The Crystal and Molecular Structure of 5,6-Dihydroisocytidine Monohydrate, $C_9H_{15}N_3O_5.H_2O$

By Biserka Kojić-Prodić, Živa Ružić-Toroš and Emil Coffou

'Ruđer Bošković' Institute, 41001 *Zagreb, Box* 1016, *Yugoslavia*

$C_9H_{15}N_3O_5.H_2O$ crystallizes in space group $P2_1$ with $a = 10\cdot112$, $b = 7\cdot262$, $c = 7\cdot980$ Å, $\beta = 101\cdot25°$, $Z = 2$. The structure was solved by direct methods and refined by full-matrix least squares to $R = 0\cdot036$. The heterocycle exhibits a half-chair conformation with C(5) and C(6) displaced by $-0\cdot436$ and $0\cdot198$ Å on either side of the nucleobase plane. The ribose moiety has the C(3′)-*endo* conformation. The glycosidic torsional angle, $77\cdot2°$ is *anti*. The conformation around C(4′)-C(5′) is *gauche–gauche*. The packing is dominated by hydrogen bonds. Sugar-sugar interaction is realized through the O(3′)-H···O(5′) ($2\cdot823$ Å) contact. Base-sugar residues are connected by O(2′)-H···N(3) ($2\cdot808$ Å) and O(5′)-H···O(4) ($2\cdot867$ Å) hydrogen bonds. The crystalline water molecule is also hydrogen-bonded to the base by N(2)-H···O(*W*) ($2\cdot816$ Å). There is no base stacking.

Introduction

The present work is part of a systematic study of nucleosides and bases containing 5,6-dihydropyrimidine derivatives to provide information on the conformation and hydrogen bonding. The presence of the saturated C(5)-C(6) bond is of a great influence on nucleobase geometry. For that reason the structure of cytidine (Furberg, Petersen & Rømming, 1965) cannot be compared with 5,6-dihydroisocytidine. The ribose moiety is in the C(3′)-*endo* conformation in both compounds and therefore its geometry is comparable to those given by Sundaralingam & Jensen (1965).

5,6-Dihydroisocytidine and its analogues were synthesized by Škarić, Gašpert, Hohnjec & Laćan (1974). The crystals for this investigation were kindly provided by Dr V. Škarić.

Experimental

The space group was determined from Weissenberg photographs recorded with Cu $K\alpha$ radiation. The

Table 1. *Crystallographic and physical data*

5,6-Dihydroisocytidine	$C_9H_{15}N_3O_5.H_2O$
F.W.	263·26
Space group	$P2_1$
a	10·112 (5)* Å
b	7·262 (3)
c	7·980 (3)
β	101·25 (5)°
U	574·7 Å³
D_c	1·423 g cm⁻³
Z	2
μ(Cu $K\alpha$)	7·14 cm⁻¹
Crystal size	0·028 × 0·057 × 0·284 mm
Crystal shape	needle

* Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digit.

diffraction symmetry and space group extinctions indicated $P2_1$ or $P2_1/m$; since the molecule is optically active, the space group is necessarily $P2_1$. Table 1 lists the crystallographic and physical data.

The intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer in the ω-scan mode (scan width $= 1\cdot2°$ θ, scan speed $= 0\cdot02°\theta$ s⁻¹) with graphite-monochromated Cu $K\alpha$ radiation. 874 independent reflexions in the range $3 < \theta < 70°$ were observed and only these were used in the calculations. Three standard reflexions were measured after every two hours to provide a check on crystal and instrumental stability and showed only the variations expected from counting statistics. The data were corrected for background, Lorentz and polarization effects, but not for absorption. A correction for monochromator polarization was included.

Structure determination and refinement

The structure was solved by the multisolution method with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). An overall temperature factor $(B = 1\cdot35$ Å²) as well as a scale factor were determined (Wilson, 1942) and used to compute normalized structure factors by routine *NORMAL* included in *MULTAN*. The solution was based on 250 reflexions with $|E| > 1\cdot1$. The E map corresponding to the solution with the best 'figure of merit' revealed the positions of 14 non-hydrogen atoms. The remaining four atoms were located from the resulting Fourier synthesis.

