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Structural Studies of Pyrimidine Cyclonucleoside Derivatives.

V. Structure of 2,2'-Anhydro-1- β -D-arabinofuranosyl-2-thiouracil

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Abstract

The title compound, $C_9H_{10}N_2O_4S$, crystallizes in space group $P2_1$ with $Z = 2$, and unit-cell dimensions $a = 8.881$ (1), $b = 6.841$ (2), $c = 8.454$ (1) Å, $\beta = 105.84$ (1)°. The structure was solved by the direct method and refined to a final R index of 0.036 (weighted $R = 0.035$). The glycosyl torsion angle χ_{CN} is 295.7° (*syn* conformation), the puckering of the ribose ring being C(4')-*endo*. The orientation of the C(5')–O(5') bond is *gauche-trans*.

Introduction

As part of a series of studies on pyrimidine cyclonucleosides, we have reported the molecular structure of 2,5'-anhydro-1-(2',3'-*O*-isopropylidene- β -D-ribofuranosyl)-2-thiouracil (2,5'-*S*-cyclo U) in a previous paper (part IV: Yamagata, Fujii, Fujiwara, Tomita & Ueda, 1980). The present paper describes the crystal and molecular structure of 2,2'-anhydro-1- β -D-arabinofuranosyl-2-thiouracil (2,2'-*S*-cyclo U) in which the cyclization occurred between C(2) and C(2'), in contrast to that between C(2) and C(5') in 2,5'-*S*-cyclo U. The conformational comparison of this compound with other related ones is not only pertinent but also informative for CD and NMR studies in solution.

Experimental

2,2'-*S*-cyclo U was synthesized from 2,2'-anhydro-1- β -D-arabinofuranosyluracil (2,2'-*O*-cyclo U) (Ueda & Shibuya, 1974). The material crystallized from an

aqueous ethanol solution as colorless prisms in the monoclinic space group $P2_1$. Unit-cell dimensions were determined by a least-squares procedure based on the 2θ values of 23 reflexions with $33^\circ \leq 2\theta \leq 45^\circ$. The density was measured by the flotation method in a carbon tetrachloride–ethylene dibromide mixture. The crystallographic data are shown in Table 1.

The intensities of 1185 independent reflexions within $\sin \theta/\lambda = 0.65$ Å⁻¹ were collected on a Rigaku automatic four-circle diffractometer with Mo $K\alpha$ radiation and corrected for Lorentz and polarization factors, but not for absorption. All numerical calculations were carried out on an ACOS-900 computer of the Computation Center of Osaka University with *The Universal Crystallographic Computing System* (1973). For structure factor calculation, the atomic scattering factors cited in *International Tables for X-ray Crystallography* (1974) were used.

Structure determination and refinement

The structure was solved by the direct method using the program *MULTAN* (Germain, Main & Woolfson,

Table 1. *Crystal data*

$C_9H_{10}N_2O_4S$	$M_r = 242.25$
Monoclinic	Space group $P2_1$
$a = 8.881$ (1) Å	$Z = 2$
$b = 6.841$ (2)	$F(000) = 252$
$c = 8.454$ (1)	$V = 494.1$ (2) Å ³
$\beta = 105.84$ (1)°	$D_m = 1.627$ (1) Mg m ⁻³
$\lambda(\text{Mo } K\alpha) = 0.71069$ Å	$D_x = 1.628$
$\mu(\text{Mo } K\alpha) = 0.327$ mm ⁻¹	

1971). A set of 200 reflexions with $E \leq 1.31$ were used for generating 1600 Σ_2 relationships. An E map revealed the positions of 10 nonhydrogen atoms in the base and sugar moieties. Subsequent Fourier syntheses using the phase angles based on these atomic positions showed the peaks for the six remaining nonhydrogen atoms. The structure was refined by a full-matrix least-squares method with isotropic temperature factors for all the nonhydrogen atoms and then by a block-diagonal least-squares method with anisotropic temperature factors. The positions of all H atoms were obtained from a difference Fourier synthesis. The final refinement including the H atoms with isotropic temperature factors reduced the R value to 0.036 ($R_w = 0.035$).^{*} Throughout the refinements each reflexion was given a weight based on counting statistics.

Results and discussion

The atomic coordinates with their estimated standard deviations are given in Tables 2 and 3. The bond lengths and angles are shown in Figs. 1 and 2.

