C2—N2—C3—C9	125.1 (2)	C1—C5—C6—C7	98.9 (3)
N2—C3—C4—O2	74.2 (2)	C1—C5—C6—N3	−83.0 (2)
N2—C3—C4—O3	−105.0 (2)		

Table 3. *Hydrogen-bond distances (Å)*

Data for normalized H-atom positions are based on bond lengths of O—H = 0.98, N—H = 1.04 and C—H = 1.08Å.

$D\cdots A$	$D\cdots A$	$H_{norm}\cdots A$
$OW1\cdots N3$	2.775 (3)	1.81
$OW1\cdots O2^{i}$	2.720 (2)	1.75
$OW2\cdots OW1$	2.744 (3)	1.80
$OW2\cdots OW1^{ii}$	2.796 (2)	1.82
$N1\cdots O3^{iii}$	2.854 (2)	1.89
$N1\cdots OW2^{iii}$	2.858 (2)	1.84
$N1\cdots O3^{iv}$	3.007 (2)	2.00
$N1\cdots O2^{iv}$	3.111 (2)	2.44
$N2\cdots OW^{i}$	2.819 (2)	1.78
$N4\cdots OW2^{v}$	2.791 (3)	1.76
$C1\cdots O1^{i}$	3.266 (3)	2.46
$C5\cdots OW1^{ii}$	3.600 (3)	2.78
$C5\cdots N3^{ii}$	3.384 (3)	2.66
$C7\cdots O3^{iv}$	3.481 (3)	2.62
$C8\cdots O1^{vi}$	3.609 (3)	2.80

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

The author is on leave from the Max-Delbrück-Centrum für Molekulare Medizin, Forschungsgruppe Kristallographie (Professor U. Heinemann), Robert Rössle Straße 10, D-13122 Berlin, Germany. He thanks Professor W. Saenger for giving him the opportunity to carry out this study in his laboratory, and the Deutsche Forschungsgemeinschaft for support (Sa 196/25-1).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1164). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Jeffrey, G. A. & Saenger, W. (1991). In *Hydrogen Bonding in Biological Structures*. Berlin: Springer-Verlag.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Steiner, Th. (1995). *Acta Cryst.* D**51**, 93–97.
Steiner, Th. (1996*a*). *Acta Cryst.* C**52**, 2266–2269.
Steiner, Th. (1996*b*). *Cryst. Rev.* In the press.
Steiner, Th. & Saenger, W. (1993). *J. Am. Chem. Soc.* **115**, 4540–4547.

Acta Cryst. (1996). C**52**, 2556–2558

α-5-Adamantyl-4′-thio-2′-deoxyuridine Methanol Solvate

MING SUN,† IVAN BASNAK, THOMAS A. HAMOR AND RICHARD T. WALKER

School of Chemistry, University of Birmingham, Birmingham B15 2TT, England. E-mail: t.a.hamor@bham.ac.uk

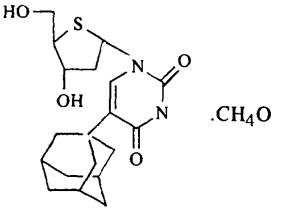
(*Received 19 February 1996; accepted 24 April 1996*)

Abstract

The thiosugar ring of the title compound, $C_{19}H_{26}N_2O_4S.CH_4O$, has the C2′-*endo*, C3′-*exo* conformation. The orientation of the C4′—C5′ bond is *trans–gauche*, and the glycosidic torsion angle S4′—C1′—N1—C6 is −26.2 (2)° (*anti*).

Comment

5-Substituted 2′-deoxy-4′-thiouridines are a relatively new group of nucleosides, possessing significant antiviral activity (Dyson, Coe & Walker, 1991; Secrist, Tiwari, Riordan & Montgomery, 1991). Syntheses provide mixtures of α- and β-anomers, of which only the β-anomers manifest antiviral activity (Rahim *et al.*, 1996). In order to provide information about structure–activity relationships in both anomeric series, the crystal structure of the title compound (I), synthesized by Basnak, Sun, Coe & Walker (1996), is presented here. As far as we are aware, it is the first reported crystal structure of an α-anomer within the 2′-deoxy-4′-thiouridine series.



