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The Structure of 2′,3′-*O*-Isopropylideneuridine

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Abstract

$C_{12}H_{16}N_2O_6$ is orthorhombic, $P2_12_12_1$, with a = 19·890 (5), b = 12·789 (2), c = 5·236 (1) Å, Z = 4, U = 1331·9 Å^3, $F(000)$ = 600. Mo $K\alpha$ (μ = 0·123 mm^{-1}) intensities for 940 unique reflections up to $\sin\theta/\lambda$ = 0·538 Å^{-1} were collected on a CAD-4 diffractometer. Final R = 0·034. The glycosidic torsion angle χ_{CN} is 3·4°, significantly smaller than that (56·5°) in 2′,3′-*O*-methoxymethyleneuridine (MMU). The ribose moiety has a C(3′)-*exo*–C(4′)-*endo* twist conformation, in contrast to the C(2′)-*endo* conformation in MMU. However, the maximum amplitudes of pucker for the ribose and dioxolane rings are very nearly the same for the two structures. The conformation about C(4′)—C(5′) is *gauche–gauche* (φ_{OO} = −68·4, φ_{OC} = 51·3°).

Introduction

We report here the crystal and molecular structure of the modified nucleoside 2′,3′-*O*-isopropylideneuridine which has an additional five-membered ring *cis* to the ribose about C(2′)—C(3′). The present investigation was undertaken to assess the effect of this modification on the conformation of the ribofuranoside ring.

Experimental

Crystals were grown by evaporation from concentrated solutions in 50/50 water–acetone mixtures (Satyanarayana, Viswamitra & Ramakrishnan, 1976). The cell dimensions and space group were determined from rotation and Weissenberg photographs. The cell parameters were later refined by least squares from 25 reflections measured on a CAD-4 diffractometer.

Mo $K\alpha$ intensities were collected for a 0·1 × 0·1 × 0·5 mm crystal on the diffractometer in the ω–2θ scan mode. Background counts were measured for a sixth of the total scan angle on either side of the Bragg peak. Two reflections were monitored during the data collection to check for crystal and instrument stability. 940 unique reflections up to $\sin\theta/\lambda$ = 0·538 Å^{-1} were collected in the *hkl* octant and corrected for Lorentz and polarization factors.

Structure solution and refinement

The structure was solved by direct methods with *SHELX* 76 (Sheldrick, 1976). An E map computed with the best set of phases showed the positions of all the atoms. Block-diagonal least-squares refinement with isotropic temperature factors reduced R to 0·100. A difference map computed at this stage revealed the positions of all the H atoms except H′(5′), which was later fixed from geometrical considerations. Further refinement with anisotropic thermal parameters for non-hydrogen, isotropic for H atoms and a Cruickshank (1961) weighting scheme converged at R = 0·034. The function minimized was $\sum w(|F_o| - k|F_c|)^2$ where $w = 1/(a + b|F_o| + c|F_o|^2)$, a = 1·990,

Table 1. *Final positional parameters* (×10^4) *and equivalent isotropic temperature factors for the non-hydrogen atoms*

E.s.d.'s are in parentheses. U_{eq} values were calculated using the expression $U_{eq} = 1/(6\pi^2)\sum_i\sum_j\beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq} (Å^2)
N(1)	3556 (1)	3891 (2)	5238 (5)	0·037
C(2)	3172 (2)	4437 (3)	3510 (6)	0·033
O(2)	2559 (1)	4326 (2)	3400 (4)	0·038
N(3)	3511 (1)	5102 (2)	1926 (6)	0·037
C(4)	4199 (2)	5245 (3)	1823 (8)	0·046
O(4)	4442 (1)	5892 (3)	342 (6)	0·069
C(5)	4568 (2)	4605 (3)	3571 (8)	0·057
C(6)	4245 (2)	3978 (3)	5209 (8)	0·047
C(1′)	3171 (1)	3311 (3)	7262 (6)	0·035
O(1′)	3632 (1)	2947 (2)	9119 (4)	0·043
C(2′)	2773 (1)	2384 (3)	6249 (6)	0·033
C(3′)	2986 (1)	1471 (3)	7967 (6)	0·038
C(4′)	3633 (2)	1816 (3)	9239 (6)	0·042
C(5′)	4261 (2)	1365 (3)	8056 (8)	0·054
O(5′)	4260 (1)	1534 (2)	5391 (5)	0·059
O(2′)	2076 (1)	2531 (2)	6723 (5)	0·043
O(3′)	2455 (1)	1432 (2)	9810 (4)	0·047
C(7)	1856 (1)	1774 (3)	8555 (7)	0·042
C(8)	1522 (2)	875 (4)	7179 (9)	0·070
C(9)	1407 (2)	2325 (4)	10470 (8)	0·073

