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α-Thymidine at 105 K

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Key indicators

Single-crystal X-ray study
T = 105 K
Mean σ(C–C) = 0.001 Å
R factor = 0.032
wR factor = 0.086
Data-to-parameter ratio = 19.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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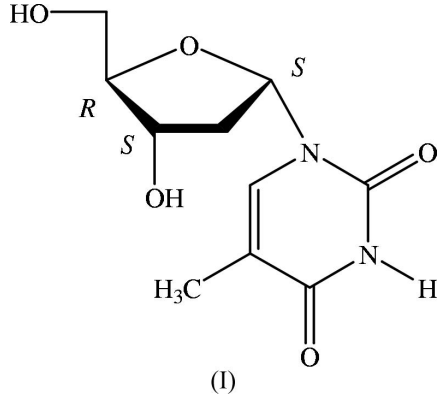
Two independent molecules in the crystal structure of the title nucleoside, 1-(2-deoxy-α-D-ribofuranosyl)-5-methyluracil, $C_{10}H_{14}N_2O_5$, form a dimer connected by two inter-base hydrogen bonds. The ring puckering modes are envelope C4′-*endo* and half-chair C3′-*exo*-C4′-*endo*, respectively, which are quite uncommon conformations for 2′-deoxyriboses.

Comment

Thymidine is one of the four major nucleosides in DNA, and its structure has been the subject of numerous studies by various experimental and theoretical techniques. The conformation of the 2′-deoxyribose sugar of the nucleosides is important for the structure of DNA. The conformation of the 2′-deoxyribose moiety with respect to the base is expected to influence which species (radicals as well as end products) are formed upon exposure of nucleosides and nucleotides to ionizing radiation. In particular, the yield of radiation-induced free radicals localized at the sugar is correlated with the yield of single-strand breaks (ssb's) in irradiated DNA (Becker & Sevilla, 2004). The processes leading to high yields of sugar radicals may be dependent on the sugar/base conformation. Radiation-induced processes in β-thymidine have been the subject of numerous studies (Sagstuen *et al.*, 1989, and references therein), whereas the isomer α-thymidine has not been investigated to date. Structural studies have also largely been limited to the β-isomer (Young *et al.*, 1969; Chekhlov, 1995; Lutz *et al.*, 2001), with only the cell parameters having been presented for the α-form (Tench, 1980). We present here a single-crystal structure analysis of α-thymidine, (I).



(I)

The asymmetric unit of (I) is shown in Fig. 1. The two α-thymidine molecules have fairly similar geometries, except that the O4—C9—C10—O5 torsion angle is 59.34 (9)° in molecule *A* and −68.49 (10)° in molecule *B* (Table 1). The