A full-matrix least-squares procedure minimizing $\sum w||F_o| - |F_c||^2$ with $w = 1/\sigma(F_o)^2$ was used.

Heavy-atom positional and isotropic thermal parameters and a scale factor were refined to an R of 0·097. Anisotropic refinement $(R = 0\cdot061)$ and a subsequent Fourier difference synthesis located the 17 H atoms. In the final refinement one scale factor, the atomic coordinates for all atoms (the y coordinates of C(4) and O(4) were kept fixed to define the origin in the polar

Table 2. *Final positional* ($\times 10^4$) *and thermal parameters* ($\times 10^3$) *for non-hydrogen atoms*

$$T = \exp\left[-2\pi^2(h^2 a^{*2}U_{11} + k^2 b^{*2}U_{22} + U_{33}l^2 c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^*)\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
N(1)	9052 (3)	5995 (7)	2412 (5)	18 (2)	17 (2)	33 (2)	−3 (2)	−3 (2)	3 (2)
C(2)	−9621 (4)	6065 (8)	3116 (6)	20 (2)	20 (3)	25 (3)	−2 (2)	0 (2)	−1 (2)
N(2)	−8914 (4)	4563 (7)	3569 (6)	26 (2)	18 (2)	54 (3)	−1 (2)	−7 (2)	0 (2)
N(3)	−8940 (4)	7655 (6)	3477 (5)	23 (2)	20 (2)	31 (2)	−1 (2)	−1 (2)	0 (2)
C(4)	−9466 (4)	9239 (0)	2739 (6)	20 (2)	19 (3)	36 (3)	−2 (2)	2 (2)	1 (2)
O(4)	−8860 (3)	725 (0)	3043 (6)	28 (2)	15 (2)	72 (3)	−6 (2)	−2 (2)	−5 (2)
C(5)	9263 (5)	9100 (9)	1403 (8)	34 (3)	30 (3)	55 (4)	−7 (3)	−13 (3)	14 (3)
C(6)	8332 (5)	7701 (9)	1883 (8)	23 (3)	23 (3)	58 (4)	1 (2)	−4 (3)	14 (3)
O(1')	7999 (3)	3705 (7)	526 (4)	16 (2)	30 (2)	32 (2)	−3 (1)	3 (1)	−7 (2)
C(1')	8291 (4)	4288 (8)	2283 (6)	21 (2)	20 (2)	28 (3)	−6 (2)	−5 (2)	−1 (2)
C(2')	6947 (5)	4415 (9)	2886 (6)	31 (2)	27 (3)	22 (3)	−5 (2)	2 (2)	0 (2)
O(2')	6717 (4)	2814 (7)	3799 (5)	38 (2)	53 (3)	28 (2)	−22 (2)	−7 (2)	16 (2)
C(3')	5908 (4)	4363 (8)	1203 (6)	18 (2)	24 (2)	23 (3)	−2 (2)	3 (2)	3 (2)
O(3')	4608 (3)	3758 (7)	1318 (5)	18 (2)	36 (2)	43 (2)	−3 (2)	6 (2)	3 (2)
C(4')	6605 (4)	3170 (8)	65 (6)	15 (2)	22 (3)	31 (3)	−1 (2)	−2 (2)	−4 (2)
C(5')	6116 (5)	3425 (9)	−1816 (7)	32 (3)	30 (3)	33 (3)	−4 (2)	2 (2)	−1 (2)
O(5')	6196 (3)	5290 (7)	−2366 (5)	26 (2)	37 (2)	37 (2)	4 (2)	6 (2)	6 (2)
O(W)	3884 (3)	4309 (9)	4812 (5)	33 (2)	69 (3)	50 (3)	7 (2)	−1 (2)	−23 (3)

space group), and anisotropic thermal parameters (isotropic for H) (229 in all) were varied. Corrections for extinction were not applied. The final agreement indices were: $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.036$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.047$.

The scattering factors given by Cromer & Mann (1968) and for H by Stewart, Davidson & Simpson (1965) were used. The calculations were carried out on the UNIVAC 1110 Computer at the University Computing Centre in Zagreb with the X-RAY 72/73 System (Stewart, Kruger, Ammon, Dickinson & Hall, 1972/73).