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

	x	y	z	U (Å^2)
H(3)	330	576	121	112
H(5)	505	471	356	57
H(6)	450	357	664	76
H(1′)	283	389	806	38
H(2′)	285	223	444	60
H(3′)	305	75	696	62
H(4′)	361	158	1097	31
H(5′)	468	178	890	35
H′(5′)	428	56	844	64
H(8)	110	112	614	65
H′(8)	187	54	592	108
H″(8)	133	32	862	98
H(9)	115	162	1136	144
H′(9)	96	267	975	90
H″(9)	155	252	1173	135

Table 3. *Bond lengths* (Å) *and angles* (°)

N(1)–C(2)	1·374 (4)	C(3′)–C(4′)	1·513 (5)
C(2)–N(3)	1·366 (4)	C(4′)–O(1′)	1·448 (5)
N(3)–C(4)	1·382 (4)	C(1′)–O(1′)	1·414 (4)
C(4)–C(5)	1·430 (5)	C(4′)–C(5′)	1·509 (5)
C(5)–C(6)	1·338 (6)	C(5′)–O(5′)	1·412 (5)
C(6)–N(1)	1·374 (4)	C(2′)–O(2′)	1·422 (4)
C(2)–O(2)	1·229 (3)	O(2′)–C(7)	1·431 (4)
C(4)–O(4)	1·232 (5)	C(7)–O(3′)	1·428 (4)
N(1)–C(1′)	1·503 (4)	O(3′)–C(3′)	1·432 (4)
C(1′)–C(2′)	1·521 (5)	C(7)–C(8)	1·511 (6)
C(2′)–C(3′)	1·533 (5)	C(7)–C(9)	1·517 (6)

C(1′)–N(1)–C(2)	115·5 (2)	C(3′)–C(2′)–O(2′)	105·5 (2)
C(1′)–N(1)–C(6)	123·7 (3)	C(2′)–C(3′)–C(4′)	105·7 (3)
C(2)–N(1)–C(6)	120·4 (3)	C(2′)–C(3′)–O(3′)	102·5 (2)
N(1)–C(2)–N(3)	116·2 (3)	C(4′)–C(3′)–O(3′)	109·9 (3)
N(1)–C(2)–O(2)	121·6 (3)	C(3′)–C(4′)–O(1′)	105·7 (3)
O(2)–C(2)–N(3)	122·1 (3)	C(3′)–C(4′)–C(5′)	114·3 (3)
C(2)–N(3)–C(4)	126·5 (3)	O(1′)–C(4′)–C(5′)	111·4 (3)
N(3)–C(4)–C(5)	113·9 (3)	C(4′)–C(5′)–O(5′)	110·2 (3)
N(3)–C(4)–O(4)	120·1 (3)	C(1′)–O(1′)–C(4′)	111·1 (2)
O(4)–C(4)–C(5)	125·9 (3)	C(2′)–O(2′)–C(7)	108·9 (2)
C(4)–C(5)–C(6)	120·5 (3)	O(2′)–C(7)–O(3′)	105·1 (2)
C(5)–C(6)–N(1)	122·2 (3)	O(2′)–C(7)–C(8)	109·2 (3)
N(1)–C(1′)–C(2′)	113·8 (2)	O(2′)–C(7)–C(9)	107·9 (3)
N(1)–C(1′)–O(1′)	108·5 (2)	O(3′)–C(7)–C(8)	110·7 (3)
O(1′)–C(1′)–C(2′)	108·7 (2)	O(3′)–C(7)–C(9)	109·2 (3)
C(1′)–C(2′)–C(3′)	104·2 (2)	C(8)–C(7)–C(9)	114·2 (3)
C(1′)–C(2′)–O(2′)	110·1 (2)	C(7)–O(3′)–C(3′)	107·1 (2)

