

Structural Studies of *S*-Cycloadenosine Derivatives.

I. The Crystal and Molecular Structure of 8,2'-Anhydro-8-mercapto-9- β -D-arabinofuranosyladenine 5'-Monophosphate Trihydrate (8,2'-*S*-cyclo 5'-AMP)

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Abstract

8,2'-Anhydro-8-mercapto-9- β -D-arabinofuranosyladenine 5'-monophosphate trihydrate ($C_{10}H_{12}N_5O_6 \cdot PS \cdot 3H_2O$) crystallizes in the tetragonal system with space group $P4_12_12$ and cell dimensions $a = b = 9.782$ (1), $c = 34.387$ (5) Å. The structure was solved by the heavy-atom method using the intensity data of 1982 independent reflections measured by Zr-filtered Mo $K\alpha$ radiation and was refined to $R = 5.0\%$. Molecules of the title compound occur in a *high-anti* conformation with a glycosidic torsion angle of 118.8° . The ribose conformation is C(4')-*endo* and the orientation of the C(5')–O(5') bond is *gauche-trans*. The bases stack along the c axis with an interplanar spacing of 3.4 Å.

Introduction

In cyclo-nucleosides and nucleotides rotation of the base about the glycosyl bond is stereochemically restricted by covalent-bond formation between the purine and furanose rings through the S or O atom. In fact, the crystal structures of some cyclonucleosides have been solved by X-ray diffraction: 8,3'-*S*-cycloadenosine (Tomita, Tanaka, Yoneda, Fujiwara & Ikehara, 1972) and 8,5'-*S*-cyclo-2',3'-isopropylideneadenosine (Tomita, Nishida, Fujiwara & Ikehara, 1970), in which the torsion angle χ about the glycosyl bond was fixed at 75° for the former crystal and 42° for the latter by ring fusion. For this reason, cyclonucleosides and cyclonucleotides may serve as suitable compounds for comparison of the molecular conformation in the crystalline form with that in aqueous solution and to find the correlation between the χ value defined by the mutual orientations of the base and sugar moieties and the corresponding spectroscopic features, especially of ORD and CD spectra (Ikehara, Kaneko, Nakahara, Yamada & Uesugi, 1971). Furthermore, as shown by the results of CD spectra, it is worthy to note that the 8,2'-*S*-cycloadenosine dinucleotide shows a Cotton effect opposite to that of

ApA and this phenomenon may support the possibility of left-handed base stacking (Ikehara, Uesugi & Yano, 1972). The conformational-energy calculation for poly(8,2'-*S*-cycloadenylic acid) strongly suggests that the sense of base stacking is left-handed (Fujii & Tomita, 1976).

In this paper, we report the structure analysis of 8,2'-anhydro-8-mercapto-9- β -D-arabinofuranosyladenine 5'-monophosphate (8,2'-*S*-cyclo 5'-AMP) and its molecular geometry, which may be useful in application to conformational studies in solution.

Experimental

A sample of 8,2'-*S*-cyclo 5'-AMP was kindly supplied by Professor M. Ikehara, Osaka University. Transparent prismatic crystals formed by slow evaporation of an aqueous solution at room temperature. Preliminary Weissenberg and precession photographs revealed the crystal to be tetragonal: systematic extinctions ($h00$, $h = 2n$; $00l$, $l = 4n$) indicated the space group to be $P4_12_12$ (No. 92) or $P4_32_12$ (No. 94), of which the former was later confirmed to be correct. The cell dimensions were obtained from the least-squares refinement of 2θ values of higher-order reflections measured on a diffractometer. The crystal data are given in Table 1. The intensities of 2292 unique reflections within $2\theta \leq 55^\circ$ were collected on a Rigaku-Denki automatic four-circle diffractometer using the ω - 2θ scan technique and Zr-filtered Mo $K\alpha$ radiation (crystal size: $0.4 \times 0.4 \times 0.3$ mm). Of these,

Table 1. *Crystal data*

Formula	$C_{10}H_{12}N_5O_6 \cdot PS \cdot 3H_2O$	V (Å ³)	3290.7 (8)
Molecular weight	415.32	Z	8
Crystal system	Tetragonal	D_m (Mg m ⁻³)	1.672 (5)
Space group	$P4_12_12$	D_x (Mg m ⁻³)	1.677
$a = b$ (Å)	9.782 (1)		
c (Å)	34.387 (5)		

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1994 were considered to have counts significantly above background. No absorption correction was applied. The density was measured by the flotation method using a carbon tetrachloride–ethylene bromide mixture.