(I)

A perspective view of the molecule with atomic numbering is shown in Fig. 1. Bond lengths are normal. The C1′—S4′ and C4′—S4′ bonds are 1.811 (2) and 1.830 (2) Å, in good agreement with accepted values (Allen *et al.*, 1987). The other bond lengths generally agree well with those found in the crystal structures of 2′-deoxyuridine (Rahman & Wilson, 1972) and α-5-acetyl-2′-deoxyuridine (Hamor, O'Leary & Walker, 1977). The thiosugar ring has the C2′-*endo*, C3′-*exo* conformation (south), these two atoms being displaced by 0.224 (3) and 0.440 (3) Å, respectively, on opposite

† Current address: Department of Chemistry, Tianjin Normal University, Tianjin 300074, People's Republic of China.

sides of the C1′—S4′—C4′ plane. The sugar ring of 2′-deoxyuridine has a similar shape; in contrast, the deoxyribose conformation in α-5-acetyl-2′-deoxyuridine is C2′-*endo* (^2E). The conformation about C4′—C5′ is *trans–gauche*; the C3′—C4′—C5′—O5′ torsion angle is −65.5 (2)°. The glycosidic torsion angle S4′—C1′—N1—C6 is −26.2 (2)° (*anti* conformation), similar to the values found in 2′-deoxyuridine (Rahman & Wilson, 1972) and α-5-acetyl-2′-deoxyuridine (Hamor *et al.*, 1977). The adamantyl group has normal bond lengths and angles (C—C bonds 1.516 to 1.544, mean 1.531 Å; C—C—C angles 107.6 to 110.7, mean 109.5°).

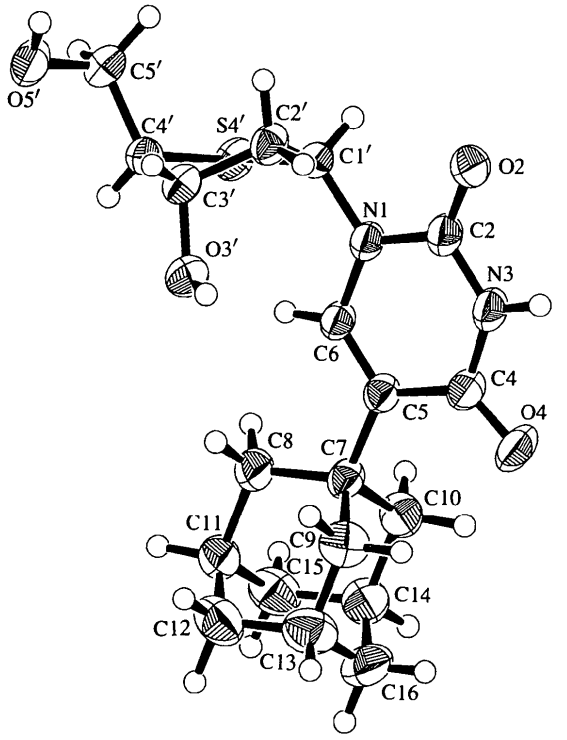


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids (*ORTEP*II; Johnson, 1976).

In the crystal, nucleoside and methanol molecules are linked through a three-dimensional network of hydrogen bonds. Atoms O3′ and O5′ of the thiosugar each donate a proton, forming bonds with, respectively, O2 of the pyrimidine base at $-\frac{1}{2}-x,-1-y,z-\frac{1}{2}$ and O7 of the methanol molecule at $-\frac{3}{2}-x,-1-y,\frac{1}{2}+z$. Relevant distances and angles are O3′···O2 2.729 (2), O5′···O7 2.852 (2) Å, O3′—H···O2 161, O5′—H···O7 149°. The methanol O atom in turn donates a proton to O4 of a different nucleoside molecule at $x-1,y,z$ [O7···O4 2.783 (3) Å, O7—H···O4 164°]. Finally, N3 donates a proton to O5′ of the thiosugar at $1+x,y,z$ [N3···O5′ 2.839 (2) Å, N3—H···O5′ 171°]. Thus, all H atoms attached to the electronegative groups are involved in hydrogen-bond formation, consistent with the principle of maximum hydrogen bonding (Robertson, 1953).

Experimental

The title compound was recrystallized from MeOH–Et_2O.

