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5′-Azido-2′,5′-dideoxythymidine

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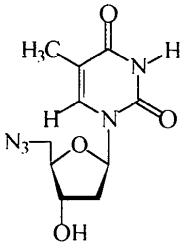
Abstract

The crystal structure of 5′-azido-2′,5′-dideoxythymidine, $C_{10}H_{13}N_5O_4$, contains two independent molecules. Both molecules are very similar, differing only in the orientation of the azido group. The sugar rings have approximately C(1′)-*exo*, C(2′)-*endo* furanose rings with the base in the *anti* conformation. The orientation about the C(4′)—C(5′) bond is *gauche–gauche* (+*sc*) for both molecules.

Comment

The synthesis of 5′-azido-2′,5′-dideoxythymidine has been reported by Hata, Yamamoto & Sekine (1975) and Yamamoto, Sekine & Hata (1980). It is an important starting material in the synthesis of 5′-amino-2′,5′-dideoxythymidine (Horwitz, Tomson, Urbanski & Chua, 1962), which is used for the syntheses of some oligonucleotide analogues with modified backbones, such as carbamates (Coull, Carlson & Weith, 1987), amides (Mesmaeker *et al.*, 1994) and phosphoramidates (Mag & Engels, 1989). Another application is the synthesis of nucleotide-dye conjugates (Smith, Fung, Hunkapillar, Hunkapillar & Hood, 1985).



(I)

A perspective view of the two independent molecules is shown in Fig. 1. Both molecules are very similar. They differ only in the orientation of the azido group. The azido group of the molecule with atom numbers appended by *A* has a *trans* orientation with respect to the C(4′*A*)—C(5′*A*) bond. The azido group of the other molecule has an orientation almost perpendicular to the C(4′)—C(5′) bond. Both thymine rings are almost planar. In each molecule the glycosyl bond has an *anti* conformation [torsion angles O(4′)—C(1′)—N(1)—C(2) −142.6 (1) and O(4′*A*)—C(1′*A*)—N(1*A*)—C(2*A*) −137.2 (1)°]. The orientation about the C(4′)—C(5′) bond is *gauche–gauche* (+*sc*) for both molecules. The sugar rings have approximately C(1′)-*exo*, C(2′)-*endo* twist conformations. The crystal packing (Fig. 2) shows no base-pairing. Instead, a two-dimensional layer structure is found with intermolecular hydrogen bonding between the thymine groups and the hydroxy groups of the sugar rings (Table 3).

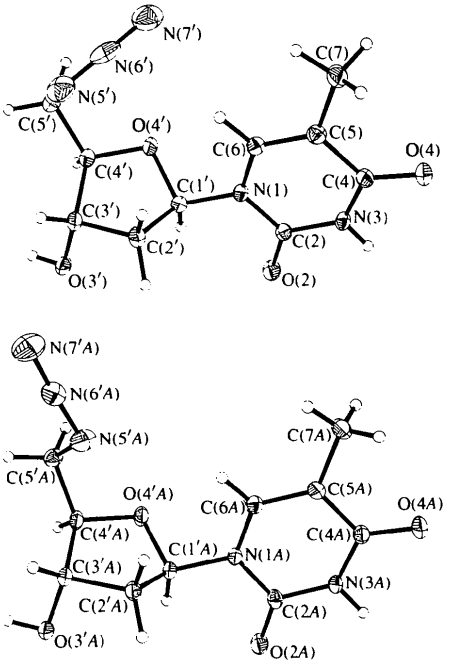


Fig. 1. Perspective views of the two independent molecules showing 50% probability ellipsoids and the atomic numbering scheme.

