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Structure of a Nucleoside Analogue: α-(1-Thyminylmethyl)-γ-butyrolactone

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Abstract

The lactone ring adopts an envelope conformation with C5' at a distance of 0.457 (4) Å from the least-squares plane containing C2', C3', O4' and C4'. The thymine base is almost perpendicular to the sugar moiety and bases are stacked together along the *b* axis forming double molecular sheets. The crystal

packing is further stabilized by N3—H···O4 hydrogen bonds across the screw axes and C—H···O close contacts.

Comment

The title compound is an acyclic analogue of thymine nucleosides in which the sugar ring is cleaved at C1' to form a butyrolactone ring. The single crystals were grown by slow evaporation from an acetone/water (1/1) solution. The crystal structure analysis of the title compound was undertaken as part of our investigation of sugar-modified nucleoside analogues with particular reference to anti-AIDS compounds.

The bond distances and angles of the thymine base are within the normal range (Saenger, 1983). In the five-membered lactone ring, the C3'—O4' bond is 0.147 (4) Å shorter than the C4'—O4' bond usually found in the sugar moieties of nucleosides (Birnbaum, Stolarski, Kazimierczuk & Shugar, 1985). O4' is not adjacent to C1', the torsion angle χ cannot be determined but C2—N1—C1'—C2' (−101°) shows that the C1'—C2' bond is approximately perpendicular to the aglycon as in other acyclonucleosides in which C1' is a secondary C atom (Birnbaum, Cygler & Shugar, 1984). The C2', C3', O4' and C4' atoms of the five-membered lactone ring are planar to within ±0.026 Å and C5' is at a distance of 0.457 (4) Å from this plane, indicating that the lactone ring has an envelope configuration. The dihedral angle between the thymine base and the planar part of the lactone ring is 65.3 (1)°.

In the crystal lattice, the thymine bases form double molecular sheets by unit translation along the *b* axis and the molecular layers are stabilized by base stacking forces. There are close contacts between the thymine bases in the two layers [O2···C5 3.550 (4), C2···C5 3.469 (4), N1···C5 3.648 (4), N1···C7
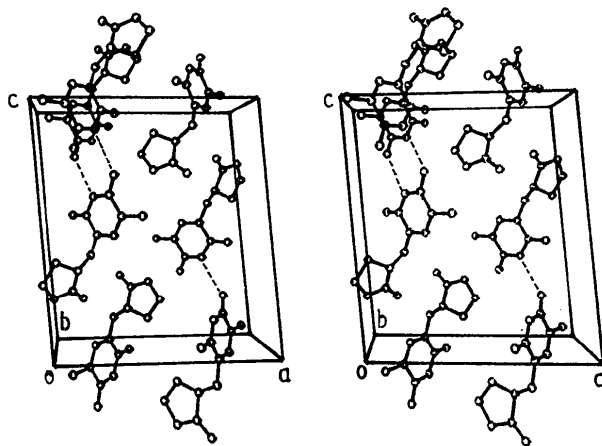

Fig. 1. Stereoscopic view of the molecular packing. Hydrogen bonds are shown by dashed lines.

3.590 (4), C2⋯C4 3.591 (4), N3⋯O4 3.587 (3), O2⋯C4 3.423 (4) Å]; the stacking distance between thymine bases is 3.4 Å. The molecules are further stabilized by N3—H⋯O4 hydrogen bonds across the screw axes and C—H⋯O close contacts (Table 3).

Experimental

Crystal data

$C_{10}H_{12}N_2O_4$
$M_r = 224.2$
Monoclinic
$P2_1/n$
$a = 14.356 (4)$ Å
$b = 4.663 (2)$ Å
$c = 15.366 (5)$ Å
$\beta = 95.20 (3)°$
$V = 1024.4 (6)$ Å^3
$Z = 4$
$D_x = 1.454$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8-17°$
$\mu = 0.1065$ mm^{-1}
$T = 293$ K
Needle
$0.80 \times 0.40 \times 0.35$ mm
Colourless

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
2425 measured reflections
1799 independent reflections
1304 observed reflections
   $[F>4\sigma(F)]$
$R_{int} = 0.053$

$\theta_{max} = 25°$
$h = -17 \rightarrow 17$
$k = 0 \rightarrow 5$
$l = 0 \rightarrow 18$
3 standard reflections
   frequency: 120 min
   intensity variation: none

Refinement

Refinement on F
Final $R = 0.055$
$wR = 0.059$
$S = 2.249$
1304 reflections
193 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F)+0.00045F^2]$

$(\Delta/\sigma)_{max} = 0.17$
$\Delta\rho_{max} = 0.236$ e Å^{-3}
$\Delta\rho_{min} = -0.232$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV Table 2.2B)

