it is rather stronger than the intermolecular hydrogen bond in (II). The dimensions of C(4)—N(7), N(7)—N(8), N(8)—C(9), *viz* 1·403 (10), 1·371 (8), 1·306 (10) Å, respectively, are similar (within experimental error) to those observed in (II). This is not unexpected as the N···O distance is considerably longer than the mean value observed in the intramolecularly hydrogen-bonded compounds.

Though there are precedents for intermolecular hydrogen bonds in phenylhydrazone derivatives involving substituted nitro groups, *e.g. para* substitution (Menczel, 1969) and *meta* substitution (Menczel, Samay & Simon, 1972), the presence of DMF solvent strongly bound to each NH centre precludes this type of interaction in the present case. As in the monomer (II) there is a considerable difference between the angles at C(9), *viz* N(8)—C(9)—C(10), N(8)—C(9)—C9$^{\rm I}$) are 124·9 (3), 112·9 (7)°, respectively, which must again be a reflection of the repulsions involving H(7). The whole dimer is closely coplanar with atom deviations less than 0·10 (1) Å. This includes the DMF solvent and indeed the dimer and the solvent planes intersect at only 3·1 (1)°.

Clearly the solvent molecule has been positioned in such a way so as to form strong hydrogen bonds. [The N···O distance of 2·96 (2) Å can be compared to a mean intramolecular hydrogen bond of 2·65 Å.] The packing diagram (Fig. 4) illustrates the way in which planes of dimers and solvent are formed. It may well be the case that the size and geometry of the DMF ligand are particularly critical to the formation of the bis adduct structure. In particular we note that two solvent molecules fit squarely in between the *p*-nitro groups of adjacent molecules. HMPA is far more bulky and will clearly not fit easily into these regular planes.

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Structural Studies of Pyrimidine Cyclonucleoside Derivatives. VII. Structure of 6,5'-Anhydro-6-hydroxy-1-β-D-ribofuranosylcytosine (6,5'-*O*-cyclo-C), $C_9H_{11}N_3O_5$

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Abstract. $M_r = 241{\cdot}2$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}047$ (1), $b = 11{\cdot}292$ (1), $c = 12{\cdot}403$ (1) Å, $V = 987{\cdot}1$ (2) Å^3, $Z = 4$, $D_m = 1{\cdot}614$ (1), $D_x = 1{\cdot}623$ Mg m^{-3}, μ(Cu $K\alpha$) = 1·17 mm^{-1}, $F(000) = 504$, $T = 293$ K, $R = 0{\cdot}053$ for 974 independent reflexions. The glycosidic torsion angle is in the *anti* range, $\chi_{\rm CN} = 64{\cdot}9$ (6)°, and the ribose-ring conformation is C(4')-*endo*.

Introduction. As a series of structural studies on pyrimidine cyclonucleosides, we have reported the structures of 2,2'-cyclonucleosides (parts II, III and V: Yamagata, Suzuki, Fujii, Fujiwara & Tomita, 1979; Yamagata, Koshibe, Tokuoka, Fujii, Fujiwara, Kanai & Tomita, 1979; Yamagata, Yoshimura, Fujii, Fujiwara, Tomita & Ueda, 1980), of a 2,5'-cyclonucleoside (part IV: Yamagata, Fujii, Fujiwara,

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Tomita & Ueda, 1980) with the cyclization between C(2) in the base and C(2′) or C(5′) in the sugar, and of a 6,2′-cyclonucleoside (part I: Yamagata, Fujii, Kanai, Ogawa & Tomita, 1979) with the cyclization between C(6) and C(2′). The present paper deals with the crystal and molecular structure of 6,5′-*O*-cyclo-C with the cyclization between C(6) and C(5′). The comparison of these molecular conformations provides us with fundamental information about the influence of cyclization on the molecular conformations.

