C(6′)	117·8 (4)	O(5′)–C(7′)–O(7′)	120·8 (5)
C(5)–C(6)–C(6′)	121·6 (4)	C(1′)–O(4′)–C(4′)	106·7 (3)
N(1)–C(1′)–C(2′)	110·2 (4)	C(5′)–O(5′)–C(7′)	115·1 (4)
N(1)–C(1′)–O(4′)	107·6 (3)		

Table 3. *The observed and calculated coupling constants* [J (Hz)] *and dihedral angles* [θ (°)]

	θ_{obs}(X-ray)	J_{calc}	J_{obs}(^{1}H NMR)	θ_{calc}
H(1′)–H(2′)	70 (5)	1·2[a]	0·0	86–90
H(1′)–H(2″)	54 (4)	3·5	4·4	49
H(2′)–H(3′)	79 (5)	0·4[b]	0·0	86–90
H(2″)–H(3′)	47 (5)	5·3	6·4	41
H(3′)–H(6′)	62 (4)	2·4[c]	1·4	69
H(3′)–H(6″)	50 (4)	4·5	3·8	54

(a) $J = 10{\cdot}1\cos^2\theta$. ($b$) $J = 11{\cdot}3\cos^2\theta$. ($c$) $J = 10{\cdot}9\cos^2\theta$.

Discussion. Tables 1 and 2 give the final atomic parameters and the bond distances and angles, respectively. Fig. 1 is an *ORTEP*II drawing (Johnson, 1976) of 6,3′-*C*-cyclo-U, and the molecular packing and hydrogen-bonding scheme are illustrated in Fig. 2.

The glycosidic torsion angle, χ_{CN}, is 265·3 (5)° which is very similar to that of 6,2′-anhydro-6-ethyl-1-β-D-arabinofuranosyluracil, 268·1 (3)° (6,2′-C_2-cyclo-U; Yamagata *et al.,* 1985), and it may correspond well to the fact that both CD patterns through the 240 to 300 nm range are very similar. The sugar ring takes the E_2 conformation with pseudorotational parameters of $P = 340{\cdot}8°$ and $\psi_m = 46{\cdot}6°$. The six-membered fused ring formed by cyclization between the sugar C(3′) and the uracil-base C(6) shows an envelope conformation with the C(2′) atom displaced by 0·883 (6) Å from the plane formed by the remaining five atoms. These conformations are quite similar to those ($\chi_{CN} = 255{\cdot}5°$, $P = 344{\cdot}6°$, $\psi_m = 44{\cdot}3°$) found in 8,3′-anhydro-8-mercapto-1-β-D-xylofuranosyladenine (8,3′-*S*-cyclo-A; Yoneda, Tanaka, Fujiwara & Tomita, 1979) which is one of the purine cyclonucleosides. This fact suggests that the overall molecular conformation including the glycosidic torsion angle and sugar and cyclic fused ring puckerings is considerably rigid both in the crystal and in solution as supported by NMR study; as shown in Table 3, the observed proton spin-coupling constants agree well with the calculated ones which are obtained from the observed dihedral angles by using the modified Karplus relation (Abraham & McLauchlam, 1962). The orientation of the O(5′) atom around the C(4′)—C(5′) bond is *trans–gauche,* not the usual *gauche–gauche* because of the prevention of the intramolecular short contacts between the O(5′) atom and the base

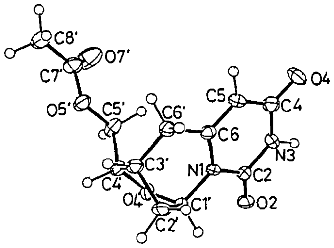

Fig. 1. Molecular conformation and atomic numbering.

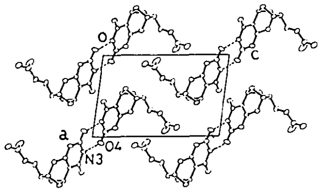

Fig. 2. Molecular packing viewed down the *b* axis. Dotted lines indicate the hydrogen bonds.

atoms as found in some cyclonucleosides (Brennan & Sundaralingham, 1973; Yamagata, Koshibe, Tokuoka, Fujii, Fujiwara, Kanai & Tomita, 1979; Yamagata, Suzuki, Fujii, Fujiwara & Tomita, 1979).

The bond distances and angles in the uracil moiety are in good agreement with standard values (Taylor & Kennard, 1982). However, in the furanose ring, the C(1')—C(2')—C(3') angle [98·5 (4)°] is significantly smaller than the average value (101·3°) of the normal furanose rings (Sundaralingam, 1973), and it is probably due to the E_2 sugar puckering strained by cyclization. Indeed, this value agrees well with the suggested one from the correlation between the endocyclic bond angles and the pseudorotational parameters (Westhof & Sundaralingam, 1980).

In the present crystal no base stacking is observed. One hydrogen bond, *i.e.* N(3)—H···O(4) [2·834 (5) Å], is found between the adjacent molecules related by twofold screw symmetry to form an infinite hydrogen-bonded column along the *b* axis.

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X-ray Structure and Molecular-Packing Analysis of 1'-(*p*-Bromophenyl)-3'-ethyl-1',3',4',5'-tetrahydro-1,2-dideoxy-D-*glycero*-α-D-*galacto*-heptofuranoso[2,1-*d*]imidazole-2'-thione Monohydrate

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Abstract. 6-(*p*-Bromophenyl)-4-ethyl-3-hydroxy-2-(1,2,3-trihydroxypropyl)-2,3,3a,5,6,6a-hexahydrofuro-[2,3-*d*]imidazole-5(4*H*)-thione monohydrate, $C_{16}H_{21}BrN_2O_5S.H_2O$, $M_r = 451·3$, orthorhombic, $P2_12_12_1$, $a = 6·073$ (3), $b = 15·977$ (8), $c = 19·213$ (9) Å, $V = 1864$ (2) Å^3, $Z = 4$, $D_m = 1·62$ (1), $D_x = 1·61$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 2·32$ mm^{-1}, $F(000) = 928$, room temperature, final $R = 0·080$ for 2147 observed reflexions. The sugar ring adopts the ^4E conformation and the dihedral angle in the bicyclic system is 115·0 (3)°. A three-dimensional network of hydrogen bonds links the molecules to stabilize the crystal structure. The lattice energy was computed in the atom–atom approach using van der Waals potential functions. These calculations account satisfactorily for all the features of the crystal packing, including rotation about selected bonds in the molecule.

Introduction. The crystal structure determination of the title compound (I) was undertaken as part of a continuing research project in this laboratory involving glucimidazoles and imidazole *C*-nucleosides. Some of these compounds, prepared in the Organic Chemistry Department of the University of Extremadura, have been studied (*e.g.* Estrada, Conde & Márquez, 1983, 1984; Conde, Millan, Conde & Márquez, 1985) in order to establish the conformational details of the molecule in the solid state. The application of aminonitrile synthesis to the preparation of the new 2-ethylamino-2-deoxyheptose having the D-*glycero*-D-

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