Atomic positional and thermal parameters are listed in Tables 2 and 3.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31462 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Positional parameters* ($\times 10^3$) *and isotropic thermal parameters* ($\times 10^2$) *for hydrogen atoms*

	x	y	z	$U(\text{Å}^2)$
H(N2)1	−789 (4)	476 (7)	398 (6)	2·3 (1·3)
H(N2)2	−913 (4)	359 (8)	327 (6)	3·1 (1·2)
H(5)1	884 (4)	45 (7)	106 (6)	2·6 (1·2)
H(5)2	948 (8)	845 (16)	16 (12)	11·8 (3·3)
H(6)1	761 (4)	751 (8)	88 (6)	3·1 (1·3)
H(6)2	785 (5)	816 (9)	298 (8)	5·7 (1·8)
H(1')	888 (4)	321 (6)	290 (6)	1·7 (1·2)
H(2')	679 (5)	576 (8)	352 (7)	3·3 (1·4)
H(O2')	732 (4)	274 (8)	459 (6)	4·2 (1·3)
H(3')	584 (4)	564 (7)	64 (6)	2·3 (1·2)
H(O3')	469 (4)	267 (8)	171 (6)	3·4 (1·3)
H(4')	650 (4)	178 (7)	40 (6)	1·8 (1·2)
H(5')1	663 (5)	259 (8)	−245 (7)	2·9 (1·3)
H(5')2	512 (4)	307 (7)	−210 (6)	2·9 (1·4)
H(O5')	692 (4)	552 (6)	−256 (6)	1·8 (1·1)
H(OW)1	427 (5)	410 (10)	418 (8)	6·1 (1·7)
H(OW)2	442 (6)	481 (10)	557 (9)	8·5 (2·2)

Description and discussion of the structure

The structural formula and numbering of the atoms are given in Fig. 1. A perspective view of the molecule
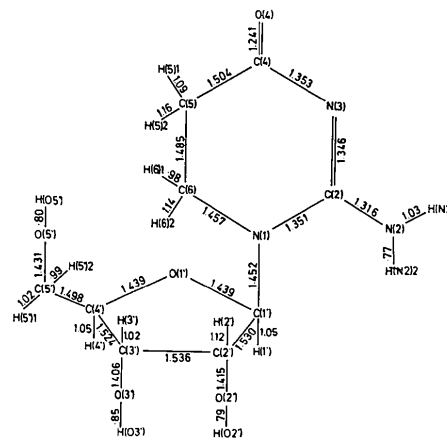

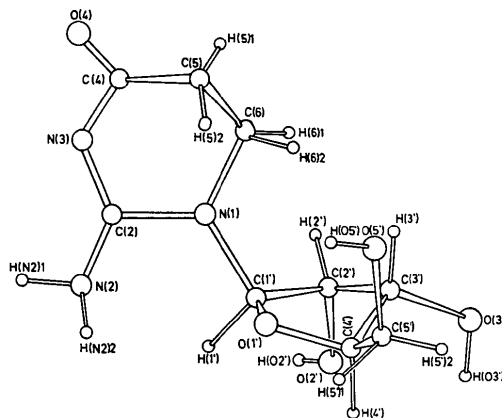Fig. 1. The structural formula and numbering of the atoms.

Fig. 2. Perspective view of the molecule.

Table 4. Bond distances (Å) and angles (°)