Crystal data

$C_{19}H_{26}N_2O_4S.CH_4O$
M_r = 410.52
Orthorhombic
$P2_12_12_1$
a = 10.5520 (10) Å
b = 24.9930 (18) Å
c = 7.9700 (10) Å
V = 2101.9 (3) Å^3
Z = 4
D_x = 1.297 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 12001 reflections (post-refined using complete data set)
θ = 2.5–25.6°
μ = 0.187 mm^{-1}
T = 293 (2) K
Irregular
0.5 × 0.4 × 0.4 mm
Colourless

Data collection

Rigaku *R*-Axis II area detector
Image-plate scans
Absorption correction: none
12001 measured reflections
3648 independent reflections [$I > \sigma(I)$]
3588 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.027
θ_{max} = 25.59°
h = −11 → 12
k = −29 → 30
l = −9 → 9

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0345
$wR(F^2)$ = 0.1049
S = 1.049
3648 reflections
364 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2 + 0.2780P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.089
$\Delta\rho_{max}$ = 0.167 e Å^{-3}
$\Delta\rho_{min}$ = −0.227 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.00 (7)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
S4′	−0.53245 (5)	−0.38812 (2)	0.37649 (6)	0.0432 (2)
O2	−0.1775 (2)	−0.47984 (7)	0.4351 (2)	0.0627 (4)
O3′	−0.50508 (14)	−0.44942 (6)	0.0330 (2)	0.0495 (4)
O4	0.03313 (14)	−0.38513 (6)	0.0393 (2)	0.0601 (4)
O5′	−0.83791 (13)	−0.48140 (6)	0.2836 (2)	0.0531 (4)
O7	−0.7716 (2)	−0.41508 (8)	−0.1759 (3)	0.0818 (6)
N1	−0.2904 (2)	−0.41958 (6)	0.2820 (2)	0.0391 (4)
N3	−0.0764 (2)	−0.43131 (7)	0.2339 (2)	0.0480 (4)
C1′	−0.4057 (2)	−0.43699 (7)	0.3775 (2)	0.0388 (4)
C2′	−0.4631 (2)	−0.48851 (7)	0.3070 (3)	0.0426 (4)
C2	−0.1805 (2)	−0.44559 (8)	0.3238 (3)	0.0453 (4)
C3′	−0.5618 (2)	−0.47275 (7)	0.1777 (2)	0.0406 (4)
C4′	−0.6433 (2)	−0.42975 (7)	0.2577 (2)	0.0381 (4)
C4	−0.0699 (2)	−0.39397 (7)	0.1039 (3)	0.0436 (4)
C5′	−0.7455 (2)	−0.45087 (8)	0.3744 (3)	0.0489 (5)
C5	−0.1906 (2)	−0.36949 (7)	0.0597 (2)	0.0395 (4)
C6	−0.2925 (2)	−0.38355 (7)	0.1511 (2)	0.0387 (4)
C7	−0.1982 (2)	−0.33025 (7)	−0.0865 (2)	0.0388 (4)
C8	−0.3350 (2)	−0.31076 (8)	−0.1170 (3)	0.0512 (5)

C9	−0.1515 (2)	−0.35676 (9)	−0.2497 (3)	0.0559 (5)
C10	−0.1160 (2)	−0.28055 (8)	−0.0493 (3)	0.0523 (5)
C11	−0.3396 (2)	−0.27130 (9)	−0.2650 (3)	0.0556 (5)
C12	−0.2925 (3)	−0.29833 (10)	−0.4234 (3)	0.0661 (7)
C13	−0.1560 (3)	−0.31685 (10)	−0.3962 (3)	0.0669 (7)
C14	−0.1221 (3)	−0.24143 (9)	0.1969 (3)	0.0615 (6)
C15	−0.2575 (3)	−0.22304 (9)	−0.2267 (3)	0.0619 (6)
C16	−0.0720 (3)	−0.26845 (12)	−0.3541 (4)	0.0743 (8)
C17	−0.7078 (4)	−0.36671 (13)	−0.2000 (4)	0.0858 (9)

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

S4′—C1′	1.811 (2)	N3—C2	1.359 (3)
S4′—C4′	1.830 (2)	N3—C4	1.396 (2)
O2—C2	1.233 (2)	C1′—C2′	1.530 (3)
O3′—C3′	1.424 (2)	C2′—C3′	1.517 (3)
O4—C4	1.223 (2)	C3′—C4′	1.517 (2)
O5′—C5′	1.434 (3)	C4′—C5′	1.519 (3)
O7—C17	1.397 (4)	C4—C5	1.456 (3)
N1—C2	1.370 (3)	C5—C6	1.346 (3)
N1—C6	1.378 (2)	C5—C7	1.525 (2)
N1—C1′	1.500 (2)		
C1′—S4′—C4′	95.21 (8)	O3′—C3′—C4′	106.77 (14)
C2—N1—C6	120.5 (2)	C2′—C3′—C4′	106.7 (2)
C2—N1—C1′	115.19 (14)	C3′—C4′—C5′	114.4 (2)
C6—N1—C1′	124.09 (14)	C3′—C4′—S4′	104.94 (12)
C2—N3—C4	127.4 (2)	C5′—C4′—S4′	109.56 (14)
N1—C1′—C2′	112.3 (2)	O4—C4—N3	118.5 (2)
N1—C1′—S4′	113.65 (12)	O4—C4—C5	126.9 (2)
C2′—C1′—S4′	105.88 (13)	N3—C4—C5	114.7 (2)
C3′—C2′—C1′	107.62 (14)	O5′—C5′—C4′	111.0 (2)
O2—C2—N3	122.8 (2)	C6—C5—C4	117.3 (2)
O2—C2—N1	121.7 (2)	C6—C5—C7	122.6 (2)
N3—C2—N1	115.5 (2)	C4—C5—C7	120.1 (2)
O3′—C3′—C2′	111.6 (2)	C5—C6—N1	124.6 (2)