Table 2. *Final positional parameters* ($\times 10^4$)

Estimated standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1')	2252 (6)	4140 (6)	653 (2)
C(2)	5930 (7)	6838 (7)	550 (2)
C(2')	1681 (6)	2665 (7)	634 (2)
C(3')	1118 (6)	2412 (6)	1054 (2)
C(4)	4763 (7)	4924 (7)	530 (2)
C(4')	1881 (6)	3482 (6)	1295 (2)
C(5)	5869 (6)	4143 (6)	418 (2)
C(5')	3212 (7)	2919 (7)	1453 (2)
C(6)	7134 (7)	4803 (7)	363 (2)
C(8)	4217 (7)	2780 (7)	462 (2)
N(1)	7087 (6)	6175 (6)	448 (2)
N(3)	4735 (6)	6290 (6)	597 (1)
N(6)	8270 (6)	4215 (6)	243 (2)
N(7)	5520 (6)	2770 (6)	371 (2)
N(9)	3706 (6)	4016 (5)	558 (1)
O(1)	6241 (5)	5189 (5)	1687 (1)
O(1')	2073 (5)	4613 (4)	1037 (1)
O(2)	6223 (6)	3070 (6)	1295 (1)
O(3)	5748 (5)	2900 (5)	2016 (1)
O(3')	-284 (5)	2724 (5)	1066 (1)
O(5')	4055 (5)	4054 (5)	1574 (1)
P	5629 (2)	3799 (2)	1662 (0)
S	3024 (2)	1469 (2)	484 (1)
O(<i>W</i> 1)	6076 (6)	6441 (2)	2409 (1)
O(<i>W</i> 2)	9011 (6)	5179 (8)	2463 (3)
O(<i>W</i> 3)	8726 (7)	5448 (6)	1295 (2)

Table 3. *Final positional parameters* ($\times 10^3$) for the hydrogen atoms

Estimated standard deviations are in parentheses. The isotropic thermal parameter is 2.38 \AA^2 . The second column shows the atom to which the H atom is bonded.

		<i>x</i>	<i>y</i>	<i>z</i>
H(1)	N(1)	779 (9)	668 (10)	40 (2)
H(2)	C(2)	609 (9)	782 (9)	61 (2)
H(6)	N(6)	900 (10)	471 (9)	16 (2)
H(6')	N(6)	827 (9)	324 (9)	17 (2)
H(1')	C(1')	173 (9)	483 (9)	48 (2)
H(2')	C(2')	99 (9)	260 (9)	47 (2)
H(3')	C(3')	133 (9)	147 (9)	117 (2)
H(3'')	O(3')	-52 (9)	198 (9)	95 (2)
H(4')	C(4')	124 (9)	384 (9)	153 (2)
H(5')	C(5')	387 (10)	225 (10)	129 (2)
H(5'')	C(5')	307 (10)	241 (9)	167 (2)
H(2'')	O(2)	631 (9)	230 (10)	132 (2)
H(<i>W</i> 1)	O(<i>W</i> 1)	632 (9)	581 (9)	258 (2)
H(<i>W</i> 1')	O(<i>W</i> 1)	621 (9)	603 (9)	219 (2)
H(<i>W</i> 2)	O(<i>W</i> 2)	883 (9)	628 (10)	235 (2)
H(<i>W</i> 2')	O(<i>W</i> 2)	843 (10)	511 (10)	256 (3)
H(<i>W</i> 3)	O(<i>W</i> 3)	903 (9)	481 (9)	116 (2)
H(<i>W</i> 3')	O(<i>W</i> 3)	782 (9)	541 (10)	139 (2)

