The individual five- and six-membered rings are planar but the molecule as a whole shows a small deviation from planarity, the rings being inclined at 1·04 (13)° to one another. An angle of 0·6° was determined in 5-bromo-2,3-dimethyl-1-benzothiophene (Hogg & Sutherland, 1974) and in 2-methyl-1-benzothiophene (Sutherland & Rawas, 1985). Cl(1) is displaced by −0·014 (9) Å and Cl(2) by 0·030 (9) Å from the five-membered ring with the Cl(1)—C(7) and Cl(2)—C(8) bonds inclined at −0·5 (9) and 1·0 (9)°, respectively, to the plane of the ring. The C—S—C bond angle of 90·0 (5)° is in good agreement with the values of 91·1 (12)° found in 2,3-dibromo-1-benzothiophene (Sutherland & Ali-Adib, 1986) and 92·4 (7)° in 2-methyl-1-benzothiophene. The C(1)—C(8) bond of 1·418 (13) Å is shorter than the corresponding values of 1·441 (1), 1·485 (17) and 1·446 (12) Å in dibenzothiophene (Schaffrin & Trotter, 1970), 2-methyl-1-benzothiophene and 5-bromo-2,3-dimethyl-1-benzothiophene, respectively. The S—C(7) bond of 1·758 (10) Å is in good agreement with the value of 1·754 (10) Å for the corresponding bond in 5-bromo-2,3-dimethyl-1-benzothiophene. The S—C(6) bond of 1·765 (10) Å is similar to the value of 1·772 (16) Å found in 2-methyl-1-benzothiophene. The C(7)—C(8) bond of 1·341 (14) Å is shorter than the corresponding values of 1·355 (14), 1·369 and 1·382 (16) Å in 5-bromo-2,3-dimethyl-1-benzothiophene, thiophene (Harshbarger & Bauer, 1970) and 2-methyl-1-benzothiophene, respectively.

The authors thank Mr G. Collier for providing the crystals.

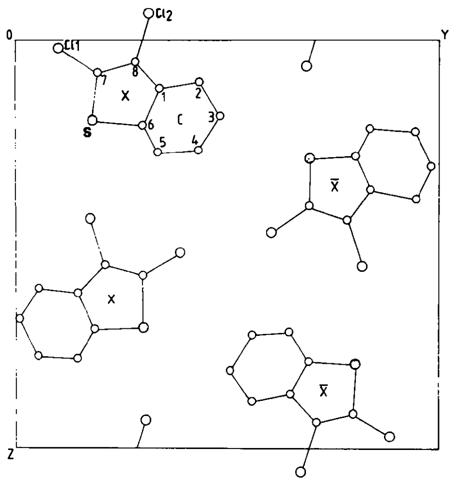

Fig. 1. The arrangement of the molecules in the unit cell viewed along **a**.

References

Harshbarger, W. R. & Bauer, S. H. (1970). *Acta Cryst.* B**26**, 1010–1020.

Hogg, J. H. C. & Sutherland, H. H. (1974). *Acta Cryst.* B**30**, 2058–2059.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Schaffrin, R. M. & Trotter, J. (1970). *J. Chem. Soc.* pp. 1561–1566.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sutherland, H. H. & Ali-Adib, Z. (1986). In preparation.

Sutherland, H. H. & Rawas, A. (1985). *Acta Cryst.* C**41**, 929–931.

Acta Cryst. (1986). C**42**, 697–700

Structure of 2′,3′,5′-Tri-*O*-acetyladenosine

By Charles C. Wilson* and Patrick Tollin

Carnegie Laboratory of Physics, University of Dundee, Dundee DD1 4HN, Scotland

and R. Alan Howie

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, Scotland

(*Received* 23 *September* 1985; *accepted* 21 *January* 1986)

Abstract. $C_{16}H_{19}N_5O_7$, $M_r = 393{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}46\,(2)$, $b = 20{\cdot}26\,(3)$, $c = 8{\cdot}42\,(1)$ Å, $U = 1955$ Å^3, $Z = 4$, $D_x = 1{\cdot}34$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}68$ cm^{-1}, $F(000) = 824$, $T = 293$ K, $R = 0{\cdot}050$ for 1926 unique reflections (including unobserveds). The molecule is *syn*, with χ[C(4)—N(9)—C(1′)—O(4′)] = 61·1 (7)°, has sugar pucker $^2T_3$, with $P = 171{\cdot}1\,(8)$°, and C(4′)—C(5′) conformation *ap* (*gauche–trans*). The structure has

---

* Present address: Neutron Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, England.