Experimental. 6,5′-*O*-Cyclo-C was synthesized in a manner similar to that described by Lipkin, Cori & Sano (1968) and crystallized from aqueous solution as colorless plates; preliminary X-ray photographs showed the crystal to be orthorhombic, space group $P2_12_12_1$; unit-cell dimensions determined by a least-squares procedure based on the 2θ values of 18 reflexions with $28° < 2\theta < 48°$ (Cu $K\alpha$); density measured by the flotation method in CCl_4–$C_2H_4Br_2$ mixture; intensities of 1023 independent reflexions with $\sin\theta/\lambda \leq 0{\cdot}60$ Å^{-1} ($0 \leq h \leq 8$, $0 \leq k \leq 13$, $0 \leq l \leq 15$) collected from a crystal 0·02 × 0·2 × 0·2 mm; Rigaku automatic four-circle diffractometer; Cu $K\alpha$ radiation; 978 reflexions had intensities greater than $2\sigma(I)$; reflexions 105, 222 and 152 monitored during data collection and their fluctuations were within 0·4% with an e.s.d. of 0·1%; all intensity data corrected for Lorentz and polarization factors, but not for absorption; structure solved by the direct method (*MULTAN*, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); first *E* map revealed the positions of all nonhydrogen atoms; structure refined by full-matrix least-squares method with anisotropic temperature factors for all nonhydrogen atoms; all H atoms located from a difference Fourier synthesis; the final refinement including H atoms with isotropic temperature factors reduced *R* to 0·053 ($R_w = 0{\cdot}048$, $S = 6{\cdot}3$);* four intense low-angle reflexions (002, 014, 121 and 140) appeared to suffer from secondary extinction and were not included in the refinement; the quantity minimized was $\sum w(|F_o| - k|F_c|)^2$, where $w = 1/\sigma^2|F_o|$ and k is the scale factor; the absolute maximum height in the final difference Fourier synthesis was 0·26 e Å^{-3}; the average and maximum ratios of parameter shift to e.s.d. after refinement were 0·06 and 0·18, respectively, for nonhydrogen atoms; all numerical calculations carried out an ACOS Series 77-700 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University with the programs of *The Universal Crystallographic Computing System – Osaka* (1979); scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic coordinates with their estimated standard deviations are given in Table 1. The bond lengths and angles are shown in Table 2. The *ORTEP* II (Johnson, 1976) stereodrawing of the molecular conformation is shown in Fig. 1 and the molecular packing projected along the *a* axis is shown in Fig. 2.

As expected, the glycosidic torsion angle [$\chi_{CN} = 64{\cdot}9\,(6)°$] is in the *anti* conformation, and differs by about 180° from the 246·4 and 244·2° found in 2,5′-anhydro-1-(2′,3′-*O*-isopropylidene-β-D-ribofuranosyl)-uracil (2,5′-*O*-cyclo-U; Delbaere & James, 1974) and 2,5′-anhydro-1-(2′,3′-*O*-isopropylidene-β-D-ribofura-

Table 1. *Final atomic coordinates of non-*H *atoms* (×10⁴) *and equivalent isotropic thermal parameters, with their estimated standard deviations in parentheses*

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

	x	*y*	*z*	B_{eq}(Å^2)
N(1)	6451 (6)	10729 (4)	9751 (3)	2·1 (2)
C(2)	8081 (8)	11334 (4)	10149 (5)	2·2 (2)
N(3)	9375 (6)	11735 (4)	9449 (4)	2·4 (2)
C(4)	9144 (7)	11592 (4)	8390 (4)	2·4 (2)
C(5)	7532 (6)	10980 (5)	7958 (5)	2·5 (2)
C(6)	6258 (7)	10554 (5)	8661 (4)	2·1 (2)
O(2)	8271 (5)	11447 (3)	11129 (3)	2·6 (2)
N(4)	10485 (7)	12014 (5)	7744 (4)	3·1 (2)
C(1′)	5108 (7)	10209 (5)	10516 (4)	2·0 (2)
C(2′)	3015 (7)	10522 (5)	10286 (5)	2·2 (2)
C(3′)	2109 (9)	9318 (5)	9995 (5)	2·9 (2)
C(4′)	3824 (9)	8569 (5)	9716 (5)	2·8 (2)
C(5′)	4516 (9)	8743 (5)	8584 (5)	2·8 (2)
O(1′)	5225 (5)	8955 (3)	10490 (3)	2·4 (1)
O(2′)	2239 (5)	10985 (3)	11261 (3)	2·7 (2)
O(3′)	1130 (7)	8829 (4)	10884 (4)	4·3 (2)
O(5′)	4685 (5)	9986 (3)	8308 (3)	2·5 (2)