C(2)—N(1)	1·351 (5)	C(2)——N(1) -C(6)	119·2 (5)	C(4) —C(5)--H(5)2	111 (4)
C(2)—N(2)	1·316 (7)	N(1)——C(2) -N(3)	123·1 (5)	C(6) —C(5)--H(5)1	116 (2)
C(2)—N(3)	1·346 (7)	N(2)——C(2) -N(1)	121·7 (5)	C(6) --C(5)--H(5)2	100 (5)
C(4)—O(4)	1·241 (5)	N(2)——C(2) -N(3)	115·1 (4)	H(5)1 -C(5)--H(5)2	106 (6)
C(4)—N(3)	1·353 (5)	C(2)——N(3) -C(4)	119·6 (4)	N(1) —C(6)—H(6)1	112 (3)
C(4)—C(5)	1·504 (6)	O(4)——C(4) -N(3)	121·1 (4)	N(1) —C(6)—H(6)2	107 (3)
C(5)—C(6)	1·485 (9)	O(4)——C(4) -C(5)	121·2 (4)	C(5)—C(6)—H(6)1	107 (3)
C(6)—N(1)	1·457 (8)	N(3)——C(4) -C(5)	117·4 (3)	C(5)—C(6)—H(6)2	113 (3)
C(1') -N(1)	1·452 (7)	C(4)——C(5) -C(6)	111·1 (5)	H(6)1 -C(6)—H(6)2	108 (4)
C(1') -C(2')	1·530 (7)	C(5)——C(6) -N(1)	110·5 (4)	N(1)—C(1') -H(1')	111 (2)
C(2') -C(3')	1·536 (6)	C(2)——N(1)-C(1')	122·1 (5)	C(2')—C(1') -H(1')	111 (2)
C(3') -C(4')	1·524 (7)	C(6)——N(1)-C(1')	118·5 (4)	O(1')—C(1') -H(1')	103 (3)
C(4') -C(5')	1·498 (7)	N(1)——C(1')-C(2')	114·7 (5)	C(1')—C(2') -H(2')	114 (3)
O(1')-C(1')	1·439 (6)	N(1)——C(1')-O(1')	109·0 (4)	C(3')—C(2') -H(2')	107 (2)
O(1')-C(4')	1·439 (5)	C(2')——C(1')-O(1')	107·4 (3)	O(2')—C(2') -H(2')	115 (3)
O(2')-C(2')	1·415 (8)	C(1')——C(2')-C(3')	102·8 (4)	C(2')—C(3')' -H(3')	110 (2)
O(3')-C(3')	1·406 (6)	C(1')——C(2')-O(2')	111·0 (5)	C(4')—C(3') -H(3')	105 (3)
O(5')-C(5')	1·431 (8)	C(3')——C(2')-O(2')	106·1 (4)	O(3')—C(3') -H(3')	109 (3)
C(5)—H(5)1	1·09 (5)	C(2')——C(3')-O(3')	116·1 (4)	C(3')—C(4') -H(4')	108 (3)
C(5)—H(5)2	1·16 (10)	C(2')——C(3')-C(4')	102·5 (4)	C(5')—C(4') -H(4')	110 (2)
C(6)—H(6)1	0·98 (4)	C(4')——C(3')-O(3')	114·1 (4)	O(1')—C(4') -H(4')	109 (2)
C(6)—H(6)2	1·14 (6)	C(3')——C(4')-C(5')	115·2 (4)	C(4')—C(5') -H(5')1	109 (3)
N(2)—H(N2)1	1·03 (4)	C(3')——C(4')-O(1')	103·8 (4)	C(4')—C(5') -H(5')2	108 (3)
N(2)—H(N2)2	0·77 (5)	C(4')——O(1')-C(1')	109·4 (4)	O(5')—C(5') -H(5')1	111 (3)
C(1') -H(1')	1·05 (4)	O(1')——C(4')-C(5')	109·8 (4)	O(5')—C(5') -H(5')2	106 (3)
C(2') -H(2')	1·12 (6)	C(4')——C(5')-O(5')	113·4 (5)	H(5')1-C(5') -H(5')2	109 (4)
C(3') -H(3')	1·02 (5)	C(2)——N(2)-H(N2)1	116 (3)	C(2')—O(2')-H(O2')	107 (4)
C(4') -H(4')	1·05 (5)	C(2)——N(2)-H(N2)2	125 (3)	C(3')—O(3')-H(O3')	107 (3)
C(5') -H(5')1	0·99 (6)	H(N2)1-N(2)-H(N2)2	115 (4)	C(5')—O(5')-H(O5')	111 (3)
C(5') -H(5')2	1·02 (4)	C(4)——C(5) -H(5)1	111 (2)	H(W)1—O(W)-H(W)2	104 (7)
O(2')-H(O2')	0·79 (4)				
O(3')-H(O3')	0·85 (5)				
O(5)—H(O5')	0·80 (4)				
O(W)-H(W)1	0·71 (7)				
O(W)-H(W)2	0·81 (6)				

Table 5. Least-squares planes through the base and sugar

Atoms included in calculations of least-squares planes are denoted by an asterisk.