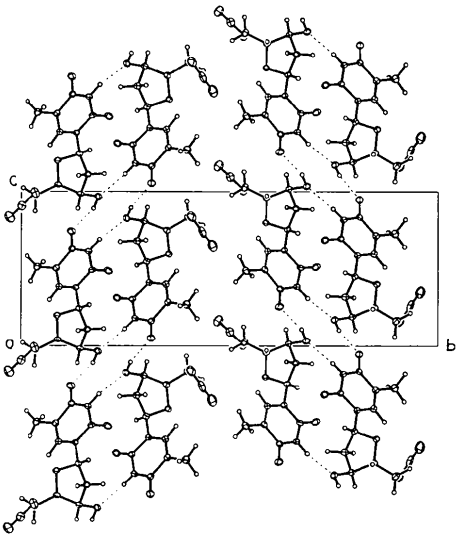


Fig. 2. Packing diagram viewed down the *a* axis.

Experimental

Crystals were grown by slow evaporation from a solution in chloroform/methanol.

Crystal data

$C_{10}H_{13}N_5O_4$
$M_r = 267.25$
Monoclinic
$P2_1$
$a = 5.381\ (1)$ Å
$b = 24.265\ (2)$ Å
$c = 8.988\ (2)$ Å
$\beta = 90.61\ (1)°$
$V = 1173.4\ (5)$ Å^3
$Z = 4$
$D_x = 1.513$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 50$–$69°$
$\mu = 0.97$ mm^{-1}
$T = 130$ K
Rod
$0.75 \times 0.28 \times 0.14$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans of 6 reflections
$T_{min} = 0.85$, $T_{max} = 1.00$
4958 measured reflections
4448 independent reflections
4447 observed reflections $[I > 0]$
$R_{int} = 0.019$
$\theta_{max} = 70°$
$h = 0 \rightarrow 6$
$k = -29 \rightarrow 29$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 92 min
intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.027$
$wR(F^2) = 0.081$
$S = 2.39$
4448 reflections
447 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F^2) + (0.03F^2)^2]$
$(\Delta/\sigma)_{max} = 0.09$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0069 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)
Absolute configuration: Flack (1983) parameter = 0.12 (10)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(3′)	0.2361 (2)	0.75170	0.1735 (1)	0.0200 (3)
O(4′)	0.1086 (2)	0.85351 (6)	0.4039 (1)	0.0181 (2)
O(2)	0.0637 (2)	0.72872 (6)	0.6883 (1)	0.0190 (2)
O(4)	−0.5528 (2)	0.81112 (6)	0.9472 (1)	0.0223 (2)
N(5′)	−0.1802 (3)	0.90726 (8)	0.1620 (2)	0.0320 (3)
N(6′)	−0.2648 (3)	0.93366 (7)	0.2614 (2)	0.0294 (3)
N(7′)	−0.3722 (3)	0.95798 (8)	0.3504 (2)	0.0380 (4)
N(1)	−0.1138 (2)	0.80644 (7)	0.5875 (1)	0.0147 (2)
N(3)	−0.2364 (2)	0.77307 (7)	0.8184 (1)	0.0159 (2)
C(1′)	0.0303 (3)	0.80008 (7)	0.4524 (2)	0.0153 (3)
C(2′)	−0.1131 (3)	0.77713 (8)	0.3187 (2)	0.0167 (3)
C(3′)	0.0548 (3)	0.79402 (7)	0.1917 (2)	0.0164 (3)
C(4′)	0.1743 (3)	0.84822 (7)	0.2497 (2)	0.0168 (3)
C(5′)	0.0956 (3)	0.90007 (8)	0.1673 (2)	0.0250 (3)
C(2)	−0.0835 (3)	0.76638 (7)	0.6968 (2)	0.0140 (3)
C(4)	−0.4218 (3)	0.81156 (7)	0.8356 (2)	0.0163 (3)
C(5)	−0.4461 (3)	0.85149 (7)	0.7161 (2)	0.0168 (3)
C(6)	−0.2937 (3)	0.84639 (7)	0.5985 (2)	0.0167 (3)
C(7)	−0.6355 (3)	0.89622 (8)	0.7294 (2)	0.0216 (3)
O(3′*A*)	0.7473 (2)	0.68407 (6)	1.0343 (1)	0.0200 (2)
O(4′*A*)	0.6326 (2)	0.58629 (6)	0.7986 (1)	0.0170 (2)
O(2*A*)	0.5588 (2)	0.70782 (6)	0.5133 (1)	0.0202 (2)
O(4*A*)	−0.0531 (2)	0.61969 (6)	0.2574 (1)	0.0240 (2)
N(5′*A*)	0.3098 (2)	0.53339 (7)	1.0103 (2)	0.0254 (3)
N(6′*A*)	0.2109 (2)	0.50112 (7)	1.0940 (2)	0.0226 (3)
N(7′*A*)	0.0981 (3)	0.47214 (8)	1.1665 (2)	0.0331 (3)
N(1*A*)	0.3861 (2)	0.63122 (6)	0.6205 (1)	0.0139 (2)
N(3*A*)	0.2578 (2)	0.66121 (7)	0.3871 (1)	0.0161 (2)
C(1′*A*)	0.5363 (3)	0.63891 (7)	0.7555 (2)	0.0142 (3)
C(2′*A*)	0.3928 (3)	0.65886 (7)	0.8900 (2)	0.0152 (3)
C(3′*A*)	0.5659 (3)	0.64180 (7)	1.0168 (2)	0.0153 (3)
C(4′*A*)	0.6826 (2)	0.58803 (7)	0.9567 (2)	0.0149 (3)
C(5′*A*)	0.5860 (2)	0.53565 (7)	1.0267 (2)	0.0171 (3)
C(2*A*)	0.4127 (3)	0.66983 (7)	0.5081 (1)	0.0147 (3)
C(4*A*)	0.0761 (3)	0.62148 (7)	0.3718 (2)	0.0158 (3)
C(5*A*)	0.0521 (3)	0.58388 (8)	0.4964 (2)	0.0162 (3)
C(6*A*)	0.2046 (3)	0.59120 (7)	0.6145 (2)	0.0156 (3)
C(7*A*)	−0.1409 (3)	0.53915 (8)	0.4881 (2)	0.0202 (3)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

