C24—N—C28	114.1 (3)	O—C20—C21	125.6 (3)
I—C14—C13	120.5 (2)	C4—C5—C6	120.4 (4)
C25—N—C28	103.7 (4)	C19—C20—C21	119.4 (3)
I—C14—C15	118.9 (2)	C5—C6—C7	120.3 (5)
C2—C1—C11	122.1 (3)	C20—C21—C22	119.7 (3)
C13—C14—C15	120.5 (3)	C6—C7—C8	118.9 (4)
C2—C1—C17	124.1 (3)	C17—C22—C21	122.5 (3)
C14—C15—C16	119.7 (3)	C3—C8—C7	122.2 (4)
C11—C1—C17	113.8 (2)	O—C23—C24	108.4 (3)
C11—C16—C15	121.4 (3)	C2—C9—C10	115.7 (4)
C1—C2—C3	121.9 (3)	N—C24—C23	112.3 (2)
C1—C17—C18	120.5 (3)	C1—C11—C12	121.4 (3)
C1—C2—C9	123.1 (4)	N—C25—C26	104.0 (4)
C1—C17—C22	122.8 (3)	C1—C11—C16	121.1 (3)
C3—C2—C9	114.9 (2)	C25—C26—C27	105.3 (4)
C18—C17—C22	116.6 (3)	C12—C11—C16	117.3 (3)
C2—C3—C4	122.5 (4)	C26—C27—C28	104.7 (5)
C17—C18—C19	121.9 (3)	N—C28—C27	103.4 (3)
C2—C3—C8	120.2 (3)		

The structure was solved using Patterson techniques. H atoms were placed at 0.96 Å from their associated C atom. They were refined in riding mode with a fixed thermal parameter of 1.2 times that of their associated C atom.

Data collection: *CAD*-4 (Enraf–Nonius, 1977). Cell refinement: *SETANG* (Enraf–Nonius, 1977). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *Ball & Stick* (Müller & Falk, 1987–1991).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Deoxyuridine Derivative

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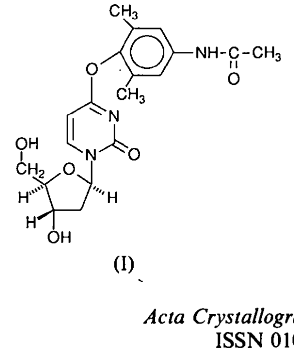
Abstract

The structure of *N*-(4-{1-[(2*R*,4*S*,5*R*)-4-hydroxy-5-(hydroxymethyl)-2-tetrahydrofuranyl]-2-oxo-1,2-dihydro-4-pyrimidinyloxy}-3,5-dimethylphenyl)acetamide chloroform solvate, $C_{19}H_{23}N_3O_6.CHCl_3$, has been determined and its geometrical features are described. This molecule plays an important role in the convertible nucleoside approach, a method of synthesizing oligodeoxynucleotides bearing tethered functionality.

Comment

Synthetic oligodeoxynucleotides are able to bind nucleic acid targets with high affinity and specificity. Unfortunately, they lack an ability to report binding or to effect chemical modification of the target sequence (MacMillan & Verdine, 1990). A method to attach non-natural ligands to synthetic DNA uses functionally tethered oligodeoxynucleotides (FTOs). When the tethered nucleophile is introduced at the monomer level of DNA synthesis the method is called 'nonconvergent'. Since this method bears some disadvantages, MacMillan & Verdine (1991) developed the 'convergent' strategy, where the tether is installed at the final step of DNA synthesis. This method leads to a variety of FTOs differing in sequence and tether structure starting from a single nucleoside precursor. The title compound, (I), is an aryl ether of uridine which can serve as a latent cytidine residue because it undergoes clean substitution when it is treated with ammonia (Zhou & Chattopadhyaya, 1986).