$b = -0{\cdot}122$ and $c = 0{\cdot}007$. Scattering factors for C, N and O were computed from the function developed by Cromer & Waber (1965) and those for H were from Stewart, Davidson & Simpson (1965).

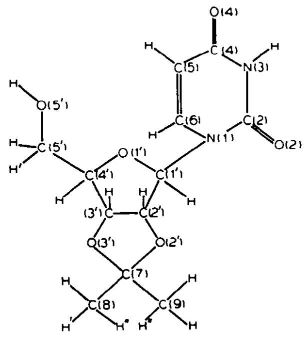

Fig. 1. Numbering in 2′,3′-*O*-isopropylideneuridine.

The positional parameters of the heavy and H atoms are given in Tables 1 and 2 respectively.* Bond distances and angles are given in Table 3. Fig. 1 shows the chemical structure and numbering scheme.

Results and discussion

Uracil base

The conformation of the uracil base about the glycosidic bond is *anti*. The torsion angle, $\chi_{CN} = 3{\cdot}4°$ (Fig. 2), is significantly small compared to the 56·5° in 2′,3′-*O*-methoxymethyleneuridine (MMU) (de Kok, Romers, de Leeuw, Altona & van Boom, 1977). The uracil base is essentially planar (Table 4) with the exocyclic O(2) and O(4) atoms deviating from the plane of the base by 0·088 (3) and 0·077 (3) Å

Table 4. *Least-squares planes and deviations of atoms* (Å)

E.s.d.'s in the atom deviations are 0·003 Å.

Uracil

Equation of plane

$$0{\cdot}0650x - 0{\cdot}7398y - 0{\cdot}6696z = 5{\cdot}0431$$

N(1)	−0·0150	C(5)	0·0240
C(2)	0·0245	C(6)	0·0020
N(3)	−0·0057	O(2)*	0·0885
C(4)	−0·0165	O(4)*	−0·0776

Ribose

Equation of plane

$$0{\cdot}6866x - 0{\cdot}1395y - 0{\cdot}7135z = -1{\cdot}0278$$

C(1′)	0·0000	C(4′)*	0·1585
C(2′)	0·0000	O(1′)	0·0000
C(3′)*	−0·1878	C(5′)*	1·5385

Dioxolane ring

Equation of plane

$$-0{\cdot}2140x - 0{\cdot}6404y - 0{\cdot}7376z = 5{\cdot}5506$$

C(7)	0·0035	C(3′)	−0·0027
O(2′)	−0·0023	O(3′)*	−0·4567
C(2′)	0·0040		

* Atoms not used in the calculation of the planes.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35698 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Torsion angles (°) involving non-hydrogen atoms*

The average e.s.d. is 1·6°.

C(6)—N(1)—C(1′)—O(1′)	3·4	C(2′)—C(3′)—C(4′)—O(1′)	21·9	C(3′)—C(4′)—C(5′)—O(5′)	51·3
C(2)—N(1)—C(1′)—O(1′)	−170·0	C(2′)—C(3′)—C(4′)—C(5′)	−101·0	C(1′)—C(2′)—O(2′)—C(7)	−112·5
O(1′)—C(1′)—C(2′)—C(3′)	7·2	O(3′)—C(3′)—C(4′)—C(5′)	149·0	C(3′)—C(2′)—O(2′)—C(7)	−0·6
O(1′)—C(1′)—C(2′)—O(2′)	120·0	O(3′)—C(3′)—C(4′)—O(1′)	−88·1	C(2′)—O(2′)—C(7)—O(3′)	19·9
C(1′)—C(2′)—C(3′)—C(4′)	−17·7	C(3′)—C(4′)—O(1′)—C(1′)	−18·1	O(2′)—C(7)—O(3′)—C(3′)	−32·6
C(1′)—C(2′)—C(3′)—O(3′)	97·5	C(4′)—O(1′)—C(1′)—C(2′)	6·7	C(7)—O(3′)—C(3′)—C(2′)	31·3
O(2′)—C(2′)—C(3′)—C(4′)	−133·7	O(1′)—C(4′)—C(5′)—O(5′)	−68·4	C(7)—O(3′)—C(3′)—C(4′)	143·4
O(2′)—C(2′)—C(3′)—O(3′)	−18·6				

