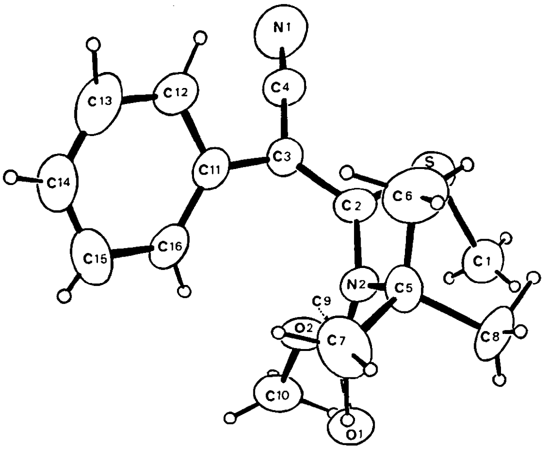

Fig. 2. *ORTEP* (Johnson, 1965) of compound (2*Z*) with atom labelling.

C(2)C(3)C(11) as important as that in (2*Z*). The distances between the methoxycarbonyl group and the phenyl ring or the cyano group are large enough to give no significant shielding or deshielding effect.

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Structure of 2′,3′,5′-Tri-*O*-acetylguanosine, $C_{16}H_{19}N_5O_8$

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(*Received* 11 *December* 1984; *accepted* 5 *March* 1985)

Abstract. $M_r = 409{\cdot}4$, monoclinic, $P2_1$, $a = 7{\cdot}414\,(3)$, $b = 11{\cdot}491\,(4)$, $c = 11{\cdot}790\,(4)$ Å, $\beta = 99{\cdot}47\,(2)°$, $U = 990{\cdot}75$ Å^3, $Z = 2$, $D_x = 1{\cdot}372$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}72$ cm^{-1}, $F(000) = 428$, $T = 293$ K, $R = 0{\cdot}053$ for 1241 unique reflections (Friedel pairs merged). The glycosidic torsion angle, χ, is $-160{\cdot}6\,(9)°$, in the *anti* range, and the sugar pucker is C(2′)-*endo* (^2E), with $P = 167{\cdot}5\,(9)°$, and $\psi_m = 28{\cdot}4\,(9)°$. The C(4′)—C(5′) conformation is g^+, with $\gamma = 50{\cdot}8\,(9)°$. There are three hydrogen bonds present, two of which base-pair symmetry-related molecules, O(6)···N(2) [2·94 (1) Å], N(7)···N(1) [2·86 (1) Å], and one is between the 5′-acetyl O atom and N(2) of a separate molecule [3·03 (1) Å]. Stacking involving the 2′-acetyl O atom between two base rings is noted.

Introduction. The structure was determined as part of our studies of nucleoside conformations, and solid-state interactions. Studies have been made of heavy-atom (halogenated) and, more recently, of acetyl-substituted pyrimidine nucleosides, which have brought to light interesting structural features. The present study continues this work, by investigating an acetyl-substituted purine nucleoside, designated TAG.

Experimental. Crystals were grown from aqueous solution, and were elongated along **a**. Cell dimensions obtained by diffractometry from crystals mounted along **a** and **b**. Intensity data collected from crystals mounted along **a** and **b**, with dimensions approximately 1·0 × 0·5 × 0·5 mm. Stoe Stadi II diffractometer (two-circle). Data collected from the *b*-axis crystal in the range $k = 0$ to 8, and from the *a*-axis crystal from $h = 0$ to 2, for scaling purposes. Max. $\sin\theta/\lambda$ 0·77 Å^{-1}. Range of indices: $-10 < h < 10$, $-14 < k < 14$, $-15 < l < 15$; No absorption corrections. One standard reflection measured every 100 reflections; intensity variation <5% from the mean. 6313 reflections measured; 2891 with $I < 3\sigma(I)$ regarded as unobserved; 1241 unique reflections used; $R_{\rm int} = 0{\cdot}042$. Structure solved by a combination of Patterson and direct methods. The orientation of the nine-membered purine base plane was obtained using the $I(\theta,\varphi)$ function of Tollin & Cochran (1964), which revealed the plane of the base ring, at $(\theta,\varphi) = (55°, 179°)$. This orientation agreed with that suggested by strong reflections $\bar{4}04$, $\bar{3}03$ and $\bar{2}02$. A one-dimensional rotation function (Tollin, 1976) carried out in this plane revealed the correct orientation of the base in this plane. The $I(\theta,\varphi)$ and rotation-function