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

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1	0.2404 (2)	0.2668 (5)	0.4836 (1)	0.038 (1)
C2	0.2011 (2)	0.3500 (7)	0.5585 (2)	0.048 (1)
N3	0.2382 (2)	0.2145 (5)	0.6330 (1)	0.041 (1)
C4	0.3061 (2)	0.0081 (6)	0.6394 (2)	0.038 (1)
C5	0.3476 (2)	−0.0582 (6)	0.5595 (2)	0.035 (1)
C6	0.3120 (2)	0.0727 (6)	0.4866 (2)	0.035 (1)
O2	0.1399 (2)	0.5281 (6)	0.5582 (1)	0.063 (1)
O4	0.3295 (1)	−0.1064 (5)	0.7100 (1)	0.053 (1)
C7	0.4272 (2)	−0.2624 (8)	0.5624 (2)	0.049 (1)
C1′	0.2057 (2)	0.3982 (7)	0.4000 (2)	0.043 (1)
C2′	0.1391 (2)	0.2012 (7)	0.3472 (2)	0.046 (1)
C5′	0.0479 (2)	0.1275 (10)	0.3822 (2)	0.056 (1)
C4′	−0.0169 (3)	0.0810 (10)	0.3003 (2)	0.061 (1)
O4′	0.0216 (2)	0.2572 (5)	0.2335 (1)	0.063 (1)
C3′	0.1074 (2)	0.3372 (8)	0.2599 (2)	0.052 (1)
O3′	0.1516 (2)	0.4922 (7)	0.2171 (1)	0.081 (1)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

N1—C2	1.382 (4)	C5—C7	1.485 (4)
N1—C6	1.367 (4)	C1′—C2′	1.508 (4)
N1—C1′	1.469 (3)	C2′—C5′	1.500 (4)
C2—N3	1.372 (4)	C2′—C3′	1.516 (4)
C2—O2	1.209 (4)	C5′—C4′	1.511 (4)
N3—C4	1.367 (4)	C4′—O4′	1.462 (4)
C4—C5	1.446 (4)	O4′—C3′	1.315 (4)
C4—O4	1.228 (3)	C3′—O3′	1.197 (4)
C5—C6	1.336 (4)		
C6—N1—C1′	120.0 (2)	C6—C5—C7	123.6 (3)
C2—N1—C1′	118.6 (2)	N1—C6—C5	124.1 (3)
C2—N1—C6	121.3 (2)	N1—C1′—C2′	111.4 (3)
N1—C2—O2	122.7 (3)	C1′—C2′—C3′	110.2 (3)
N1—C2—N3	114.1 (3)	C1′—C2′—C5′	118.6 (3)
N3—C2—O2	123.1 (3)	C5′—C2′—C3′	102.2 (2)
C2—N3—C4	127.2 (2)	C2′—C5′—C4′	103.0 (2)
N3—C4—O4	120.4 (2)	C5′—C4′—O4′	105.1 (3)
N3—C4—C5	115.8 (2)	C4′—O4′—C3′	110.2 (2)
C5—C4—O4	123.8 (3)	C2′—C3′—O4′	110.6 (3)
C4—C5—C7	119.1 (3)	O4′—C3′—O3′	122.0 (3)
C4—C5—C6	117.3 (3)	C2′—C3′—O3′	127.4 (3)
C6—N1—C1′—C2′	80.8 (3)	C3′—C2′—C5′—C4′	28.4 (3)
C2—N1—C1′—C2′	−101.1 (3)	C5′—C2′—C3′—O4′	−21.3 (4)
N1—C1′—C2′—C3′	−177.8 (3)	C5′—C2′—C3′—O3′	160.1 (4)
N1—C1′—C2′—C5′	65.0 (4)	C2′—C3′—O4′—C4′	4.2 (4)
C1′—C2′—C5′—C4′	149.8 (3)	O3′—C3′—O4′—C4′	−177.2 (3)
C1′—C2′—C3′—O3′	33.2 (5)	C3′—O4′—C4′—C5′	14.7 (4)
C1′—C2′—C3′—O4′	−148.3 (3)	O4′—C4′—C5′—C2′	−27.1 (4)

Table 3. *Geometries of intermolecular hydrogen bonds and C—H⋯O close contacts* (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3⋯O4^i	0.95 (4)	1.86 (4)	2.808 (3)	178 (3)
C2′—H2′⋯O3′^{ii}	1.06 (4)	2.70 (4)	3.390 (4)	123 (3)
C6—H6⋯O3′^{ii}	1.03 (3)	2.24 (3)	3.242 (4)	165 (2)
C5′—H5′2⋯O2^{iii}	1.03 (4)	2.60 (4)	3.337 (4)	129 (3)
C4′—H4′2⋯O4^{iv}	0.99 (4)	2.66 (4)	3.336 (5)	126 (3)

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x, -y+1, -z+1$; (iv) $x-\frac{1}{2}, -y-\frac{1}{2}, z-\frac{1}{2}$

Data collection: CAD-4 diffractometer software. Program used to solve structure: *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Program used to refine structures: *SHELXTL* (Sheldrick, 1990). Program used to draw figure: *OR-TEP* (Johnson, 1976). Most calculations were performed using *PARST* (Nardelli, 1983).