0108-2701/86/060697-04$01.50 © 1986 International Union of Crystallography

base-paired symmetry-related molecules, with hydrogen bonds between the 6-amino group and N(1) and N(7). The base-pair shows a propeller twist, defined as the angle between the base planes about a line joining them, of 17 (1)°.

Introduction. The structural study of the title compound (TAA) was undertaken in continuation of our studies of acetylated nucleosides, induced base-pairing and studies of propeller-twisting in mononucleoside crystals.

Experimental. Crystals from aqueous ethanol solution, elongated along **c**; space group and initial cell dimensions from Weissenberg photographs. Data collected on a Nicolet P3 (four-circle) diffractometer in Aberdeen, by RAH; crystal cut to cube shape of side 0·4 mm. Cell dimensions obtained from the 262, 351 and symmetry-related reflections; 1926 reflections measured, Mo $K\alpha$ radiation; $0° < 2\theta < 50°$, using $\theta/2\theta$ scans, with a 2θ scan range of 2·42–2·72°, depending on 2θ value. Range of indices: h 0/13, k 0/24, l 0/10; reflections 262 and 330 measured every 50 reflections, no significant change in their intensities. No absorption or extinction corrections. The Patterson methods program *PATMET* (Wilson & Tollin, 1985) was used to obtain an oriented model of the adenine base in the molecule. Calculation of the $I(\theta,\varphi)$ function (Tollin & Cochran, 1964) showed this plane to be in the orientation $(\theta,\varphi) = (88°, 18°)$. This orientation was not entirely unambiguously indicated, but was confirmed by noting that the very strong reflections 320, 310 and 330 all represent an orientation with $\theta = 90°$. Use of the rotation function (Tollin, 1976) from *PATMET*, in this plane, completed the definition of the orientation of the group.

This oriented model was used as *ab initio* structural knowledge (Main, 1976) in the direct-methods package *MITHRIL* (Gilmore, 1983), using E values calculated with *SHELX*76 (Sheldrick, 1976). This led to the appearance of most non-hydrogen atoms in the best E map. Fourier recycling completed the definition of the structure; least-squares refinement on F with *SHELX*76; difference Fourier maps revealed all H atoms, except the 3′ and 5′ methyl hydrogens. These H atoms included at calculated positions with fixed $U_{\rm iso} = 0·05$ Å^2; remaining H atoms refined isotropically. Anisotropic temperature factors used for all non-hydrogen atoms; refinement converged at $R = 0·050$, $wR = 0·048$, using unit weights. 305 parameters refined; max. shift/e.s.d. $<0·02$; max. difference peak, 0·21 e Å^{-3}, min. –0·28 e Å^{-3}. Scattering factors taken from *International Tables for X-ray Crystallography* (1974). Also used were the program packages *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978). All calculations carried out on the Dundee University DEC-10 computer.