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Table 1. *Fractional coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å² × 10³) *for non-hydrogen atoms 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)	566 (7)	−2770	577 (4)	35 (1)
C(2)	1729 (8)	−3043 (5)	1572 (5)	33 (1)
N(2)	2039 (10)	−4204 (6)	1772 (5)	59 (2)
N(3)	2517 (7)	−2283 (5)	2341 (4)	34 (1)
C(4)	2061 (8)	−1170 (6)	1995 (5)	29 (1)
C(5)	961 (8)	−796 (6)	1018 (5)	30 (1)
C(6)	82 (8)	−1630 (6)	218 (4)	30 (1)
O(6)	−939 (6)	−1463 (4)	−715 (3)	42 (1)
N(7)	899 (8)	423 (5)	977 (4)	40 (1)
C(8)	1963 (9)	756 (6)	1913 (5)	35 (1)
N(9)	2703 (6)	−161 (4)	2578 (3)	32 (1)
C(1′)	4030 (7)	−143 (6)	3648 (4)	29 (1)
C(2′)	6010 (7)	−248 (6)	3440 (4)	31 (1)
O(2′)	6611 (6)	−1432 (4)	3574 (3)	41 (1)
C(2′1)	7054 (10)	−1992 (8)	2646 (7)	55 (2)
O(2′1)	6908 (10)	−1534 (7)	1739 (5)	101 (3)
C(2′2)	7699 (13)	−3206 (8)	2949 (10)	92 (4)
C(3′)	7085 (7)	530 (6)	4380 (4)	29 (1)
O(3′)	7598 (5)	−146 (4)	5419 (3)	36 (1)
C(3′1)	9238 (8)	−731 (6)	5517 (5)	41 (2)
O(3′1)	10286 (6)	−613 (5)	4868 (4)	63 (1)
C(3′2)	9436 (9)	−1533 (9)	6539 (5)	66 (2)
C(4′)	5681 (7)	1440 (5)	4612 (4)	30 (1)
C(5′)	5807 (8)	2603 (6)	4054 (5)	41 (2)
O(5′)	5848 (6)	2400 (4)	2846 (3)	50 (1)
C(5′1)	5607 (10)	3352 (9)	2150 (7)	67 (3)
O(5′1)	5386 (9)	4295 (6)	2525 (6)	94 (2)
C(5′2)	5628 (11)	3024 (11)	933 (8)	96 (4)
O(4′)	3891 (5)	944 (3)	4177 (3)	33 (1)

calculations employed locally written programs. The *MITHRIL* (Gilmore, 1983) direct-methods program was then used with the oriented model included. Also used were the programs *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978); all calculations carried out on the Dundee University DEC-10 computer. Refinement (on F) by blocked-matrix least squares with *SHELX76* (Sheldrick, 1976). Non-hydrogen atoms refined anisotropically; H(21) and H(22) on N(2) were included at positions indicated by a difference map and during refinement had their bond distances from N(2) constrained close to 0·900 Å. Remaining H atoms included at calculated positions, with fixed isotropic temperature factors 1·5 times that of the parent atom. 267 parameters refined, $R = 0{\cdot}053$, $wR = 0{\cdot}070$, $w = 1{\cdot}4016/[\sigma^2(F) + 0{\cdot}002957F^2]$; max. $\Delta/\sigma = 0{\cdot}076$; max. difference-map peak 0·28 e Å^{-3}, min. −0·23 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction.

Discussion. Atomic coordinates are given in Table 1,* with bond lengths and angles in Table 2. The atomic numbering used is shown in the perspective drawing (Fig. 1). Bond lengths and angles are unexceptional, being broadly similar to that in guanosine dihydrate (GD) (Thewalt, Bugg & Marsh, 1970), and the acetyl geometry is as previously noted (Low & Wilson, 1984), showing short C=O bonds [C(2′1)—O(2′1) 1·181 (10), C(3′1)—O(3′1) 1·184 (8), and C(5′1)—O(5′1) 1·192 (13) Å]. The purine base is approximately planar, with C(8) [0·029 (8) Å] and C(4) [−0·027 (8) Å] showing greatest deviation from the mean plane. All three acetyl groups are planar to within 0·006 (11) Å.