		Displacement (Å)
Heterocycle	N(1)*	0·034
	C(2)*	−0·070
	N(3)*	0·069
	C(4)*	−0·033
	N(2)	−0·259
	O(4)	0·087
	C(5)	−0·436
	C(6)	0·198
	C(1')	0·093
	H(N2)1	1·618
	H(N2)2	−0·502
	H(5)1	−1·565
	H(5)2	−1·556
	H(6)1	−0·228
	H(6)2	1·312
Ribose	C(1')*	−0·049
	C(2')*	0·029
	C(4')*	−0·031
	O(1')*	0·051
	C(3')*	0·552
	C(5')	0·689
	O(2')	−1·263
	O(3')	0·261
	O(5')	2·080

Table 6. Dihedral angles describing the conformation of the molecule

The positive sense of the rotation is clockwise while looking along the *BC* bond. Greek letters correspond to Sundara-lingam's (1969) notation.

	A	B	C	D	Angles (°)
χ	O(1')—C(1')-N(1) -C(6)				77·2 (5)
τ₀	C(4')—O(1')-C(1')-C(2')				−9·3 (6)
τ₁	O(1')—C(1')-C(2')-C(3')				−14·6 (6)
τ₂	C(1')—C(2')-C(3')-C(4')				31·4 (6)
τ₃	C(2')—C(3')-C(4')-O(1')				−37·6 (5)
τ₄	C(3')—C(4')-O(1')-C(1')				29·6 (6)
	O(1')—C(1')-N(1) -C(2)				102·8 (3)
	C(2)—N(1)-C(6) -C(5)				179·6 (6)
	N(3)—C(4) -C(5) -C(6)				10·2 (5)
	C(4)--C(5) -C(6) -N(1)				−177·5 (7)
	C(2')—C(1')-N(1) -C(2)				−17·5 (3)
	C(2')—C(1')-N(1) -C(6)				−43·1 (6)
	O(2')—C(2')-C(3')-O(3')				39·9 (6)
	O(5')—C(5')'-C(4')-O(1')				−60·7 (6)
ψ	O(5')—C(5')-C(4')-C(3')				56·0 (6)
	N(1)—C(1')-C(2')-O(2')				−140·4 (4)
	N(1)—C(1')-C(2')-C(3')				106·6 (5)
	N(1)—C(1')-O(1')-C(4')				−134·0 (4)
ψ'	C(5')—C(4')-C(3')-O(3')				76·0 (6)
	C(5')—C(4')-C(3')-C(2')				−157·6 (5)
	C(5')—C(4')-O(1)'-C(1')				153·3 (5)
	H(2')—C(2')-O(2')-H(O2')				−71·5 (5)
	H(3')—C(3')-O(3')-H(O3')				175 (5)
	H(5')1-C(5')-O(5')-H(O5')				−37 (5)
	H(5')2-C(5')-O(5')-H(O5')				−155 (5)

is shown in Fig. 2. Molecular packing and hydrogen bonds are illustrated in Fig. 3.

Interatomic distances and angles are listed in Table 4, displacements of the atoms from the least-squares planes through the base and ribose in Table 5 and Fig. 4. Dihedral angles defining the conformation are presented in Table 6.

Base

The nucleobase is not planar due to the saturation of C(5)–C(6). The puckering of the base is illustrated in Fig. 4 and can be numerically described by the dihedral angles N(3)–C(4)–C(5)–C(6) of 10·2° and C(2)–N(1)–C(6)–C(5) of 179·6°. The displacements of C(5) and C(6) from the best least-squares plane defined by N(1), C(2), N(3), C(4) are −0·436 and 0·198 Å. The base exists in a twisted half-chair conformation. O(4) and N(2) are displaced from the least-squares plane by 0·087 and −0·259 Å, respectively. The C(4)–O(4) distance of 1·241 (5) Å indicates the keto form. According to the lengths C(2)–N(3) of 1·346 (7) Å and C(2)–N(2) of 1·316 (7) Å, the presence of a double bond in the ring is obvious. The amino tautomeric