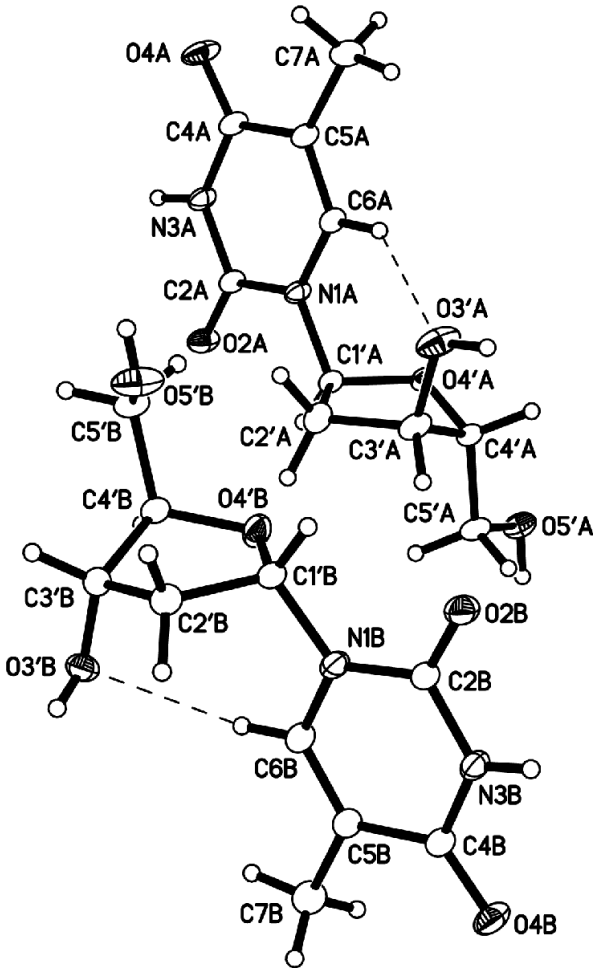


Figure 1
The asymmetric unit of (I) with the atomic numbering. Displacement ellipsoids are shown at the 50% probability level.

puckering of the five-membered rings can be classified as envelope C4′-*endo* and half-chair C3′-*exo*-C4′-*endo* for molecules *A* and *B*, respectively. Neither puckering mode is particularly common for furanose rings. The conformations of the 2′-deoxyribose ring in the crystal structures of α-cytidine (Post *et al.*, 1977) and β-thymidine are C2′-*exo*-C3′-*endo* and C3′-*exo*, respectively. The preferred sugar puckering modes in DNA are C2′-*endo* and C3′-*endo*.

Fig. 1 indicates the presence of equivalent pyrimidine–ribose intramolecular hydrogen bonds for both molecules, constraining the O4′—C1′—N1—C2 torsion angles to about 124° (Table 1). The crystal structures of various β-nucelosides also contain intramolecular C—H···O and/or C—H···N interactions between the base and the sugar (Chekhlov, 1995), but not the structure of α-cytidine.

The crystal packing is illustrated in Fig. 2. *A* and *B* molecules form dimers connected by N3*A*—H3*A*···O2*B* and N3*B*—H3*B*···O2*A* hydrogen bonds (Table 2). This motif is not present in the structure of the β-isomer of thymidine, but occurs in about 60 substituted thymine and uracil structures the Cambridge Structural Database (Version 5.26, November 2004; Allen, 2002).

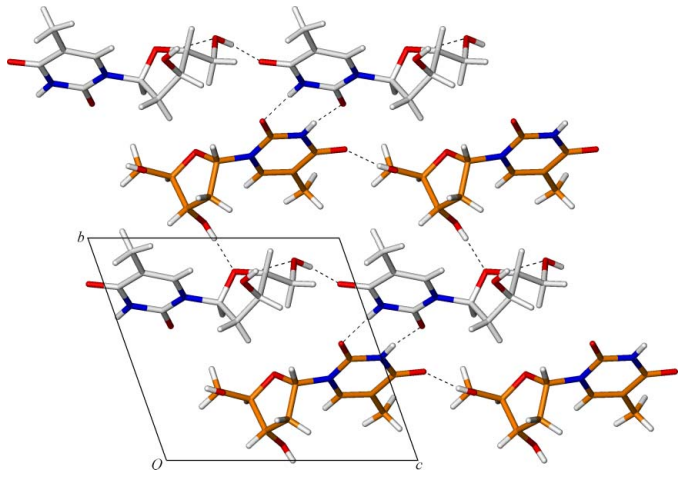


Figure 2
The molecular packing and unit cell of (I), viewed along the *a* axis. The C atoms in molecule *B* have been coloured orange. Hydrogen bonds are indicated by dotted lines.

For both molecules, atom (O5′-)H5′ is donated to atom O4 in a molecule of the same type related by translation along the *b* axis. The only qualitative difference between the hydrogen-bonding connectivities of molecules *A* and *B* resides with O3′—H3′, as atom H3′*A* is donated to atom O5′*A*($x-1, y, z$), while atom H3*B* is donated to atom O4′*A*($x-1, y-1, z$).

Experimental

α-Thymidine was obtained from Sigma–Aldrich. Crystals were prepared by slow evaporation of saturated aqueous solutions at room temperature.