(I)

The crystal structure analysis was carried out in order to determine the orientation of the phenyl ring relative to the base moiety, which turned out to be 74.7°. The deoxyribose ring adopts the $C_{(1')}$-*exo*-$C_{(2')}$-*endo* conformation. Relative to the sugar moiety the base appears in the *anti* conformation, with the dihedral angle χ [O(4′)—C(1′)—N(1)—C(2)] −148.4 (3)°. The exocyclic bond C(4′)—C(5′) exhibits the +*sc* conformation. The intermolecular packing is stabilized by two hydrogen bonds: O(5′)···O(2$^{\mathrm{i}}$) 2.722 (4) Å, O(5′)—H(5′O)···O(2$^{\mathrm{i}}$) 174.0 (2)° and N(4″)···O(5″$^{\mathrm{ii}}$) 2.957 (4) Å, N(4″)—H(4″)···O(5″$^{\mathrm{ii}}$) 178.2 (1)°. For the hydroxyl group O(3′)—H(3′O) no hydrogen bonds were found, only two contacts to a chloroform molecule: O(3′)···Cl(1$^{\mathrm{iii}}$) 3.553 (4) Å, O(3′)—H(3′O)···Cl(1$^{\mathrm{iii}}$) 158.2 (1)° and O(3′)···Cl(2$^{\mathrm{iii}}$) 3.946 (5) Å, O(3′)—H(3′O)···Cl(2$^{\mathrm{iii}}$) 144.1 (1)°, but the angles at the Cl atoms [C(1*L*)—Cl(1)···H(3′O$^{\mathrm{iv}}$) 80.5 (2), C(1*L*)—Cl(2)···H(3′O$^{\mathrm{iv}}$) 66.8 (2)°] do not confirm the existence of hydrogen bonds [symmetry codes: (i) $x-1, y, z$; (ii) $3-x, y-\frac{1}{2}, 1-z$; (iii) $x-1, y, z-1$; (iv) $1+x, y, 1+z$]. The packing diagram shows that the phenyl residues of neighbouring molecules form nearly planar layers (the angle between the phenyl rings is 10.6°), which are stacked in such a way that short contacts from the centre of the aromatic ring to a methyl group are found [C(6″)···centre(phenyl) 3.619 Å, C(5″)—C(6″)···centre(phenyl) 93.4°].

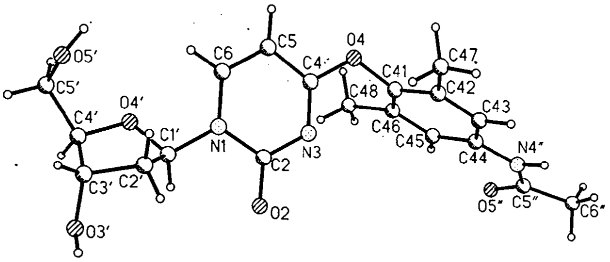


Fig. 1. Perspective view of the title compound with the atom-numbering scheme.

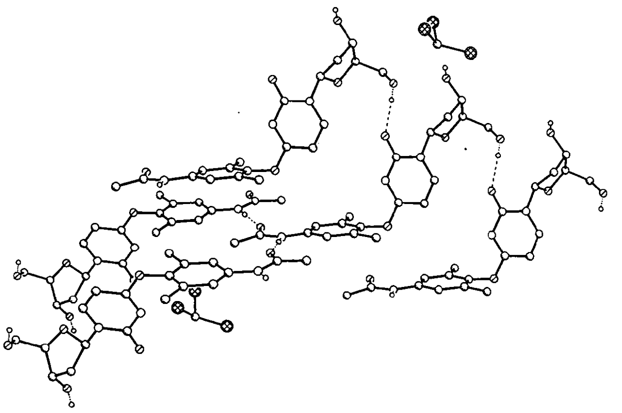


Fig. 2. Packing diagram showing the hydrogen bonds as dashed lines.

Experimental

Crystal data

$C_{19}H_{23}N_3O_6.CHCl_3$
$M_r = 508.8$
Monoclinic
$P2_1$
$a = 6.592$ (1) Å
$b = 9.831$ (1) Å
$c = 18.053$ (1) Å
$\beta = 97.00$ (1)°
$V = 1161.1$ (1) Å^3
$Z = 2$
$D_x = 1.455$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 28$–48°
$\mu = 4.00$ mm^{-1}
$T = 293$ K
Transparent block
0.3 × 0.3 × 0.1 mm
Colourless
Crystal source: chloroform/methanol

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
6651 measured reflections
3351 independent reflections
3307 observed reflections [$|F| > 3\sigma(F)$]

$R_{\mathrm{int}} = 0.053$
$\theta_{\max} = 60°$
$h = -7 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 92 min
intensity variation: insignificant