state is thus confirmed in the crystal, in agreement with UV spectroscopic data (Škarić *et al.*, 1974). Bond distances N(1)–C(2) of 1·351 (5), N(3)–C(4) of 1·353 (5) and C(4)–C(5) of 1·504 (6) Å can be compared with the values found in saturated derivatives, *e.g.* 5,6-dihydrouracil (Rohrer & Sundaralingam, 1970), 5,6-dihydrouridine (Suck, Saenger & Zechmeister, 1972), 5,6-dihydro-2-thiouridine (Kojić, Liminga, Šljukić & Ružić-Toroš, 1974), 5,6-dihydro-2,4-dithiouridine (Kojić, Kvick & Ružić-Toroš, 1976) and 5,6-dihydro-2-thiouracil (Kojić, Ružić-Toroš & Coffou, 1976). The C(5)–C(6) distance of 1·485 (9) Å is significantly shorter than the sp^3 single bond value of 1·533 Å (Bartell, 1959). The shortening of this length is also observed in 5,6-dihydro-2-thiouracil (Kojić, Ružić-Toroš & Coffou, 1976).

Ribose moiety

Intramolecular dimensions (Table 4) are generally comparable to the values found in compounds containing C(3')-*endo* ribose (Sundaralingam & Jensen, 1965). Among calculated least-squares planes, the best is defined by C(1'), O(1'), C(2'), C(4') (Table 5). C(3')
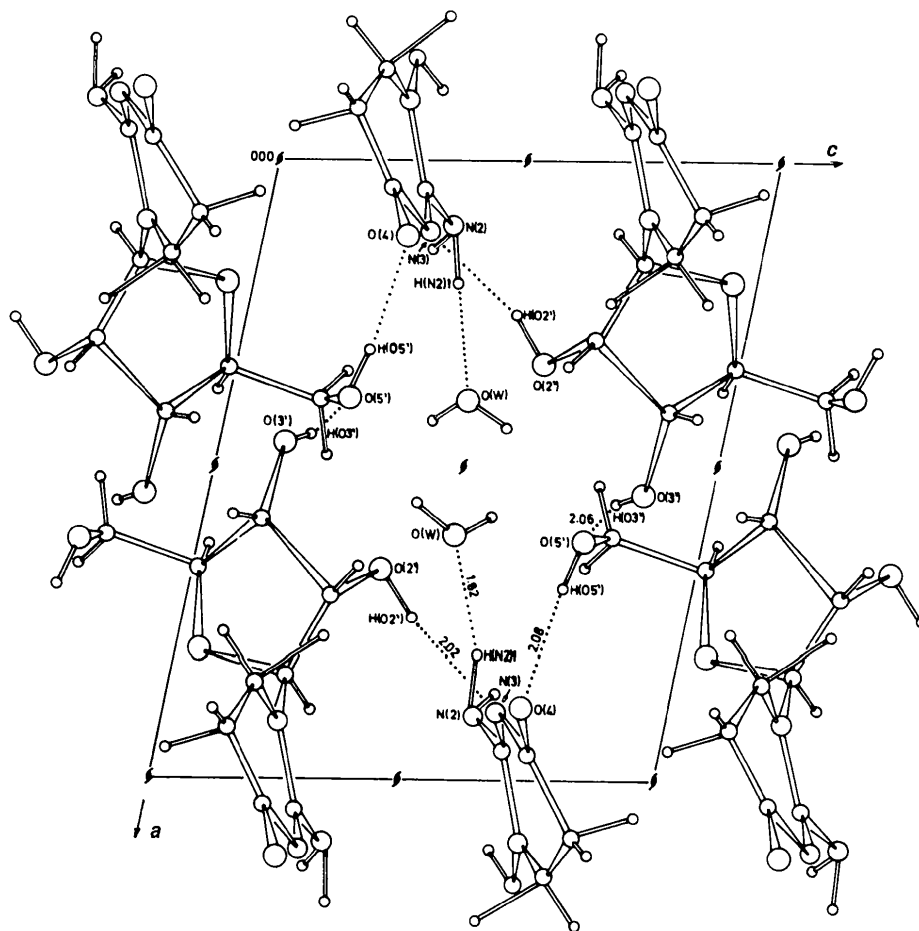

Fig. 3. Molecular packing and hydrogen bonds.