Table 1. *Fractional coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N(1)	−7591 (3)	−4234 (2)	−7902 (4)	42 (1)
C(2)	−7844 (5)	−3610 (2)	−8250 (5)	46 (1)
N(3)	−8217 (3)	−3129 (2)	−7325 (4)	43 (1)
C(4)	−8310 (3)	−3338 (2)	−5816 (4)	30 (1)
C(5)	−8050 (3)	−3959 (2)	−5251 (4)	29 (1)
C(6)	−7676 (4)	−4433 (2)	−6373 (5)	36 (1)
N(6)	−7455 (5)	−5059 (2)	−6011 (5)	51 (1)
N(7)	−8272 (3)	−4000 (2)	−3624 (4)	33 (1)
C(8)	−8674 (4)	−3417 (2)	−3262 (4)	32 (1)
N(9)	−8712 (3)	−2989 (1)	−4520 (4)	32 (1)
C(1′)	−9223 (3)	−2330 (2)	−4495 (5)	32 (1)
C(2′)	−8436 (3)	−1805 (2)	−5209 (4)	32 (1)
O(2′)	−7662 (2)	−1555 (1)	−4044 (3)	38 (1)
C(2′1)	−6662 (4)	−1263 (2)	−4619 (6)	45 (1)
O(2′1)	−6416 (3)	−1269 (2)	−5985 (4)	66 (1)
C(2′2)	−5992 (5)	−954 (3)	−3316 (8)	65 (2)
C(3′)	−9344 (4)	−1294 (2)	−5756 (5)	40 (1)
O(3′)	−9743 (3)	−944 (1)	−4365 (4)	53 (1)
C(3′1)	−9182 (6)	−366 (3)	−4019 (8)	74 (2)
O(3′1)	−8498 (5)	−118 (2)	−4900 (7)	104 (2)
C(3′2)	−9516 (6)	−149 (3)	−2365 (9)	106 (3)
C(4′)	−10337 (4)	−1726 (2)	−6324 (5)	37 (1)
C(5′)	−10221 (5)	−1878 (3)	−8076 (5)	51 (1)
O(5′)	−11175 (3)	−2298 (2)	−8517 (3)	53 (1)
C(5′1)	−11001 (5)	−2669 (3)	−9821 (6)	55 (1)
O(5′1)	−10125 (4)	−2626 (2)	−10579 (5)	95 (1)
C(5′2)	−12034 (5)	−3085 (3)	−10178 (6)	71 (1)
O(4′)	−10254 (2)	−2333 (1)	−5421 (3)	40 (1)

Table 2. *Interatomic distances* (Å) *and angles* (°)

C(2)–N(1)	1·330 (5)	C(3′)–C(2′)	1·538 (5)
C(6)–N(1)	1·354 (5)	C(2′1)···O(2′)	1·378 (5)
N(3)–C(2)	1·319 (5)	C(2′1)–C(2′1)	1·185 (6)
C(4)–N(3)	1·344 (5)	C(2′2)–C(2′1)	1·479 (8)
C(5)–C(4)	1·378 (5)	O(3′)–C(3′)	1·445 (5)
N(9)–C(4)	1·380 (5)	C(4′)–C(3′)	1·513 (6)
C(6)–C(5)	1·413 (5)	C(3′1)–O(3′)	1·368 (6)
N(7)–C(5)	1·396 (5)	O(3′1)–C(3′1)	1·191 (8)
N(6)–C(6)	1·328 (5)	C(3′2)–C(3′1)	1·510 (10)
C(8)–N(7)	1·304 (5)	C(5′)–C(4′)	1·513 (6)
N(9)–C(8)	1·369 (5)	O(4′)–C(4′)	1·449 (5)
C(1′)–N(9)	1·458 (5)	C(5′)–C(5′)	1·436 (6)
C(2′)–C(1′)	1·519 (5)	C(5′1)–O(5′)	1·346 (6)
O(4′)–C(1′)	1·415 (5)	O(5′1)–C(5′1)	1·193 (7)
O(2′)–C(2′)	1·417 (5)	C(5′2)–C(5′1)	1·484 (8)
C(6)–N(1)–C(2)	118·5 (3)	C(3′)–C(2′)–O(2′)	113·0 (3)
N(3)–C(2)–N(1)	130·0 (4)	C(2′1)–O(2′)–C(2′)	115·5 (3)
C(4)–N(3)–C(2)	110·6 (3)	O(2′1)–C(2′1)–O(2′)	122·3 (4)
C(5)–C(4)–N(3)	126·7 (3)	C(2′2)–C(2′1)–O(2′)	110·7 (4)
N(9)–C(4)–N(3)	127·8 (3)	C(2′2)–C(2′1)–O(2′1)	127·0 (4)
N(9)–C(4)–C(5)	105·5 (3)	O(3′)–C(3′)–C(2′)	107·5 (3)
C(6)–C(5)–C(4)	117·0 (3)	C(4′)–C(3′)–C(2′)	102·4 (3)
N(7)–C(5)–C(4)	110·7 (3)	C(4′)–C(3′)–O(3′)	107·6 (3)
N(7)–C(5)–C(6)	132·2 (3)	C(3′1)–O(3′)–C(3′)	116·4 (4)
C(5)–C(6)–N(1)	117·1 (3)	O(3′1)–C(3′1)–O(3′)	122·5 (6)
N(6)–C(6)–N(1)	119·3 (4)	C(3′2)–C(3′1)–O(3′)	109·1 (5)
N(6)–C(6)–C(5)	123·5 (4)	C(3′2)–C(3′1)–O(3′1)	128·3 (5)
C(8)–N(2)–C(5)	104·0 (3)	C(5′)–C(4′)–C(3′)	111·1 (4)
N(9)–C(8)–N(7)	113·8 (3)	O(4′)–C(4′)–C(3′)	106·0 (3)
C(8)–N(9)–C(4)	106·1 (3)	O(4′)–C(4′)–C(5′)	109·5 (3)
C(1′)–N(9)–C(4)	127·9 (3)	O(5′)–C(5′)–C(4′)	107·8 (4)
C(1′)–N(9)–C(8)	125·5 (3)	C(5′1)–O(5′)–O(5′)	115·4 (4)
C(2′)–C(1′)–N(9)	113·3 (3)	O(5′1)–C(5′1)–O(5′)	121·4 (5)
O(4′)–C(1′)–N(9)	108·9 (3)	C(5′2)–C(5′1)–O(5′)	111·3 (4)
O(4′)–C(1′)–C(2′)	106·3 (3)	C(5′2)–C(5′1)–O(5′1)	127·2 (5)
O(2′)–C(2′)–C(1′)	110·4 (3)	C(4′)–O(4′)–C(1′)	109·9 (3)
C(3′)–C(2′)–C(1′)	100·8 (3)		