Refinement

Refinement on F
$R = 0.069$
$wR = 0.081$
$S = 2.29$
3307 reflections
289 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.67$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
N(1)	0.4822 (4)	0.5400 (3)	0.1194 (2)	0.037 (1)
C(2)	0.6830 (5)	0.5091 (4)	0.1489 (2)	0.036 (1)
O(2)	0.8226 (4)	0.5324 (3)	0.1110 (1)	0.047 (1)
N(3)	0.7171 (4)	0.4588 (3)	0.2188 (2)	0.041 (1)
C(4)	0.5615 (5)	0.4301 (4)	0.2546 (2)	0.040 (1)
C(5)	0.3547 (6)	0.4479 (4)	0.2253 (2)	0.045 (1)
C(6)	0.3214 (5)	0.5042 (4)	0.1573 (2)	0.041 (1)
C(1′)	0.4507 (6)	0.6092 (4)	0.0476 (2)	0.039 (1)
O(4′)	0.2759 (4)	0.6943 (3)	0.0460 (1)	0.048 (1)
C(2′)	0.4040 (6)	0.5183 (4)	−0.0199 (2)	0.044 (1)
C(3′)	0.3052 (6)	0.6190 (5)	−0.0769 (2)	0.046 (1)
O(3′)	0.4562 (5)	0.6970 (5)	−0.1087 (2)	0.078 (1)
C(4′)	0.1958 (5)	0.7160 (4)	−0.0296 (2)	0.042 (1)
C(5′)	−0.0333 (6)	0.6984 (5)	−0.0377 (3)	0.059 (1)
O(5′)	−0.0921 (5)	0.5609 (4)	−0.0319 (2)	0.070 (1)
O(4)	0.5950 (4)	0.3833 (3)	0.3243 (1)	0.048 (1)
C(41)	0.7996 (6)	0.3741 (4)	0.3589 (2)	0.042 (1)
C(42)	0.8829 (6)	0.2444 (4)	0.3689 (2)	0.044 (1)
C(47)	0.7657 (9)	0.1207 (5)	0.3388 (3)	0.066 (2)
C(43)	1.0773 (6)	0.2349 (4)	0.4082 (2)	0.045 (1)
C(44)	1.1836 (5)	0.3482 (4)	0.4360 (2)	0.039 (1)
C(45)	1.0940 (6)	0.4768 (4)	0.4249 (2)	0.042 (1)
C(46)	0.8995 (6)	0.4901 (4)	0.3860 (2)	0.041 (1)

C(48)	0.8030 (8)	0.6294 (5)	0.3745 (3)	0.057 (1)
N(4″)	1.3766 (5)	0.3270 (3)	0.4772 (2)	0.040 (1)
C(5″)	1.5123 (7)	0.4161 (4)	0.5101 (2)	0.043 (1)
O(5″)	1.4869 (5)	0.5409 (3)	0.5057 (2)	0.058 (1)
C(6″)	1.6977 (7)	0.3570 (5)	0.5541 (2)	0.055 (1)
Cl(1)	1.7879 (2)	0.5720†	0.7659 (1)	0.084 (1)
Cl(2)	1.5131 (2)	0.3519 (2)	0.7841 (1)	0.098 (1)
Cl(3)	1.9438 (3)	0.3019 (2)	0.7859 (2)	0.130 (1)
C(1*L*)	1.7593 (8)	0.4150 (5)	0.8084 (3)	0.065 (2)

† Coordinate fixed to define origin.

Table 2. *Selected geometric parameters* (Å, °)