Table 7. *Hydrogen-bond distances* (Å) *and angles* (°)

X–H···Y	X···Y	X–H	H···Y	∠X–H···Y	Symmetry operation		
N(2)–H(N2)1···O(W)	2·816 (4)	1·03 (4)	1·82 (4)	162 (4)	xyz; x−1,	y,	z
O(2')–H(O2')····N(3)	2·808 (5)	0·79 (4)	2·02 (4)	176 (5)	xyz; x̄,	(½+y)−1,	1−z
O(3')–H(O3')····O(5')	2·823 (5)	0·85 (5)	2·06 (5)	149 (4)	xyz; 1−x,	(½+y)−1,	z̄
O(5')–H(O5')····O(4)	2·867 (5)	0·80 (4)	2·08 (4)	172 (4)	xyz; x̄,	½+y,	z̄

is displaced by 0·552 Å from this plane on the same side as C(5'). The ribose exists in the envelope C(3')-*endo* form. The conformation of the ribose part is described by means of dihedral angles listed in Table 6. The values of the angles $\tau_0, \tau_1, \tau_2, \tau_3, \tau_4$ are in good agreement with those in 4-thiouridine monohydrate (Saenger & Scheit, 1970). Shefter & Trueblood (1965) have defined φ_{OO} and φ_{OC} as the dihedral angles O(5')-C(5')-C(4')-O(1') and O(5')-C(5')-C(4')-C(3') respectively. In the present compound these $\varphi_{OO} = -60·7$ and $\varphi_{OC} = 56·0°$ so that the hydroxymethyl group O(5')-C(5') is *gauche* to C(4')-O(1') and also *gauche* to C(4')-C(3').

Conformation of the molecule

The orientation of the base relative to the sugar ring, described in terms of rotation about the C(1')-N(1) glycosidic bond for the sequence O(1')-C(1')-N(1)-C(6) is 77·2° (Sundaralingam, 1969; Altona &

Sundaralingam, 1972) and the molecule is *anti*. The large χ value is probably caused by the puckering of the base due to the presence of the saturated C(5)-C(6) bond (Sundaralingam, 1969).

Hydrogen bonding and molecular packing

The molecules are connected by hydrogen bonds between sugar-sugar, base-sugar and base-water forming a three-dimensional network. Base stacking does not occur.

Each molecule is involved in four independent hydrogen bonds to the neighbouring molecules (Table 7 and Fig. 3). The hydroxyl groups in the ribose moiety are engaged in hydrogen bonds O(2')-H···N(3) of 2·808 (5), O(3')-H···O(5') of 2·823 (5) and O(5')-H···O(4) of 2·867 (5) Å. The crystalline water molecule is hydrogen-bonded to the base by N(2) H(N2)1···O(W) of 2·816 (4) Å. There is one short contact O(W)···O(2') of 2·888 (8) Å and O(W)-H-O(2') angle of 105°.

The intensities were collected on a Philips PW 1100 diffractometer at the Department of General and Inorganic Chemistry, Faculty of Science, University of Zagreb. The authors thank Magistar Milenko Bruvo for collecting the data.
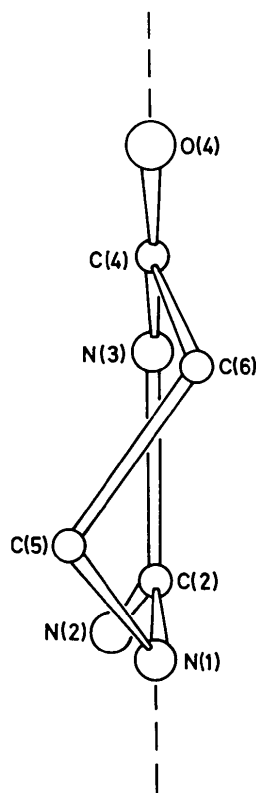

Fig. 4. Schematic view of the base parallel to the plane defined by N(1), C(2), N(3), C(4), illustrating the displacements of C(5) and C(6).