Crystal data

$C_{10}H_{14}N_2O_5$
$M_r = 242.23$
Triclinic, *P*1
$a = 5.838$ (2) Å
$b = 9.883$ (4) Å
$c = 10.576$ (4) Å
$\alpha = 107.225$ (14)°
$\beta = 100.203$ (14)°
$\gamma = 98.894$ (14)°
$V = 559.5$ (4) Å^3
$Z = 2$
$D_x = 1.438$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7621 reflections
$\theta = 2.1$–40.5°
$\mu = 0.12$ mm^{-1}
$T = 105$ (2) K
Block, colourless
0.85 × 0.75 × 0.55 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Thin-slice ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.802$, $T_{max} = 0.938$
10 979 measured reflections
6311 independent reflections
6021 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 40.5°$
$h = -9 \rightarrow 10$
$k = -17 \rightarrow 17$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.086$
$S = 1.07$
6311 reflections
327 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 0.0016P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O4′*A*—C1′*A*	1.4361 (11)	O4′*B*—C1′*B*	1.4257 (12)
O4′*A*—C4′*A*	1.4523 (10)	O4′*B*—C4′*B*	1.4514 (12)
C2*A*—N1*A*—C1′*A*—O4′*A*	124.84 (8)	C2*B*—N1*B*—C1′*B*—O4′*B*	123.87 (9)
C4′*A*—O4′*A*—C1′*A*—C2′*A*	17.59 (8)	C4′*B*—O4′*B*—C1′*B*—C2′*B*	8.61 (9)
O4′*A*—C1′*A*—C2′*A*—C3′*A*	5.50 (8)	O4′*B*—C1′*B*—C2′*B*—C3′*B*	10.72 (9)
C1′*A*—C2′*A*—C3′*A*—C4′*A*	−24.58 (8)	C1′*B*—C2′*B*—C3′*B*—C4′*B*	−24.45 (8)
C2′*A*—C3′*A*—C4′*A*—O4′*A*	35.38 (8)	C2′*B*—C3′*B*—C4′*B*—O4′*B*	30.05 (9)
C3′*A*—C4′*A*—O4′*A*—C1′*A*	−33.64 (8)	C3′*B*—C4′*B*—O4′*B*—C1′*B*	−24.65 (9)
O4′*A*—C4′*A*—C5′*A*—O5′*A*	59.34 (9)	O4′*B*—C4′*B*—C5′*B*—O5′*B*	−68.49 (10)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3′*A*—H3′*A*···O5′*A*^{i}	0.83 (3)	2.00 (2)	2.7923 (14)	161 (3)
O5′*A*—H5′*A*···O4*A*^{ii}	0.84 (2)	1.93 (2)	2.7546 (12)	170 (2)
N3*A*—H3*A*···O2*B*^{iii}	0.87 (2)	1.98 (2)	2.8531 (12)	178 (2)
C6*A*—H61*A*···O3′*A*	0.95	2.43	3.2371 (15)	143
O3′*B*—H3′*B*···O4′*A*^{iv}	0.84 (2)	2.09 (2)	2.9144 (12)	166 (2)
O5′*B*—H5′*B*···O4*B*^{v}	0.72 (3)	2.09 (3)	2.7893 (13)	162 (3)
N3*B*—H3*B*···O2*A*^{vi}	0.86 (2)	1.96 (2)	2.8078 (12)	170 (2)
C6*B*—H61*B*···O3′*B*	0.95	2.35	3.1682 (16)	144

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z+1$; (iii) $x+1, y, z-1$; (iv) $x-1, y-1, z$; (v) $x-1, y, z-1$; (vi) $x-1, y, z+1$.

Positional parameters were refined for H atoms bonded to O and N atoms. H atoms bonded to C atoms were positioned with idealized geometry and fixed C—H distances in the range 0.95–1.00 Å. U_{iso}(H) values were $1.2U_{eq}$ or $1.5U_{eq}$ (–OH, methyl) of the carrier atom. In the absence of significant anomalous scattering effects, 2937 Friedel pairs were merged. The absolute configuration was known for the purchased material.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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