Structure determination and refinement

The structure of 8,2'-*S*-cyclo 5'-AMP was solved by the heavy-atom method. A sharpened Patterson map showed clearly the positions of two heavy atoms (S and P). The fact that all the non-hydrogen atoms considered as a molecule containing the β -anomer of the D-arabinofuranose ring were properly located on successive Fourier maps indicated the correct space group to be $P4_12_12$. The structure was refined to an *R* value of 0.065 by a least-squares method with programs using the block-diagonal approximation (*UNICS*, 1973) with isotropic thermal parameters and then the full-matrix least-squares method (Busing, Martin & Levy, 1962) with anisotropic thermal parameters. At this stage, 12 reflections having large discrepancies between observed and calculated structure factors were omitted and a difference Fourier synthesis was calculated which revealed the locations of all H atoms. They were included in the final refinement with anisotropic temperature factors for non-hydrogen atoms and isotropic for H atoms, and the final *R* value was 0.050 (0.074 including $F_o = 0$). The final positional parameters are listed in Tables 2 and 3.* Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and all numerical calculations were carried out on a NEAC 2200-700 computer at this university.

Results and discussion

The bond lengths and angles are given in Fig. 1. As expected, some of these deviate somewhat from the standard values. In Table 4, selected bond lengths and

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34123 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Comparison of bond lengths* (\AA) and bond angles ($^\circ$) in 8,2'-*S*-cyclo 5'-AMP with those in 5'-AMP

	8,2'- <i>S</i> - cyclo- 5'-AMP	Ortho- rhombic 5'-AMP	Mono- clinic 5'-AMP
N(7)–C(8)	1.312	1.326	1.32
N(9)–C(8)	1.349	1.392	1.39
C(1')–C(2')	1.549	1.534	1.50
C(2')–C(3')	1.566	1.526	1.54
C(1')–N(9)	1.465	1.489	1.49
C(1')–N(9)–C(4)	134.1	124.2	123.8
C(1')–N(9)–C(8)	119.2	127.4	128.6
N(7)–C(8)–N(9)	115.1	111.8	111.8
C(8)–N(9)–C(4)	106.6	108.3	107.1
N(9)–C(1')–C(2')	105.2	113.0	112.6

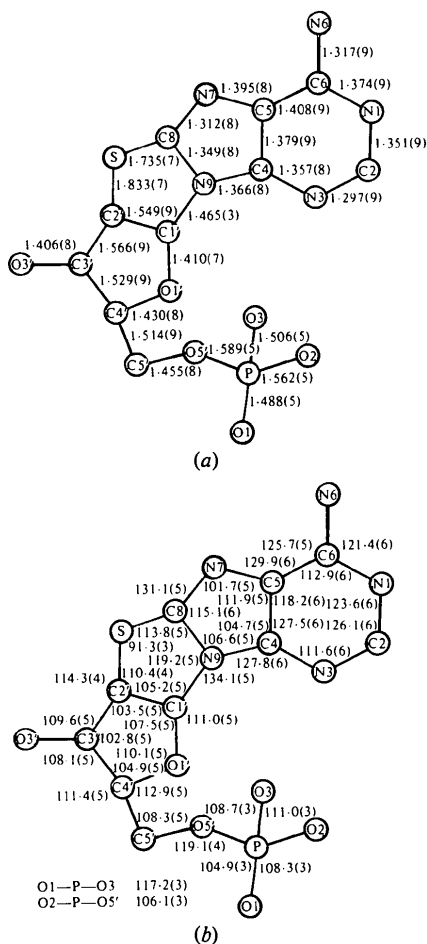


Fig. 1. Molecular geometry: (a) bond lengths (Å); (b) bond angles (°). Standard deviations are given in parentheses.

angles are compared with corresponding values in orthorhombic 5'-AMP (Neidle, Kühlbrandt & Achari, 1976) and also in monoclinic 5'-AMP (Kraut & Jensen, 1963). For example, in 8,2'-*S*-cyclo 5'-AMP, the N(9)—C(8) bond is shorter by 0.04 Å, the C(1')—N(9)—C(4) bond angle is larger by 10°, C(1')—N(9)—C(8) is smaller by 9° and N(9)—C(1')—C(2') is smaller by 8° compared to those of 5'-AMP. These deviations might be due to strains induced by cyclization.