O(3′)—C(3′)	1.427 (2)	O(3′*A*)—C(3′*A*)	1.424 (2)
O(4′)—C(1′)	1.433 (2)	O(4′*A*)—C(1′*A*)	1.430 (2)
O(4′)—C(4′)	1.439 (2)	O(4′*A*)—C(4′*A*)	1.444 (2)
O(2)—C(2)	1.212 (2)	O(2*A*)—C(2*A*)	1.212 (2)
O(4)—C(4)	1.232 (2)	O(4*A*)—C(4*A*)	1.236 (2)
N(5′)—N(6′)	1.194 (2)	N(5′*A*)—N(6′*A*)	1.213 (2)
N(5′)—C(5′)	1.494 (2)	N(5′*A*)—C(5′*A*)	1.493 (2)
N(6′)—N(7′)	1.154 (2)	N(6′*A*)—N(7′*A*)	1.139 (2)
N(1)—C(1′)	1.456 (2)	N(1*A*)—C(1′*A*)	1.462 (2)
N(1)—C(2)	1.390 (2)	N(1*A*)—C(2*A*)	1.387 (2)
N(1)—C(6)	1.374 (2)	N(1*A*)—C(6*A*)	1.378 (2)
N(3)—C(2)	1.385 (2)	N(3*A*)—C(2*A*)	1.379 (2)
N(3)—C(4)	1.376 (2)	N(3*A*)—C(4*A*)	1.379 (2)
C(1′)—C(2′)	1.526 (2)	C(1′*A*)—C(2′*A*)	1.521 (2)
C(2′)—C(3′)	1.520 (2)	C(2′*A*)—C(3′*A*)	1.521 (2)
C(3′)—C(4′)	1.552 (2)	C(3′*A*)—C(4′*A*)	1.548 (2)
C(4′)—C(5′)	1.518 (2)	C(4′*A*)—C(5′*A*)	1.513 (2)
C(4)—C(5)	1.451 (2)	C(4*A*)—C(5*A*)	1.452 (2)
C(5)—C(6)	1.351 (2)	C(5*A*)—C(6*A*)	1.346 (2)
C(5)—C(7)	1.494 (2)	C(5*A*)—C(7*A*)	1.503 (2)
C(1′)—O(4′)—C(4′)	106.8 (1)	C(1′*A*)—O(4′*A*)—C(4′*A*)	107.7 (1)
N(6′)—N(5′)—C(5′)	115.2 (1)	N(6′*A*)—N(5′*A*)—C(5′*A*)	113.9 (1)
N(5′)—N(6′)—N(7′)	172.3 (2)	N(5′*A*)—N(6′*A*)—N(7′*A*)	173.8 (2)
C(1′)—N(1)—C(2)	117.1 (1)	C(1′*A*)—N(1*A*)—C(2*A*)	117.3 (1)
C(1′)—N(1)—C(6)	121.1 (1)	C(1′*A*)—N(1*A*)—C(6*A*)	120.5 (1)
C(2)—N(1)—C(6)	121.3 (1)	C(2*A*)—N(1*A*)—C(6*A*)	121.7 (1)
C(2)—N(3)—C(4)	127.3 (1)	C(2*A*)—N(3*A*)—C(4*A*)	127.3 (1)
O(4′)—C(1′)—N(1)	108.6 (1)	O(4′*A*)—C(1′*A*)—N(1*A*)	107.8 (1)
O(4′)—C(1′)—C(2′)	103.8 (1)	O(4′*A*)—C(1′*A*)—C(2′*A*)	104.7 (1)
N(1)—C(1′)—C(2′)	115.2 (1)	N(1*A*)—C(1′*A*)—C(2′*A*)	114.8 (1)
C(1′)—C(2′)—C(3′)	101.1 (1)	C(1′*A*)—C(2′*A*)—C(3′*A*)	101.4 (1)
O(3′)—C(3′)—C(2′)	107.7 (1)	O(3′*A*)—C(3′*A*)—C(2′*A*)	107.5 (1)
O(3′)—C(3′)—C(4′)	111.5 (1)	O(3′*A*)—C(3′*A*)—C(4′*A*)	111.4 (1)
C(2′)—C(3′)—C(4′)	102.9 (1)	C(2′*A*)—C(3′*A*)—C(4′*A*)	102.4 (1)
O(4′)—C(4′)—C(3′)	107.1 (1)	O(4′*A*)—C(4′*A*)—C(3′*A*)	107.2 (1)
O(4′)—C(4′)—C(5′)	109.0 (1)	O(4′*A*)—C(4′*A*)—C(5′*A*)	108.9 (1)
C(3′)—C(4′)—C(5′)	115.2 (1)	C(3′*A*)—C(4′*A*)—C(5′*A*)	114.9 (1)
N(5′)—C(5′)—C(4′)	112.6 (1)	N(5′*A*)—C(5′*A*)—C(4′*A*)	109.6 (1)
O(2)—C(2)—N(1)	123.7 (1)	O(2*A*)—C(2*A*)—N(1*A*)	123.9 (1)
O(2)—C(2)—N(3)	122.2 (1)	O(2*A*)—C(2*A*)—N(3*A*)	122.2 (1)
N(1)—C(2)—N(3)	114.2 (1)	N(1*A*)—C(2*A*)—N(3*A*)	114.0 (1)
O(4)—C(4)—N(3)	120.5 (1)	O(4*A*)—C(4*A*)—N(3*A*)	120.0 (1)
O(4)—C(4)—C(5)	124.1 (1)	O(4*A*)—C(4*A*)—C(5*A*)	124.5 (1)
N(3)—C(4)—C(5)	115.5 (1)	N(3*A*)—C(4*A*)—C(5*A*)	115.5 (1)
C(4)—C(5)—C(6)	117.8 (1)	C(4*A*)—C(5*A*)—C(6*A*)	117.8 (1)
C(4)—C(5)—C(7)	118.8 (1)	C(4*A*)—C(5*A*)—C(7*A*)	118.8 (1)
C(6)—C(5)—C(7)	123.3 (1)	C(6*A*)—C(5*A*)—C(7*A*)	123.3 (1)
N(1)—C(6)—C(5)	123.7 (1)	N(1*A*)—C(6*A*)—C(5*A*)	123.3 (1)