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Etude Structurale des Halogeno-Chalcogenures d'Etain(II).
I. Structure Cristalline de la Phase α de l'Iodosulfure d'Etain, 'Sn₂SI₂'

PAR NGUYEN-HUY-DUNG ET F. THÉVET

Laboratoire de Physique (Laboratoire de Chimie Structurale associé au CNRS N° 200), Faculté des Sciences Pharmaceutiques et Biologiques de Paris-Luxembourg, 4 avenue de l'Observatoire, 75270 Paris Cedex 06, France

The crystal structure of α-'Sn₂SI₂' was determined by the symbolic addition method. The cell is monoclinic, space group $B2/m$ with $a = 14·305$ (6); $b = 17·281$ (4); $c = 4·435$ (8) Å; $\gamma = 110°28$ (3)'; $Z = 6$. Atomic parameters were refined to a final $R = 0·045$. This structure, slightly deficient in SnS, is characterized by large and pseudo hexagonal columns of I atoms around mixed S and Sn positions. The remaining Sn atoms are in trigonal prism sites.

Les dérivés binaires de l'étain(II) ont déjà fait l'objet d'études structurales, notamment pour les chalcogénures SnS (Mosburg, Ross, Bethke & Toulmin, 1961), SnSe (Okazaki & Ueda, 1956), et les halogénures SnBr₂ (Masson & Howie, 1972), SnI₂ (Howie, Moser & Trevena, 1972). Quant aux halogénochalcogénures stanneux, peu de travaux leur ont été consacrés. L'étude systématique des systèmes ternaires Sn–X–X' (X=S, Se; X'=Br, I) nous a permis de mettre en évidence les composés stanneux suivants: les iodosulfures Sn₂SI₂ α et β, l'iodoséléniure Sn₃SeI₄ et le bromosulfure Sn₂SBr₂ (Thévet, Nguyen-Huy-Dung & Dagron, 1972, 1973; Thévet, 1975).

Novoselova, Tordiya, Odin & Popovkin (1971) ont publié le diagramme de phases du système SnS–SnI₂ et décrit deux composés définis: Sn₂S₀,₉₀I₂,₂₀ et Sn₃SI₄. Notre étude de ce même système n'a révélé qu'un seul iodosulfure de formule approchée Sn₂SI₂ mais qui présente un dimorphisme (Thévet *et al.*, 1972, 1973). Nous avons ensuite entrepris de résoudre la structure cristalline de ces deux variétés Sn₂SI₂, ce qui nous a conduit à modifier le diagramme de phases (Thévet, 1975).

L'article I de cette série décrit la structure de 'Sn₂SI₂' α. Ce composé est préparé par union directe du soufre et de l'iodure d'étain dans une ampoule de silice scellée sous vide en chauffant à 300°C. Il faut noter que cette phase α n'est obtenue uniquement qu'en présence d'un léger excès d'iodure d'étain SnI₂. Des monocristaux se forment par un recuit de treize jours à 315 ± 4°C.

Données expérimentales

L'iodosulfure 'Sn₂SI₂' α cristallise le plus souvent en aiguilles rouges très fines. Nous avons choisi un monocristal de forme parallélépipédique allongée suivant l'axe [001] et de dimensions 160 × 220 × 450 μm.

Les constantes du réseau sont: $a = 14,305$ (6); $b = 17,281$ (4); $c = 4,435$ (8) Å; $\alpha = \beta = 90°$; $\gamma = 110°28$ (3)' $Z = 6$; $\varrho_{exp} = 5,21$ g cm⁻³ et $\varrho_{cal} = 5,08$ g cm⁻³. $\mu = 170$ cm⁻¹ (λMo $K\alpha$).

Les réflexions hkl sont telles que $h + l = 2n$, ce qui est caractéristique des groupes spatiaux $B2$, Bm et $B2/m$.

Les intensités de 1427 réflexions indépendantes sont collectées jusqu'à l'angle $2\theta = 56°$ sur un diffractomètre automatique à 4 cercles Nonius CAD-4 en utilisant le rayonnement $K\alpha$ du molybdène filtré à partir d'un monochromateur de graphite et un balayage sur ω–2θ dont l'amplitude s est fonction de l'angle θ selon $s = 1,20 + 0,50$ tg θ. Elles sont ensuite corrigées des facteurs de Lorentz et de polarisation puis mises en échelle absolue par la méthode statistique de Wilson.

Les facteurs de structure normalisés E sont calculés pour toutes les réflexions en prenant comme facteur