The conformation of the molecule is shown by the stereoscopic representation in Fig. 2. The calculated least-squares planes are given in Table 5. The purine ring and the fused five-membered ring (*S*-cyclo ring) are almost coplanar with maximum deviations of 0.038 Å. The dihedral angles between purine and sugar rings and between purine and *S*-cyclo rings are 59.2 and 0.9°, respectively. The conformation of the sugar ring can be assessed on the basis of the endocyclic torsion angles in Table 6. The phase angle of pseudorotation

(Altona & Sundaralingam, 1972), $P = 232.7^\circ$, corresponds to C(4')-*endo* pucker (4E) and the displacement of atom C(4') from the least-squares plane through the other four atoms in the ring is 0.486 Å. The glycosidic torsion angle $\chi[\text{O}(1')\text{—C}(1')\text{—N}(9)\text{—C}(8)]$ is 118.8° (*high-anti*). The orientation of the C(5')—O(5') bond is *gauche-trans*. There is no short contact between a phosphate O atom and any atom of the base ring. The contact between C(5') and O(2) is 3.210 Å which is roughly equal to the sum of the van der Waals radii of the atoms involved. The base planes stack along the *c* axis with much overlapping, as shown in Fig. 3, and with an interplanar spacing of 3.4 Å.

Several intermolecular hydrogen bonds found in the crystal are summarized in Table 7. The molecular packing is shown in Fig. 4, where 8,2'-*S*-cyclo 5'-AMP molecules are linked to each other by strong hydrogen bonds through three water molecules.

The torsion angles of H(1')—C(1')—C(2')—H(2'), H(2')—C(2')—C(3')—H(3') and H(3')—C(3')—C(4')—H(4') are important in the determination of the conformation of the furanose ring in aqueous solution using the spin-spin coupling constants of PMR spectra. The torsion angles (φ) computed from idealized H atom positions obtained by assuming a normal tetrahedral angle around the relevant C atom and a C—H bond length of 1.08 Å, and the observed torsion angles (φ')

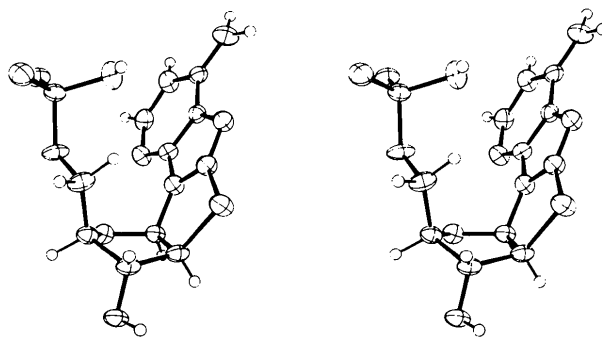


Fig. 2. Stereoscopic view of the molecule; the thermal ellipsoids correspond to 50% probability.

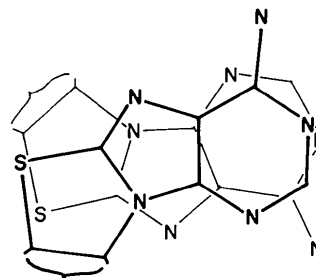


Fig. 3. The superposition of the stacked-ring portions of 8,2'-*S*-cyclo 5'-AMP molecules projected onto the upper adenine ring (heavy lines).

Table 5. *Least-squares planes*

Atoms marked with an asterisk are those used in the determination of the best planes. Deviations from the planes are in Å.