(a) Bond lengths and angles

The cyclization between S and C(2') causes significant alteration of the bond lengths and angles involved in the uracil-ring moiety compared to those of 2-thiouridine (Hawkinson, 1977). For example, in 2,2'-*S*-cyclo U the C(2)—N(3) bond (1.297 Å) is shorter than

^{*} Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34855 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final atomic coordinates for the non-hydrogen atoms ($\times 10^4$) with their estimated standard deviations in parentheses*

	x	y	z
S	8644 (1)	6805 (1)	4450 (1)
N(1)	7973 (2)	7392 (3)	1424 (2)
C(2)	9209 (2)	7068 (3)	2757 (3)
N(3)	10661 (2)	6980 (3)	2731 (3)
C(4)	11015 (2)	7220 (4)	1250 (3)
C(5)	9720 (3)	7506 (4)	-220 (3)
C(6)	8250 (3)	7602 (4)	-85 (3)
O(4)	12404 (2)	7195 (3)	1210 (2)
C(1')	6385 (2)	7457 (4)	1673 (3)
C(2')	6586 (2)	7114 (4)	3522 (2)
C(3')	5883 (2)	8974 (4)	4086 (3)
C(4')	5922 (2)	10461 (4)	2766 (3)
O(1')	5702 (2)	9307 (3)	1275 (2)
O(3')	4344 (2)	8610 (3)	4209 (2)
C(5')	7376 (2)	11718 (4)	3067 (2)
O(5')	7202 (2)	13195 (3)	1851 (2)

Table 3. *Final atomic coordinates for the hydrogen atoms ($\times 10^3$) with their estimated standard deviations in parentheses*

	x	y	z
H(5)	983 (3)	772 (5)	-131 (3)
H(6)	737 (3)	784 (5)	-98 (3)
H(1')	569 (3)	655 (6)	97 (3)
H(2')	605 (3)	580 (5)	384 (3)
H(3')	658 (3)	934 (5)	522 (3)
H(4')	497 (3)	1137 (5)	252 (3)
H(5')	841 (3)	1090 (5)	307 (3)
H(5'')	760 (3)	1237 (5)	421 (3)
H(O3')	373 (3)	796 (5)	324 (3)
H(O5')	707 (3)	1285 (5)	83 (3)

The overall isotropic temperature factor is 2.7 \AA^2 .

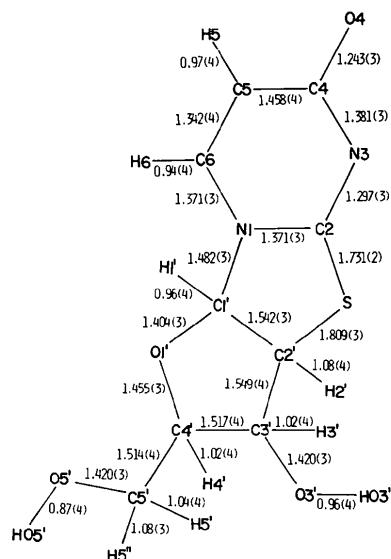


Fig. 1. Bond lengths (Å) with estimated standard deviations in parentheses.

that found in 2-thiouridine (1.360 Å), but the C(4)—C(5) bond (1.458 Å) is a little longer. Similarly, the N(1)—C(2)—N(3) angle is larger by 9° and C(2)—N(3)—C(4) is smaller by 8° than those found in 2-thiouridine. Similar alterations were found in 2,5'-*S*-cyclo U (Yamagata, Fujii, Fujiwara, Tomita & Ueda, 1980) and 2,2'-*O*-cyclo U (Delbaere & James, 1973; Suck & Saenger, 1973). It is interesting to compare the bond lengths around S in 2,2'-*S*-cyclo U with those in related compounds: the C(2)—S bond (1.731 Å) is shorter than that of 2,5'-*S*-cyclo U (1.769 Å) and a similar tendency is found in *S*-cycloadenosine derivatives, *i.e.* the C(8)—S bond lengths of 8,2'-*S*-cyclo 5'-AMP (Tanaka, Fujii, Fujiwara & Tomita, 1979), 8,3'-*S*-cycloadenosine (Yoneda, Tanaka, Fujiwara & Tomita, 1979) and 8,5'-*S*-cyclo-2',3'-*O*-isopropylideneadenosine (Tomita, Nishida, Fujiwara &