C(4′)—O(4′)—C(1′)—C(2′)	−38.1 (1)
C(1′)—O(4′)—C(4′)—C(3′)	17.8 (1)
C(4′A)—O(4′A)—C(1′A)—C(2′A)	−32.4 (1)
C(1′A)—O(4′A)—C(4′A)—C(3′A)	10.4 (1)
N(6′)—N(5′)—C(5′)—C(4′)	91.6 (2)
C(2)—N(1)—C(1′)—O(4′)	−142.6 (1)
C(2)—N(1)—C(1′)—C(2′)	101.6 (2)
C(6)—N(1)—C(1′)—O(4′)	45.2 (2)
C(6)—N(1)—C(1′)—C(2′)	−70.6 (2)
N(6′A)—N(5′A)—C(5′A)—C(4′A)	−162.1 (2)
C(2A)—N(1A)—C(1′A)—O(4′A)	−137.2 (1)
C(2A)—N(1A)—C(1′A)—C(2′A)	106.5 (2)
C(6A)—N(1A)—C(1′A)—O(4′A)	50.7 (2)
C(6A)—N(1A)—C(1′A)—C(2′A)	−65.6 (2)
O(4′)—C(1′)—C(2′)—C(3′)	42.9 (2)
C(1′)—C(2′)—C(3′)—C(4′)	−30.8 (2)
C(2′)—C(3′)—C(4′)—O(4′)	9.5 (2)
O(4′)—C(4′)—C(5′)—N(5′)	−65.7 (2)
C(3′)—C(4′)—C(5′)—N(5′)	54.6 (2)
O(4′A)—C(1′A)—C(2′A)—C(3′A)	41.2 (1)
C(1′A)—C(2′A)—C(3′A)—C(4′A)	−33.3 (1)
C(2′A)—C(3′A)—C(4′A)—O(4′A)	15.4 (1)
O(4′A)—C(4′A)—C(5′A)—N(5′A)	−64.6 (2)
C(3′A)—C(4′A)—C(5′A)—N(5′A)	55.6 (2)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(3′)—H(O3′)···O(4^{i})	0.81 (2)	1.98 (3)	2.749 (2)	159 (2)
O(3′A)—H(O3′A)···O(4A^{ii})	0.90 (2)	1.92 (2)	2.751 (2)	152 (2)
N(3)—H(O3)···O(3′A^{iii})	0.88 (3)	2.05 (3)	2.905 (2)	163 (2)
N(3A)—H(O3A)···O(3′)	0.94 (3)	1.99 (3)	2.918 (2)	167 (2)