Adenine ring (plane I)					
N(1)*	-0.026 (11)	C(6)*	0.019 (11)	S	-0.038 (10)
C(5)*	0.002 (11)	N(6)	0.068 (11)	C(4)*	0.002 (11)
N(9)*	-0.008 (11)	N(3)*	0.016 (11)	C(8)*	-0.009 (12)
C(2')	-0.043 (12)	N(7)*	0.006 (11)	C(1')	0.013 (11)
C(2)*	-0.001 (12)				
Sugar ring (plane II)					
C(1')*	0.012 (16)	C(2')*	-0.012 (16)	C(3')*	0.008 (16)
C(4')	-0.482 (16)	C(5')	-1.988 (16)	O(1')*	-0.005 (15)
<i>S</i> -cyclo ring (plane III)					
S*	0.001 (6)	N(1)	-0.077 (8)	C(6)	-0.013 (8)
C(2')*	-0.015 (9)	C(5)	-0.013 (8)	C(1')*	0.017 (8)
C(4)	-0.018 (8)	N(9)*	-0.010 (8)	N(3)	-0.025 (8)
N(7)	0.012 (8)	C(2)	-0.055 (9)	N(6)	0.039 (8)
C(8)*	0.004 (9)				
Adenine ring and <i>S</i> -cyclo ring (plane IV)					
N(1)*	-0.038 (7)	C(6)*	0.017 (7)	S*	-0.004 (4)
C(5)*	0.009 (7)	N(6)	0.069 (7)	C(4)*	0.005 (7)
N(9)*	0.004 (6)	N(3)*	0.008 (7)	C(8)*	0.012 (7)
C(2')*	-0.016 (7)	N(7)*	0.024 (7)	C(1')*	0.027 (7)
C(2)*	-0.016 (8)				

The equations for the least-squares planes are in the form:

$$px + qy + rz + s = 0.$$

	<i>p</i>	<i>q</i>	<i>r</i>	<i>s</i>
Plane I	-0.223	0.169	-0.960	1.975
Plane II	-0.890	0.373	-0.261	1.048
Plane III	-0.228	0.155	-0.961	2.053
Plane IV	-0.225	0.162	-0.961	2.028

The dihedral angles between: planes I and II 59.2 (2)°
planes I and III 0.9 (2)

Table 6. *Selected torsion angles* (°)

C(1')-C(2')-C(3')-C(4')	-20.5 (6)
C(2')-C(3')-C(4')-O(1')	32.2 (6)
C(3')-C(4')-O(1')-C(1')	-33.1 (6)
C(4')-O(1')-C(1')-C(2')	19.4 (6)
O(1')-C(1')-C(2')-C(3')	2.0 (6)
N(9)-C(1')-C(2')-S	-2.3 (6)
O(1')-C(1')-C(2')-S	-120.8 (4)
O(1')-C(1')-N(9)-C(8)	118.8 (6)
O(1')-C(1')-N(9)-C(4)	-63.0 (8)
C(8)-S-C(2')-C(3')	-114.9 (5)
S-C(2')-C(3')-C(4')	99.6 (5)
S-C(2')-C(3')-O(3')	-145.6 (4)
C(1')-C(2')-C(3')-O(3')	94.3 (6)
O(1')-C(4')-C(5')-O(5')	45.4 (7)
C(3')-C(4')-C(5')-O(5')	163.2 (5)
C(4')-C(5')-O(5')-P	-166.3 (4)
C(5')-O(5')-P-O(1)	167.3 (5)
C(5')-O(5')-P-O(2)	52.8 (5)
C(5')-O(5')-P-O(3)	-66.7 (5)

using the H atom coordinates found in a difference Fourier map, are summarized in Table 8 together with those of related compounds.