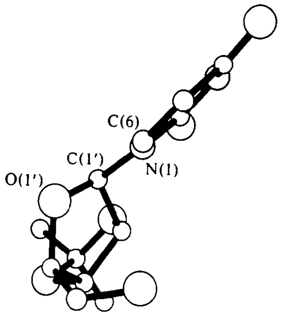

Fig. 2. View down *a* showing the low-*anti* conformation about C(1′)—N(1).

respectively on either side of the ring. These deviations could be due to the involvement of the keto O atoms in hydrogen bonds.

Ribose

The torsion angles about the furanose ring bonds are listed in Table 5. The ribose moiety has a C(3′)-*exo*–C(4′)-*endo* twist conformation, as shown by the phase angle of pseudorotation $P = 216{\cdot}3°$ (Fig. 3). This is in contrast to the C(2′)-*endo* conformation of the ribose moiety in MMU (de Kok *et al.*, 1977). C(3′) and C(4′) are displaced by 0·188 (3) and 0·158 (3) Å respectively from the plane of the other atoms. The maximum amplitude of pucker, $\tau_{m,\max} = 23{\cdot}70°$, is close to that of MMU (23·1°). However, it differs significantly from the average value of 38·0° for *S*-type rings (Altona & Sundaralingam, 1972) indicating a flattening of the ribose moiety. This could be due to the *cis* connection of the ribose and dioxolane rings about C(2′)—C(3′). The torsion angle O(3′)—C(3′)—C(2′)—O(2′) = −18·6° is much smaller than the normally observed range of ±45 to 65° (Saenger & Eckstein, 1970).

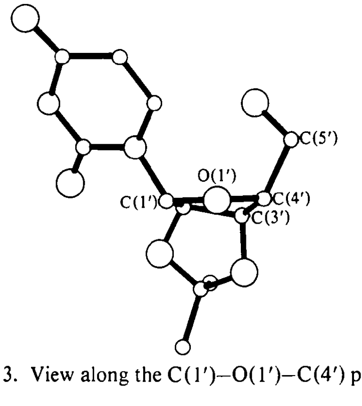

Fig. 3. View along the C(1′)—O(1′)—C(4′) plane.

Dioxolane ring

The five-membered dioxolane ring C(2′)—O(2′)—C(7)—O(3′)—C(3′) has an envelope conformation. O(3′) is displaced by 0·457 (3) Å from the plane of the other atoms (Table 4). C(3′), C(2′), O(2′) and C(7) form the best plane, as evidenced by the torsion angle

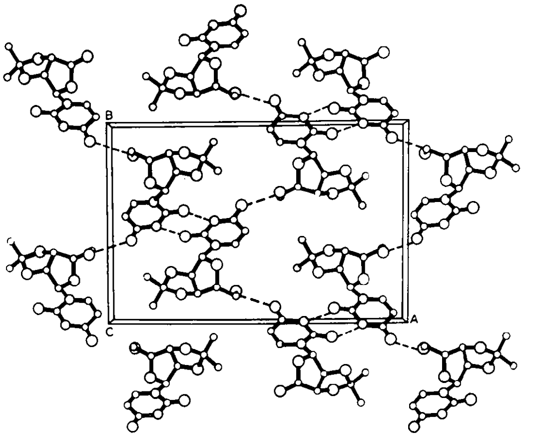

Fig. 4. Packing of the molecules viewed down *c*. Hydrogen bonds are shown as broken lines.