C2—N1—C1′—C2′	−80.6 (2)
C6—N1—C1′—C2′	94.0 (2)
C2—N1—C1′—S4′	159.24 (14)
C6—N1—C1′—S4′	−26.2 (2)
C4′—S4′—C1′—C2′	−8.74 (14)
S4′—C1′—C2′—C3′	33.1 (2)
C1′—C2′—C3′—C4′	−47.8 (2)
C2′—C3′—C4′—S4′	39.2 (2)
C1′—S4′—C4′—C3′	−17.45 (13)
C3′—C4′—C5′—O5′	−65.5 (2)
S4′—C4′—C5′—O5′	176.94 (12)

Image-plate scans were recorded covering 180° of rotation in 3° frames about one axis, with crystal–detector distance 78 mm and exposure time 10 min frame^{-1}. The resulting data contains *ca* 86% of the theoretically accessible independent reflections. Coordinates and anisotropic displacement parameters were refined for non-H atoms. H atoms, except those of the methanol methyl group, were located from a difference map and were refined with isotropic displacement parameters. The methanol methyl H atoms were placed in calculated positions and only their isotropic displacement parameters were refined.

Data collection: *R-Axis II Software* (Rigaku Corporation, 1994). Cell refinement: *R-Axis II Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

We thank the EPSRC and the University of Birmingham for funds to purchase the X-ray diffractometer and the British Council (Sino–British Friendship Scholarship to MS).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1160). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Basnak, I., Sun, M., Coe, P. L. & Walker, R. T. (1996). *Nucleosides Nucleotides*, **15**, 121–134.
Dyson, M. R., Coe, P. L. & Walker, R. T. (1991). *J. Med. Chem.* **34**, 2782–2786.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hamor, T. A., O'Leary, M. K. & Walker, R. T. (1977). *Acta Cryst.* B**33**, 1218–1223.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Rahim, S. G., Trivedi, N., Bobunovic-Batchelor, M. V., Hardy, G. W., Mills, G., Selway, J. W. T., Snowden, W., Littler, E., Coe, P. L., Basnak, I., Whale, R. F. & Walker, R. T. (1996). *J. Med. Chem.* **39**, 789–795.
Rahman, A. & Wilson, H. R. (1972). *Acta Cryst.* B**28**, 2260–2270.
Rigaku Corporation (1994). *R-Axis II Software*. Rigaku Corporation, Tokyo, Japan.
Robertson, J. M. (1953). *Organic Crystals and Molecules*. Ithaca: Cornell University Press.
Secrist, J. A. III, Tiwari, K. N., Riordan, J. M. & Montgomery, J. A. (1991). *J. Med. Chem.* **34**, 2361–2366.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 2558–2561

(2a*S*,3*S*,6*S*,7*S*,7b*R*)-7-[(Dimethylphenyl)-silyl]-2-oxo-6-[(1*R*,2*S*)-2-phenylcyclo-hexyloxy]-2a,3,6,7,7a,7b-hexahydro-2*H*-1,4,5-trioxa-4a-azacyclopenta[*cd*]indene-3-carboxylic Acid 1-Methylethyl Ester

Atli Thorarensen, Kevin A. Swiss* and Scott E. Denmark*

Department of Chemistry, Roger Adams Laboratory, University of Illinois, 600 South Mathews Avenue, Urbana, Illinois 61801, USA. E-mail: denmark@aries.scs.uiuc.edu

(*Received 15 February 1996; accepted 29 April 1996*)

Abstract

The structure of the title compound, $C_{31}H_{39}NO_7Si$, was determined and found to be a fused tricyclic nitroso acetal. Remarkable features include a twist-boat