From X-ray studies it is known that the furanose ring of usual nucleotides occurs in two conformations,

Table 7. *Distances* (Å) and *angles* (°) involved in hydrogen bonds

Standard deviations are in parentheses.
The superscripts refer to the equivalent positions:

(i)	x, y, z	(v)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
(ii)	$1 + x, y, z$	(vi)	$\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z$
(iii)	$1 - y, 1 - x, \frac{1}{2} - z$	(vii)	$\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} + z$
(iv)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$		

<i>D</i> ' H... <i>A</i>	<i>D</i> ... <i>A</i>	H... <i>A</i>	$\angle D-H\cdots A$	$\angle H-D\cdots A$
N(1)-H(1)...O(3') ⁱⁱ	2.711 (7)	1.89 (9)	158 (8)	15 (6)
O(3')-H(3')...O(1) ^{iv}	2.790 (7)	1.95 (9)	166 (8)	10 (6)
N(6)-H(6')...O(W1) ⁱⁱ	2.837 (8)	1.89 (9)	159 (8)	14 (5)
N(6)-H(6'')...O(W2) ⁱⁱⁱ	2.726 (10)	1.82 (9)	167 (8)	8 (5)
O(2)-H(2'')...O(W3) ⁱ	2.584 (8)	1.85 (9)	161 (9)	13 (7)
O(W1)-H(W1)...O(3) ⁱⁱⁱ	3.082 (7)	2.12 (9)	175 (8)	4 (6)
O(W1)-H(W1')...O(1) ⁱ	2.773 (7)	1.91 (9)	172 (8)	6 (6)
O(W2)-H(W2)...N(7) ⁱⁱ	2.820 (9)	1.76 (9)	149 (7)	19 (4)
O(W2)-H(W2')...O(3) ⁱⁱⁱ	2.744 (9)	2.12 (9)	156 (10)	18 (8)
O(W3)-H(W3)...O(3') ⁱⁱ	2.942 (8)	2.17 (9)	153 (8)	20 (6)
O(W3)-H(W3')...O(1) ⁱ	2.790 (8)	1.86 (9)	166 (8)	9 (5)

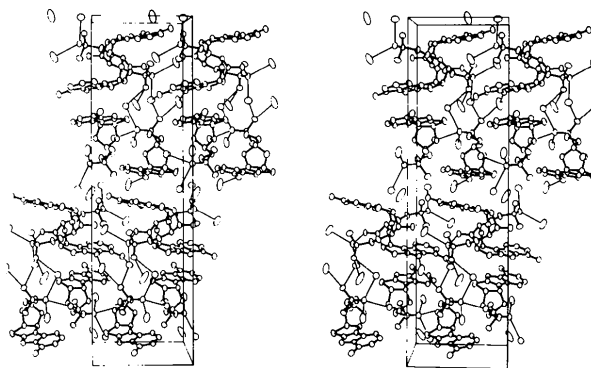


Fig. 4. Stereoscopic view of the molecular packing viewed along the *b* axis. Thin lines indicate the hydrogen bonds.

C(2')-endo and *C*(3')-endo. In solution the furanose ring seems to be in a state of rapid equilibrium between these two conformations (Altona & Sundaralingam, 1973). But in the case of cyclonucleotides, as shown in Table 8, the conformation of the furanose ring is classified as being in the *C*(4')-endo and *C*(4')-exo forms and, therefore, the furanose ring of the cyclonucleotide in solution is in an equilibrium state involving both the *C*(4')-endo and *C*(4')-exo forms. Table 9 shows the mean torsion angles of *C*(4')-endo and *C*(4')-exo, and the coupling constants calculated by the modified Karplus equation (Altona & Sundaralingam, 1973). As shown in Table 9, $J_{H1'-H2'}(\text{obs})$ is apparently smaller than $J_{H1'-H2'}(\text{calc})$. This result is consistent with the fact that the observed coupling constant between *cisoidal* protons in arabinose rings is smaller than that calculated by use of the modified Karplus equation (Jaworski, Ekiel & Shugar, 1978). Furthermore, in the case of 8,2'-*S*-cyclo 5'-AMP, in which *C*(2') is connected to a S atom instead of the O atom found in usual arabinose rings, the difference in the electronegativity resulting from the substitution of