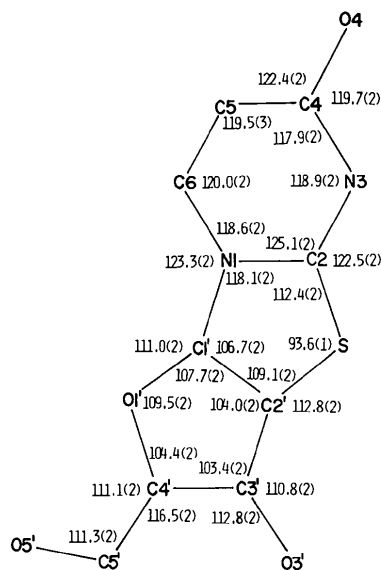


Fig. 2. Bond angles ($^{\circ}$) with estimated standard deviations in parentheses.

Ikehara, 1970) are 1.73, 1.75 and 1.78 Å, respectively, indicating that the bond length increases in turn. These increases may result from the difference in the extent of steric distortions and in the magnitude of the base resonance effect, depending upon the number of atoms in the newly formed fused ring resulting from cyclization. On the other hand, the S—C(X) (X = 2', 3' and 5') bond lengths are similar. The large distortions in the angles around N(1), C(1') and C(2') of 2,2'-*O*-cyclonucleosides (Brennan & Sundaralingam, 1973; Yamagata, Koshibe, Tokuoka, Fujii, Fujiwara, Kanai & Tomita, 1979; Yamagata, Suzuki, Fujii, Fujiwara & Tomita, 1979) are not found in 2,2'-*S*-cyclo U, because C—S bond lengths are apparently longer than C—O bond lengths and the bond angles around S and O(2) differ.

(b) Molecular conformation

A stereographic representation of the molecular conformation is shown in Fig. 3.

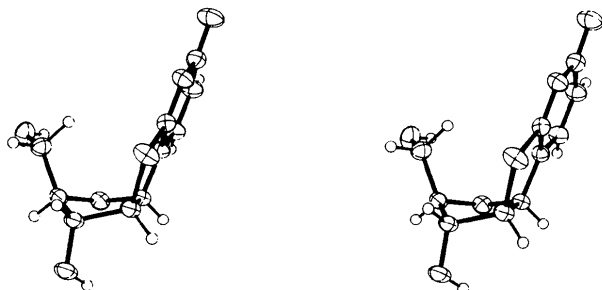


Fig. 3. Stereoview (Johnson, 1965) of the molecular conformation.

Table 4. Deviations (Å) of atoms from least-squares planes through several parts of the molecule

x , y and z refer to the orthogonal coordinate system (Å) with x along a , y along b and z along c^* . A dagger indicates atoms included in the calculation of the least-squares plane.

(a) Base and part of the sugar

	(I)	(II)	(III)
N(1)	-0.007 (2)†	-0.002 (2)†	-0.009 (2)†
C(2)	0.009 (3)†	0.005 (3)†	0.002 (2)†
N(3)	0.003 (3)†	0.001 (4)	-0.003 (3)†
C(4)	-0.014 (3)†	-0.004 (5)	-0.013 (3)†
C(5)	0.013 (3)†	0.033 (5)	0.021 (3)†
C(6)	0.003 (3)†	0.020 (4)	0.008 (3)†
S	0.017 (3)	-0.001 (1)†	0.001 (1)†
O(4)	-0.058 (4)	-0.047 (6)	-0.056 (3)
C(1')	-0.004 (4)	-0.002 (3)†	-0.008 (3)†
C(2')	0.016 (4)	0.005 (3)†	0.004 (3)†

Equations of the planes

$$\begin{aligned} \text{(I)} & -0.0526x - 0.9874y - 0.1490z + 5.5139 = 0.0 \\ \text{(II)} & -0.0516x - 0.9861y - 0.1579z + 5.5160 = 0.0 \\ \text{(III)} & -0.0519x - 0.9866y - 0.1545z + 5.5099 = 0.0 \end{aligned}$$

(b) Sugar

	(IV)	(IV)	(IV)
C(1')	0.010 (3)†	O(1')	-0.004 (3)†
C(2')	-0.010 (3)†	C(4')	-0.482 (4)
C(3')	0.007 (4)†	C(5')	-1.974 (4)

Equation of plane

$$\text{(IV)} \quad -0.8766x - 0.4258y - 0.2245z + 7.1200 = 0.0$$

Table 5. Torsion angles ($^{\circ}$)