Discussion. The atomic numbering is shown in the perspective drawing (Fig. 1); atomic parameters, and bond lengths and angles are given in Tables 1* and 2.

Bond lengths and angles are unexceptional, being broadly similar to expected values, and with acetyl groups showing short C=O bonds in the range 1·18 (1) to 1·195 (8) Å.

The purine base is approximately planar, with C(5) showing the greatest deviation [0·044 (7) Å] from the mean plane.

This plane has (θ,φ) values of (80°, 16°), which means that the θ value detected in the $I(\theta,\varphi)$ function is 8° too large. Nonetheless, the coordinates generated by the rotation function are still in approximately the correct orientation, as verified by the final solution.

As expected, the acetyl groups are all planar, to within 0·02 Å.

Conformation of the molecule

Purine nucleosides show less restriction than pyrimidines to rotation about the N-glycosidic bond, but are more often found in the *anti* conformation. For TAA, however, the N-glycosidic torsion angle χ is 61·1 (7)°, in the *syn* range. The sugar pucker, $^2T_3$, is normal, with $P = 171{\cdot}1$ (8)°, and $\psi_m = 37{\cdot}5$ (8)°.

The C(4′)—C(5′) conformation, [$\gamma = 178{\cdot}8$ (9)°, $\gamma' = 62{\cdot}0$ (9)°] is *ap* (*gauche–trans*). Purine nucleosides whose structures have been determined are roughly equally divided between the +*sc* and *ap* conformations about this bond, so these results are quite normal. Relevant torsion angles have been deposited. The conformational parameters used follow the guidelines of the IUPAC–IUB Joint Commission on Biochemical Nomenclature (1983).

Hydrogen bonding

There are two crystallographically independent hydrogen bonds present in the structure of TAA (Table 3).

The hydrogen bonding is especially interesting, since, as in the case of 3′,5′-di-*O*-acetylthymidine (Wilson, Low, Tollin & Wilson, 1984), the acetylated nucleoside adopts a base-paired conformation whereas the parent, adenosine, does not (Lai & Marsh, 1972).