N(1)—C(2)	1.399 (4)	N(1)—C(6)	1.375 (5)
N(1)—C(1′)	1.457 (4)	C(2)—O(2)	1.233 (4)
C(2)—N(3)	1.348 (4)	N(3)—C(4)	1.308 (5)
C(4)—C(5)	1.411 (5)	C(4)—O(4)	1.333 (4)
C(5)—C(6)	1.341 (5)	C(1′)—O(4′)	1.421 (5)
C(1′)—C(2′)	1.512 (5)	O(4′)—C(4′)	1.419 (4)
C(2′)—C(3′)	1.517 (5)	C(3′)—O(3′)	1.430 (6)
C(3′)—C(4′)	1.520 (6)	C(4′)—C(5′)	1.509 (5)
C(5′)—O(5′)	1.413 (6)	O(4)—C(41)	1.418 (4)
C(41)—C(42)	1.391 (6)	C(41)—C(46)	1.378 (5)
C(42)—C(47)	1.506 (6)	C(42)—C(43)	1.390 (5)
C(43)—C(44)	1.377 (5)	C(44)—C(45)	1.400 (5)
C(44)—N(4″)	1.409 (4)	C(45)—C(46)	1.390 (5)
C(46)—C(48)	1.513 (6)	N(4″)—C(5″)	1.339 (5)
C(5″)—O(5″)	1.239 (4)	C(5″)—C(6″)	1.492 (6)
Cl(1)—C(1*L*)	1.743 (5)	Cl(2)—C(1*L*)	1.743 (5)
Cl(3)—C(1*L*)	1.732 (6)		
C(2)—N(1)—C(6)	120.5 (3)	C(2)—N(1)—C(1′)	117.7 (3)
C(6)—N(1)—C(1′)	121.8 (3)	N(1)—C(2)—O(2)	119.0 (3)
N(1)—C(2)—N(3)	118.5 (3)	O(2)—C(2)—N(3)	122.4 (3)
C(2)—N(3)—C(4)	119.4 (3)	N(3)—C(4)—C(5)	124.6 (3)
N(3)—C(4)—O(4)	119.4 (3)	C(5)—C(4)—O(4)	115.9 (3)
C(4)—C(5)—C(6)	115.9 (3)	N(1)—C(6)—C(5)	120.7 (3)
N(1)—C(1′)—O(4′)	108.6 (3)	N(1)—C(1′)—C(2′)	115.7 (3)
O(4′)—C(1′)—C(2′)	104.3 (3)	C(1′)—O(4′)—C(4′)	108.3 (3)
C(1′)—C(2′)—C(3′)	100.9 (3)	C(2′)—C(3′)—O(3′)	111.1 (3)
C(2′)—C(3′)—C(4′)	102.8 (3)	O(3′)—C(3′)—C(4′)	106.9 (4)
O(4′)—C(4′)—C(3′)	107.4 (3)	O(4′)—C(4′)—C(5′)	109.0 (3)
C(3′)—C(4′)—C(5′)	114.3 (3)	C(4′)—C(5′)—O(5′)	112.5 (4)
C(4)—O(4)—C(41)	118.5 (3)	O(4)—C(41)—C(42)	117.1 (3)
O(4)—C(41)—C(46)	119.5 (3)	C(42)—C(41)—C(46)	123.3 (3)
C(41)—C(42)—C(47)	121.1 (4)	C(41)—C(42)—C(43)	116.9 (3)
C(47)—C(42)—C(43)	122.0 (4)	C(42)—C(43)—C(44)	121.9 (3)
C(43)—C(44)—C(45)	119.4 (3)	C(43)—C(44)—N(4″)	117.3 (3)
C(45)—C(44)—N(4″)	123.2 (3)	C(44)—C(45)—C(46)	120.3 (3)
C(41)—C(46)—C(45)	118.2 (3)	C(41)—C(46)—C(48)	121.7 (3)
C(45)—C(46)—C(48)	120.1 (3)	C(44)—N(4″)—C(5″)	130.5 (3)
N(4″)—C(5″)—O(5″)	122.8 (4)	N(4″)—C(5″)—C(6″)	116.1 (3)
O(5″)—C(5″)—C(6″)	121.1 (4)	Cl(1)—C(1*L*)—Cl(2)	110.6 (3)
Cl(1)—C(1*L*)—Cl(3)	110.4 (3)	Cl(2)—C(1*L*)—Cl(3)	111.8 (3)

Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Refinement was carried out by full-matrix least-squares methods with *XLS* (Sheldrick, 1987). All H atoms were located by a difference synthesis and positioned with fixed individual displacement parameters [$U(\mathrm{H}) = 1.5 \times U_{\mathrm{eq}}(\mathrm{C_{methyl}})$ or $U(\mathrm{H}) = 1.2 \times U_{\mathrm{eq}}(\mathrm{C, N, O})$] using a riding model with C—H = 0.96, N—H 0.90 and O—H 0.85 Å. An empirical isotropic extinction correction was applied for which $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-0.25}$, where χ refined to a value of 0.012 (2). The absolute configuration was determined by η-refinement (Rogers, 1981) starting from both configurations [η = 0.94 (4) for the correct structure].

I thank Professor G. Verdine (Harvard University, Cambridge, USA) for providing the sample.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: SE1052). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6-Oxa-3,9-dithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene

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Abstract

The title molecule, $C_{12}H_{16}OS_2$, is partially disordered with the O and H atoms of the —CH_2—O—CH_2— group occupying two positions. The molecule assumes C_2 symmetry and the twofold axis is located midway through the triene group and across the two partially occupied O-atom positions.

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