	Designation	
χ	O(1')—C(1')—N(1)—C(6)	295.7 (3)
τ_0	C(4')—O(1')—C(1')—C(2')	19.2 (2)
τ_1	O(1')—C(1')—C(2')—C(3')	1.7 (2)
τ_2	C(1')—C(2')—C(3')—C(4')	-20.4 (2)
τ_3	C(2')—C(3')—C(4')—O(1')	31.8 (2)
τ_4	C(3')—C(4')—O(1')—C(1')	-32.6 (2)
ψ_{OO}	O(1')—C(4')—C(5')—O(5')	67.3 (3)
ψ_{CO}	C(3')—C(4')—C(5')—O(5')	-173.2 (2)

The glycosyl torsion angle χ_{CN} , 295.7°, is similar to those found in other 2,2'-cyclonucleosides (observed values: 291 ~ 302°), while that of 2,5'-*S*-cyclo U is 244.2°. The pyrimidine ring in 2,2'-*S*-cyclo U is essentially planar and S is on this plane (Table 4), while S of 2,5'-*S*-cyclo U is displaced from this plane by 0.10 Å.

The five-membered fused ring formed by cyclization between S and C(2') is also essentially planar. The conformation of the sugar puckering is C(4')-*endo*, where C(4') is displaced by 0.48 Å from the least-squares plane calculated by the other four atoms, and this conformation is usually found in 2,2'-cyclopyrimidine-nucleosides. The orientation of the C(5')—O(5') bond is *gauche-trans* [O(1')—C(4')—C(5')—O(5') = 67.3°,

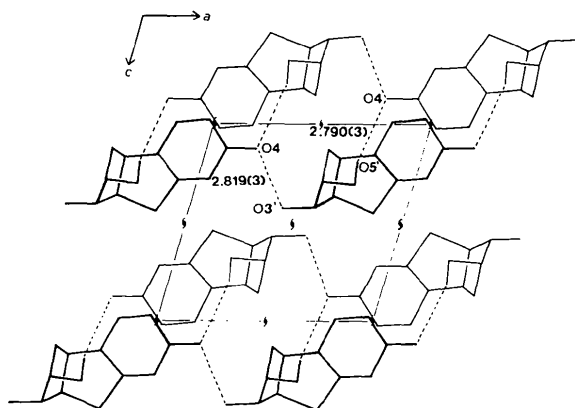


Fig. 4. Molecular packing along the *b* axis. Dashed lines indicate the hydrogen bonds.

$C(3')-C(4')-C(5')-O(5') = -173.2^\circ$; Table 5], introducing no short contacts between $O(5')$ and the base atoms in contrast to the 2,2'-(*O*)-cyclocytidine derivatives (Brennan & Sundaralingam, 1973; Yamagata, Koshibe, Tokuoaka, Fujii, Fujiwara, Kanai & Tomita, 1979; Yamagata, Suzuki, Fujii, Fujiwara & Tomita, 1979) where the $C(5')-O(5')$ bond relative to the sugar ring is *gauche-gauche*.

(c) Molecular packing

The molecular packing along the *b* axis is shown in Fig. 4.

The base plane is nearly parallel to (010), but no base stacking is observed. There are two kinds of hydrogen bond, as shown in Fig. 4, *i.e.* $O(3')-H \cdots$

$O(4)$ (2.819 Å) and $O(5')-H \cdots O(4)$ (2.790 Å), where $O(4)$ participates in hydrogen bonding as a unique acceptor.

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The Structures of 5-Phenyl-2,4-pentadienoic Acid (PPA) and 1,5-Diphenyl-2,4-pentadien-1-one (DPO)

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Abstract

The crystal structures of PPA and DPO have been determined from visually estimated $Cu K\alpha$ data, and refined to *R* values of 0.096 and 0.098 for 1973 and 804 non-zero reflexions, respectively. The unit cells are:

0567-7408/80/020346-08\$01.00

Pcab, $a = 10.49$ (1), $b = 37.47$ (6), $c = 9.50$ (2) Å, $Z = 16$ for PPA; and *Pcab*, $a = 15.49$ (2), $b = 16.51$ (3), $c = 10.34$ (2) Å, $Z = 8$ for DPO. The molecules take *trans-trans-s-cis* conformations in both crystals. Two molecules in PPA form a noncentrosymmetric hydrogen-bonded dimer, which takes a propeller-like

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