In this case (Fig. 2), each TAA molecule is involved in four hydrogen bonds, two with each of two translationally related bases, forming a chain of paired bases along **c**, similar to the situation in 2′,3′,5′-tri-*O*-acetylguanosine (Wilson, Low & Tollin, 1985).

The hydrogen-bond scheme involves N(1)···N(6) and N(6)···N(7) pairing between neighbouring bases.

In recent studies of single crystals of oligonucleotides, it has become apparent that many base-pairs show a significant rotation of the bases with respect to each other, about an axis joining them, termed 'propeller twist' (Dickerson, 1983). This twist has been found to have a significant magnitude in many single-crystal studies of mononucleosides (Wilson, 1985). In the present structure, the TAA base-pair shows a propeller twist of 17 (1)°.

Table 3. *Hydrogen bonding and close contact distances* (Å) *and angles* (°)

Hydrogen-bond geometry			
N(1)···N(6^{i})	3·00 (1)	N(1)···H(61^{i})–N(6^{i})	168 (1)
N(1)···H(61^{i})	2·24 (1)		
N(6)···N(7^{i})	3·04 (1)	N(6)–H(62)···N(7^{i})	180 (1)
H(62)···N(7^{i})	2·24 (1)		
Acetyl–base stacking			
O($2'1^{\text{ii}}$)···N(7)	3·66 (1)		
···C(8)	3·27 (1)		
···N(9)	3·47 (1)		

Symmetry code: (i) $-1\frac{1}{2}-x, -1-y, -\frac{1}{2}+z$; (ii) $-\frac{1}{2}+x, -\frac{1}{2}-y, -1-z$.

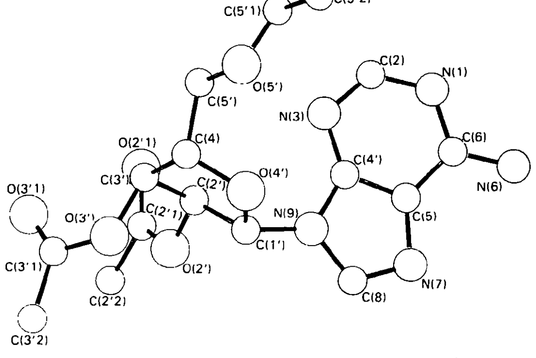

Fig. 1. Perspective drawing and atomic numbering.

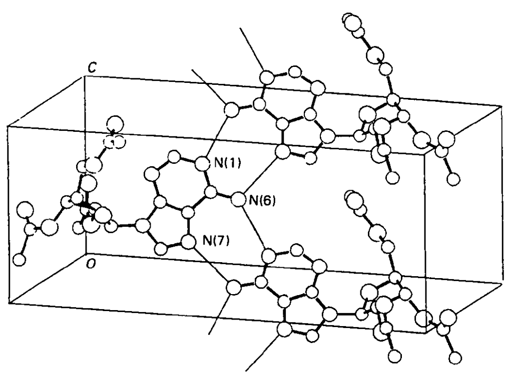

Fig. 2. Perspective drawing of the unit cell showing the hydrogen bonding.

---

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42778 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

A very weak stacking interaction of the 2′-acetyl group with a neighbouring base occurs, but is less pronounced than others in this series (Wilson, Low & Tollin, 1985) and, unusually, is above the indole ring of the purine base, rather than above the six-membered ring. Details are given in Table 3.

The authors would like to thank Dr J. N. Low for discussion and assistance. One of us (CCW) thanks the University of Dundee for the award of the Elizabeth Nicoll-Lindsay Postgraduate Scholarship.

References

DICKERSON, R. E. (1983). *J. Mol. Biol.* **166**, 419–441.

GILMORE, C. G. (1983). *MITHRIL*. A computer program for the automatic solution of crystal structures from X-ray data. Univ. of Glasgow.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

IUPAC–IUB JOINT COMMISSION ON BIOCHEMICAL NOMENCLATURE (1983). *Pure Appl. Chem.* **55**, 1273–1280.