Table 2. *Bond distances* (Å) *and angles* (°) *for the nonhydrogen atoms*

N(1)–C(2)	1·424 (7)	C(1′)–O(1′)	1·419 (7)
N(1)–C(6)	1·372 (7)	C(1′)–C(2′)	1·544 (8)
C(2)–N(3)	1·339 (7)	C(2′)–C(3′)	1·545 (9)
N(3)–C(4)	1·333 (7)	C(2′)–O(2′)	1·426 (7)
C(4)–C(5)	1·433 (8)	C(3′)–O(3′)	1·413 (8)
C(4)–N(4)	1·327 (8)	C(3′)–C(4′)	1·515 (9)
C(5)–C(6)	1·341 (8)	C(4′)–O(1′)	1·445 (7)
N(1)–C(1′)	1·464 (7)	C(4′)–C(5′)	1·499 (9)
C(2)–O(2)	1·229 (7)	C(5′)–O(5′)	1·450 (8)
C(6)–O(5′)	1·353 (7)		

C(2)–N(1)–C(6)	119·4 (5)	C(6)–O(5′)–C(5′)	116·7 (4)
C(2)–N(1)–C(1′)	119·3 (4)	N(1)–C(1′)–C(2′)	114·0 (5)
C(6)–N(1)–C(1′)	121·1 (4)	N(1)–C(1′)–O(1′)	110·4 (4)
N(1)–C(2)–N(3)	119·1 (5)	C(2′)–C(1′)–O(1′)	106·2 (4)
N(1)–C(2)–O(2)	118·7 (5)	C(1′)–C(2′)–C(3′)	103·7 (5)
N(3)–C(2)–O(2)	122·1 (5)	C(1′)–C(2′)–O(2′)	107·0 (4)
C(2)–N(3)–C(4)	121·0 (5)	C(3′)–C(2′)–O(2′)	111·2 (5)
N(3)–C(4)–C(5)	121·6 (5)	C(2′)–C(3′)–C(4′)	102·4 (5)
N(3)–C(4)–N(4)	117·6 (5)	C(2′)–C(3′)–O(3′)	111·4 (5)
C(5)–C(4)–N(4)	120·8 (5)	C(4′)–C(3′)–O(3′)	110·4 (5)
C(4)–C(5)–C(6)	117·4 (5)	C(3′)–C(4′)–C(5′)	113·6 (5)
N(1)–C(6)–C(5)	121·5 (5)	C(3′)–C(4′)–O(1′)	103·0 (5)
N(1)–C(6)–O(5′)	117·9 (5)	C(5′)–C(4′)–O(1′)	111·2 (5)
C(5)–C(6)–O(5′)	120·5 (5)	C(4′)–C(5′)–O(5′)	112·0 (5)
		C(1′)–O(1′)–C(4′)	106·1 (4)

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* 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 38262 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

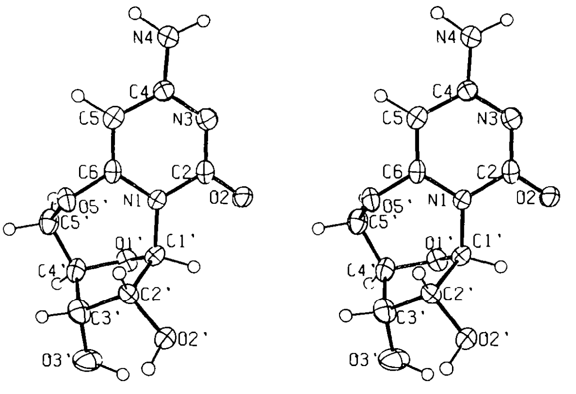

Fig. 1. Stereoview of the molecular conformation.