Table 8. Torsion angles ($^{\circ}$) involving hydrogen atoms as obtained from the X-ray diffraction studies (φ , φ' , see text)

	H(1')-H(2')		H(2')-H(3')		H(3')-H(4')			Reference
	φ	φ'	φ	φ'	φ	φ'		
8,2'- <i>S</i> -cyclo 5'-AMP	2	1	92	104	84	91	C(4')-endo	This work
2,2'- <i>O</i> -cyclo 5-S(CH ₃) ₂ 6-oxo C ⁱ	7	14	111	92	103	103	C(4')-endo	<i>a</i>
2,2'- <i>O</i> -cyclo 5-Cl 6-oxo C ⁱⁱ	4	23	100	83	100	98	C(4')-endo	<i>a</i>
2,2'- <i>O</i> -cyclo U ⁱⁱⁱ (I)	7	2	93	96	88	101	C(4')-endo	<i>b</i>
(II)	15	12	81	88	81	91	C(4')-endo	<i>b</i>
2,2'- <i>O</i> -cyclo 4-pyridone ^{iv} (I)	7	13	95	93	90	91	C(4')-endo	<i>c</i>
(II)	9	8	129	138	146	166	C(4')-exo	<i>c</i>
6,2'- <i>O</i> -cyclo C ^v	8	10	129	131	154	154	C(4')-exo	<i>d</i>

(i) 2,2'-Anhydro-1- β -D-arabinofuranosyl-6-oxocytosine-5-dimethylsulfonium chloride. (ii) 2,2'-Anhydro-1-3',5'-di-*O*-acetyl- β -D-arabinofuranosyl-5-chloro-6-oxocytosine. (iii) 2,2'-Anhydro-1- β -D-arabinofuranosyluracil. (iv) 2,2'-Anhydro-2-hydroxy-1- β -D-arabinofuranosyl-4-pyridone. (v) 6,2'-Anhydro-1- β -D-arabinofuranosyl-6-hydroxycytosine.

(*a*) Yamagata, Koshibe, Tokuoaka, Fujii, Fujiwara, Kanai & Tomita (1979). (*b*) Suck & Saenger (1973). (*c*) Hutcheon & James (1977). (*d*) Yamagata, Fujii, Kanai, Ogawa & Tomita (1979).

Table 9. Torsion angles of the C(4')-endo and C(4')-exo conformations, and a comparison of the observed and the calculated spin-spin coupling constants

Torsion angles ($^{\circ}$)	H(1')-H(2')		H(2')-H(3')		H(3')-H(4')	
	φ	φ'	φ	φ'	φ	φ'
C(4')-endo	7 (4)	11 (8)	95 (10)	93 (7)	91 (9)	96 (6)
C(4')-exo	9 (1)	9 (1)	129 (0)	135 (5)	150 (6)	160 (8)
Coupling constants (Hz)						
J_{calc} [C(4')-endo]	9.2	8.9	0.2	0.1	0.0	0.2
J_{calc} [C(4')-exo]	9.1	9.1	4.9	6.1	8.9	10.2
$J_{\text{obs}}^{(a)}$	6.7		2.7		3.3	

(*a*) Dingra, Sarma, Uesugi & Ikehara (1978).

the S atom could not be neglected. However, such an effect on $J_{\text{H}3'-\text{H}4'}$ is thought to be the smallest of the three coupling constants, and therefore the populations of the C(4')-endo and C(4')-exo conformers in aqueous solution were tentatively calculated to be 60 or 70% and 40 or 30%, respectively, when described by φ or φ' . In the stable sugar conformation of a cyclonucleotide such as 8,2'-*S*-cyclo 5'-AMP in aqueous solution it is plausible that the furanose ring is in equilibrium between the C(4')-endo and C(4')-exo conformations but not between the C(2')-endo and C(3')-endo conformations predicted by Dingra, Sarma, Uesugi & Ikehara (1978).

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