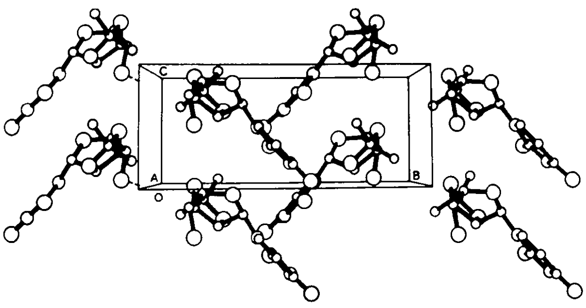

Fig. 5. Molecular packing viewed down *a*.

about C(2′)—O(2′) which is only −0·6°. The pseudorotation parameters for the dioxolane ring are P = 124°, $\lambda_{m,\max}$ = 33·9° (Sprang, Rohrer & Sundaralingam, 1978). This value is close to that of the dioxolane ring in MMU (32·3°).

The conformation about the exocyclic C(4′)—C(5′) bond is *gauche–gauche* with the torsion angles φ_{OO} = −68·4 and φ_{OC} = 51·3°.

Molecular packing

The packing of the molecules in the unit cell is shown viewed down c and a in Figs. 4 and 5 respectively. The molecules run in a helical fashion parallel to c. This is stabilized by the intermolecular hydrogen bond N(3)—H···O(2) (2·906 Å). Neighbouring helical columns are linked through the other hydrogen bond O(4)···H—O(5′) (2·720 Å). These are the only hydrogen bonds in the extended crystal structure.

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References

ALTONA, C. & SUNDARALINGAM, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

CRUICKSHANK, D. W. J. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Oxford: Pergamon Press.

KOK, A. J. DE, ROMERS, C., DE LEEUW, H. P. M., ALTONA, C. & VAN BOOM, J. H. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 487–493.

SAENGER, W. & ECKSTEIN, F. (1970). *J. Am. Chem. Soc.* **92**, 4712–4718.

SATYANARAYANA, M., VISWAMITRA, M. A. & RAMAKRISHNAN, P. (1976). *Curr. Sci.* **45**, 826–827.

SHELDRICK, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

SPRANG, S., ROHRER, D. C. & SUNDARALINGAM, M. (1978). *Acta Cryst.* B**34**, 2803–2810.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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The *trans-anti* Photodimer of 1-Methylthymine: Direct Evidence of X-ray Cleavage of Dimer into Monomers in the Crystalline State*

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Abstract

The title compound, $(C_6H_8N_2O_2)_2$, is monoclinic, $P2_1/c$, with a = 7·5420 (3), b = 6·2277 (2), c = 14·4633 (5) Å, β = 117·039 (3)°, Z = 2. Other pertinent information: D_x = 1·538 Mg m^{-3}, U = 605·08 Å^3, $F(000)$ = 296, μ(Cu $K\alpha$) = 1·0026 mm^{-1}, transmission = 0·800–0·922, T = 297 K. The structure was solved by direct methods. Refinement yielded $R(F)$ = 0·039 for 1052 nonzero counter data to 0·84 Å. The dimer is of the *trans-anti* type, having a crystallographic center of symmetry at the center of its cyclobutane ring. The pyrimidine ring is folded along the N(1)···C(4) line with a dihedral angle of 163·6 (1)° between two planes each consisting of four ring atoms. About 4% of the molecules exist in the monomeric form, presumably because of prolonged X-irradiation. E.s.d.'s of bond lengths and angles involving C, N, O atoms are 0·002 Å and 0·1°. Through pairs of centrosymmetrically related N(3)H···O(2) hydrogen bonds, the dimers form infinite chains in the [1$\bar{1}$0] direction.

Introduction

When frozen solutions of pyrimidines or N-methylated pyrimidines are irradiated by UV light, dimerization across the 5,6-double bonds takes place. Depending on the geometrical arrangement of pyrimidines with respect to the cyclobutane ring thus formed, and on the type of 5,6 : 5′,6′ linkage for the two pyrimidines, it was proposed that four different stereoisomers could be

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