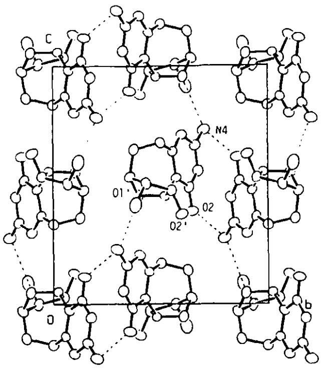

Fig. 2. Molecular packing viewed down the *a* axis. Dashed lines indicate the hydrogen bonds. The dashed lines from O(2′) to O(2) are omitted because O(2′) and O(2) are almost overlapped when viewed down the *a* axis.

Table 3. *Conformational parameters* (°) *for 5′-cyclonucleosides*

	6,5′-*O*-cyclo-C	2,5′-*O*-cyclo-U[(*a*)]	2,5′-*S*-cyclo-U[(*b*)]
Glycosidic torsion angle			
χ_{CN}	64·9 (6)	246·4	244·2 (7)
Sugar-ring torsion angles			
τ_0	31·8 (5)	34·9	28·4 (8)
τ_1	−6·9 (6)	−14·3	−9·2 (8)
τ_2	−18·8 (6)	−9·9	−11·7 (8)
τ_3	37·9 (5)	30·5	28·6 (7)
τ_4	−44·2 (5)	−41·6	−35·8 (7)
Pseudorotation parameters [(*c*)]			
Phase angle, *P*	244	256	251
Maximum amplitude, τ_m	44	41	36
Conformation about C(4′)–C(5′)			
$\psi_{OO(OS)}$	−67·8 (6)	−73·5	−73·8 (7)
$\psi_{CO(CS)}$	47·8 (7)	41·6	44·6 (9)

References: (*a*) Delbaere & James (1974); (*b*) Yamagata, Fujii *et al.* (1980); (*c*) Altona & Sundaralingam (1972).

nosyl)-2-thiouracil (2,5′-*S*-cyclo-U: Yamagata, Fujii *et al.*, 1980), as shown in Table 3. In all these 5′-cyclonucleosides, the O(5′) or S atom is located over the center of the sugar ring (the *endo* form) and the newly formed seven-membered rings all have chair forms. This suggests that the *endo* form is stereochemically more stable than the *exo* form where the seven-membered ring takes the boat form.

The sugar ring is puckered in a typical C(4′)-*endo* conformation ($P = 244°$, $\tau_m = 44°$; Table 3), where C(4′) is displaced by 0·620 (8) Å from the least-squares plane calculated through the other four atoms. As shown in Table 3, the sugar conformation is similar but not identical to that found in the other 5′-cyclonucleosides because of small distortions caused by the attached isopropylidene group, *i.e.* the other 5′-cyclonucleosides have an O(1′)-*exo*-like C(4′)-*endo* puckering with small τ_m values. The unusual C(4′)-*endo* puckering is also observed in 2,2′-cyclonucleosides (Delbaere & James, 1973; Yamagata, Koshibe *et al.*, 1979; Yamagata, Suzuki *et al.*, 1979; Yamagata, Yoshimura *et al.*, 1980). However, the τ_m for C(4′)-*endo* sugar puckering of these 2,2′-cyclonucleosides with a *gauche–gauche* conformation about the C(4′)–C(5′) bond is *ca* 20°, which is apparently smaller than those found in 5′-cyclonucloesides, because several short contacts between O(5′) and some atoms in the base should be released.

The bond distances and angles (Table 1) are in good agreement with those of related cyclonucleosides. In spite of cyclization, those in the cytosine moiety differ little from those of cytosine derivatives (Tougard & Lefebvre-Soubeyran, 1974).

In this crystal no base stacking is observed. There are four protons in a molecule available as hydrogen-bond donors; of these, three participate in hydrogen bonding, *i.e.* N(4)–H···O(2) [2·972 (7) Å], O(2′)–H···O(2) [2·849 (5) Å] and N(4)–H···O(1′) [3·044 (7) Å].

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