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (B. A. Frenz & Associates Inc., 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,4,7-Trimethyl-2,3-dihydro-4*H*-pyrido-[4,3-*e*]-1,2,4-thiadiazinium 1,1-Dioxide Iodide

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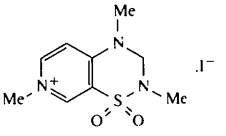
Abstract

The title compound, $C_9H_{14}N_3O_2S^+.I^-$, is a new drug developed as a structural derivative of the antihypertensive agent diazoxide. The C atom at the 3 position is sp^3 hybridized, whereas in the related compounds for which the structures have been determined so far it is sp^2 hybridized. The distances and angles around the N atom in the aromatic ring are consistent with a pyridinium cationic moiety.

Comment

The title compound, (I), is structurally related to diazide diuretics and diazoxide (Bandoli & Nicolini, 1977).



(I)

The cationic heterocycle exhibits an opening of the intra-cyclic angle C7—N8—C9 [118.3 (9)°] and a lengthening of C7—N8 and N8—C9 with respect to the values usually observed in a pyridine ring. This was also observed for 1-isopropyl-3-{[4-(1-piperidylamino)-3-pyridyl]sulfonyl}urea hydrogen nitrate (Dupont, Dideberg, Delarge, Dive & Thunus, 1982). Further examples