LAI, T. F. & MARSH, R. E. (1972). *Acta Cryst.* B**28**, 1982–1989.

MAIN, P. (1976). *Crystallographic Computing Techniques*, edited by F. R. AHMED, K. HUML & B. SEDLACEK, pp. 97–105. Copenhagen: Munksgaard.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

ROBERTS, P. & SHELDRICK, G. M. (1975). *XANADU*. Program for torsion-angle, mean-plane and libration-correction calculations. Univ. of Cambridge, England.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

TOLLIN, P. (1976). *Crystallographic Computing Techniques*, edited by F. R. AHMED, K. HUML & B. SEDLACEK, pp. 212–221. Copenhagen: Munksgaard.

TOLLIN, P. & COCHRAN, W. (1964). *Acta Cryst.* **17**, 1322–1324.

WILSON, C. C. (1985). PhD thesis, Univ. of Dundee.

WILSON, C. C., LOW, J. N. & TOLLIN, P. (1985). *Acta Cryst.* C**41**, 1123–1125.

WILSON, C. C., LOW, J. N., TOLLIN, P. & WILSON, H. R. (1984). *Acta Cryst.* C**40**, 1712–1715.

WILSON, C. C. & TOLLIN, P. (1985). *PATMET*. Program for determination of orientation and position of a known molecular fragment within a unit cell. Univ. of Dundee.

Acta Cryst. (1986). C**42**, 700–703

Structure of 2′,3′,5′-Tri-*O*-acetylguanosine (Orthorhombic Form)

BY JOHN N. LOW, PATRICK TOLLIN AND CHARLES C. WILSON*

Department of Physics, University of Dundee, Dundee DD1 4HN, Scotland

AND SHEELAGH N. SCRIMGEOUR

Department of Chemistry, University of Dundee, Dundee DD1 4HN, Scotland

(*Received* 1 *October* 1985; *accepted* 30 *January* 1986)

Abstract. $C_{16}H_{19}N_5O_8$, $M_r = 409·4$, orthorhombic, $P2_12_12_1$, $a = 14·346\,(4)$, $b = 11·135\,(4)$, $c = 22·606\,(9)$ Å, $U = 3611·1$ Å^3, $Z = 8$, $D_x = 1·51$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 0·79$ cm^{-1}, $F(000) = 1712$, $T = 293$ K, $R = 0·091$ for 2835 unique observed reflections (Friedel pairs merged). The asymmetric unit consists of two molecules, *A* and *B*, of the title compound. *A*: the *N*-glycosidic torsion angle, χ, is $-158\,(1)°$, in the *anti* range, the sugar pucker is ^2_1T, with $P = 147\,(1)°$, $\psi_m = 44\,(1)°$ and the C(4′)—C(5′) conformation is $+sc$ with $\gamma = 49\,(1)°$. *B*: χ is $179\,(1)°$, in the *anti* range, the sugar pucker is $_4T^3$, with $P = 44\,(1)°$, $\psi_m = 42\,(1)°$ and the C(4′)—C(5′) conformation is $+sc$ with $\gamma = 46\,(1)°$. Each of these molecules is base-paired to one of their symmetry-related molecules by hydrogen bonds involving O(6)···N(2) [2·87 (1) Å (*A*), 2·82 (1) Å (*B*)] and N(7)···N(1) [2·83 (1) Å (*A*), 2·87 (1) Å (*B*)]. These base-paired molecules form ribbons which run through the crystal parallel to **b**.

Introduction. The structure determination resulted from an experiment in which an attempt was made to co-crystallize the title compound, designated TAG, with 3-deazauracil (Low & Wilson, 1983), to find out if the latter could intercalate between the stacked bases of TAG. This did not happen, an orthorhombic form of TAG with two molecules in the asymmetric unit being formed instead. This continues our study of conformations and base-pairing patterns of acetyl-substituted nucleosides. A monoclinic form of TAG has already been described by Wilson, Low & Tollin (1985).

---

* Present address: Neutron Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, England.

0108-2701/86/060700-04$01.50

© 1986 International Union of Crystallography