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5-Chloro-2-hydroxycarbonylmethoxy-1,3-xylyl-18-crown-5 and 5-Chloro-2-ethoxycarbonylmethoxy-1,3-xylyl-18-crown-5

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Abstract

In the acid (1) {19-chloro-3,6,9,12,15-pentaoxabicyclo-[15.3.1]henicosa-1(21),17,19-trien-21-yloxyacetic acid} there exists an intramolecular O—H···O hydrogen bond [O···O 2.658(3) Å], which is achieved with considerable distortion of the macrocycle ring. The macroring of the ethyl ester (2) has an essentially undistorted crown ether conformation, in which the side chain overhangs the macrocycle cavity with the carbonyl O atom directed *exo*.

Comment

As part of a programme of study of synergism in ion binding between strategically placed functional groups and macrocyclic receptors, we have studied crown ethers with pendant phenolic groups and have demonstrated cooperation in binding of ammonia and primary amines leading, *via* proton transfer, to the formation of ammonium phenoxide complexes (Browne, Ferguson, McKervey, Mulholland, O'Connor & Parvez, 1985; Ferguson, Kaitner, Browne & McKervey, 1988). The calixarene family of macrocycles, in which several phenolic functions are organized in metacyclophane arrays, also provides important examples of synergism in ion binding.

That carboxylic acid and ester functions can participate effectively in ion binding, particularly when attached to oxygenated macrocycles, is well known. We have extended our study of functionalized macrocycles to include carboxylic acids and esters attached to crown ethers and we describe here two such compounds, the chloro-acid (1) and its ethyl ester (2) in a metacyclophane environment. A search of the 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) shows that there is only one other report of a 1,3-xylyl-18-crown-5 moiety and that is for an aqua-nitrato samarium(III) complex of 2-methoxy-1,3-xylyl-18-crown-5 (Tomat, Valle, Cassol & di Bernardo, 1983).
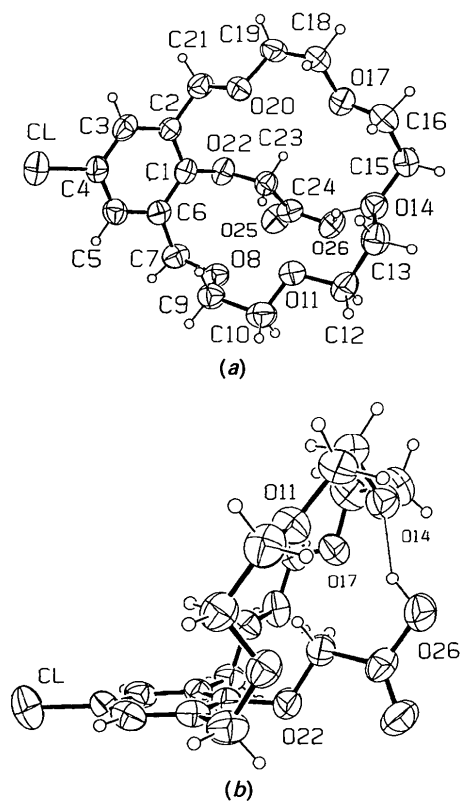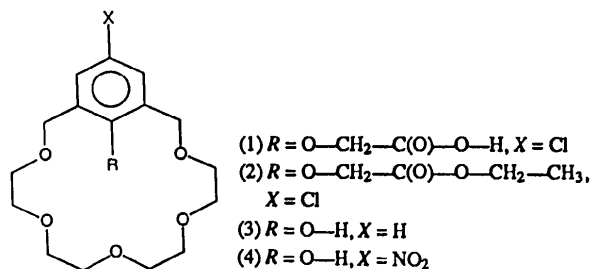

(1) $R = O—CH_2—C(O)—O—H$, $X = Cl$
(2) $R = O—CH_2—C(O)—O—CH_2—CH_3$, $X = Cl$
(3) $R = O—H$, $X = H$
(4) $R = O—H$, $X = NO_2$

Fig. 1. Views of molecule (1): (*a*) plan view and (*b*) side-on view showing the general conformation and the intramolecular hydrogen bonding with the crystallographic numbering scheme. The non-H atoms are shown with thermal ellipsoids drawn at the 50% probability level. For clarity the H atoms are drawn as small spheres of an arbitrary size.