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

C(2)—N(1)	1·374 (7)	C(3′)—C(2′)	1·540 (8)
C(6)—N(1)	1·404 (6)	C(2′1)—O(2′)	1·356 (10)
N(2)—C(2)	1·367 (9)	O(2′1)—C(2′1)	1·181 (10)
N(3)—C(2)	1·324 (7)	C(2′2)—C(2′1)	1·499 (13)
C(4)—N(3)	1·368 (8)	O(3′)—C(3′)	1·448 (6)
C(5)—C(4)	1·367 (8)	C(4′)—C(3′)	1·532 (8)
N(9)—C(4)	1·391 (8)	C(3′1)—O(3′)	1·378 (7)
C(6)—C(5)	1·425 (8)	O(3′1)—C(3′1)	1·184 (8)
N(7)—C(5)	1·402 (8)	C(3′2)—C(3′1)	1·505 (10)
O(6)—C(6)	1·244 (6)	C(5′)—C(4′)	1·500 (9)
C(8)—N(7)	1·304 (8)	O(4′)—C(4′)	1·458 (6)
N(9)—C(8)	1·373 (8)	O(5′)—C(5′)	1·449 (7)
C(1′)—N(9)	1·466 (6)	C(5′1)—O(5′)	1·361 (11)
C(2′)—C(1′)	1·533 (8)	O(5′1)—C(5′1)	1·192 (13)
O(4′)—C(1′)	1·408 (7)	C(5′2)—C(5′1)	1·486 (13)
O(2′)—C(2′)	1·432 (8)		
C(6)—N(1)—C(2)	124·4 (4)	C(3′)—C(2′)—C(1′)	103·6 (4)
N(2)—C(2)—N(1)	115·8 (5)	C(3′)—C(2′)—O(2′)	110·9 (4)
N(3)—C(2)—N(1)	125·3 (5)	C(2′1)—O(2′)—C(2′)	118·3 (5)
N(3)—C(2)—N(2)	118·9 (5)	O(2′1)—C(2′1)—O(2′)	121·4 (8)
C(4)—N(3)—C(2)	110·7 (5)	C(2′2)—C(2′1)—O(2′)	111·1 (7)
C(5)—C(4)—N(3)	129·0 (5)	C(2′2)—C(2′1)—O(2′1)	127·5 (9)
N(9)—C(4)—N(3)	125·8 (5)	O(3′)—C(3′)—C(2′)	109·3 (5)
N(9)—C(4)—C(5)	105·2 (5)	C(4′)—C(3′)—C(2′)	103·8 (4)
C(6)—C(5)—C(4)	119·4 (6)	C(4′)—C(3′)—O(3′)	107·9 (4)
N(7)—C(5)—C(4)	110·8 (5)	C(3′1)—O(3′)—C(3′)	116·0 (4)
N(7)—C(5)—C(6)	129·8 (5)	O(3′1)—C(3′1)—O(3′)	123·7 (6)
C(5)—C(6)—N(1)	111·2 (4)	C(3′2)—C(3′1)—O(3′)	109·5 (5)
O(6)—C(6)—N(1)	120·0 (5)	C(3′2)—C(3′1)—O(3′1)	126·8 (6)
O(6)—C(6)—C(5)	128·8 (6)	C(5′)—C(4′)—C(3′)	115·9 (5)
C(8)—N(7)—C(5)	104·6 (5)	O(4′)—C(4′)—C(3′)	106·0 (4)
N(9)—C(8)—N(7)	112·8 (5)	O(4′)—C(4′)—C(5′)	108·2 (4)
C(8)—N(9)—C(4)	106·6 (4)	O(5′)—C(5′)—C(4′)	107·5 (5)
C(1′)—N(9)—C(4)	124·3 (5)	C(5′1)—O(5′)—C(5′)	116·2 (6)
C(1′)—N(9)—C(8)	129·0 (5)	O(5′1)—C(5′1)—O(5′)	121·3 (8)
C(2′)—C(1′)—N(9)	112·7 (4)	C(5′2)—C(5′1)—O(5′)	110·9 (9)
O(4′)—C(1′)—N(9)	107·8 (4)	C(5′2)—C(5′1)—O(5′1)	127·8 (10)
O(4′)—C(1′)—C(2′)	106·4 (5)	C(4′)—O(4′)—C(1′)	112·0 (4)
O(2′)—C(2′)—C(1′)	110·2 (5)		

Selected torsion angles (°)

C(4)—N(9)—C(1′)—O(4′)	−160·6 (9)	χ
C(4′)—O(4′)—C(1′)—C(2′)	−15·0 (9)	ν_0
O(4′)—C(1′)—C(2′)—C(3′)	26·6 (9)	ν_1
C(1′)—C(2′)—C(3′)—C(4′)	−27·7 (9)	ν_2
C(2′)—C(3′)—C(4′)—O(4′)	19·6 (9)	ν_3
C(3′)—C(4′)—O(4′)—C(1′)	−3·1 (9)	ν_4
C(3′)—C(4′)—C(5′)—O(5′)	50·8 (9)	γ
O(4′)—C(4′)—C(5′)—O(5′)	−68·1 (9)	

Distances involved in close ring contacts (Å)

O(2′1)···N(1)(x+1, y, z)	3·53 (1)	O(2′1)···N(3)(x, y, z)	3·55 (1)
···C(5)(x+1, y, z)	3·36 (1)	···C(4)(x, y, z)	3·68 (1)
···C(6)(x+1, y, z)	3·19 (1)	···N(9)(x, y, z)	3·77 (1)
···O(6)(x+1, y, z)	3·53 (1)		

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42109 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Conformation

The conformation of the molecule is not unusual for a purine nucleoside, with χ[C(4)–N(9)–C(1′)–O(4′)] = −160·6 (9)°, in the high *anti* range, and sugar pucker described by $P = 167{\cdot}5$ (9)°, $\psi_m = 28{\cdot}4$ (9)°, ${}^2E$ [C(2′)-*endo*] conformation. The C(4′)–C(5′) conformation is g^+ (*gauche–gauche*), with relevant torsion angles, γ[C(3′)–C(4′)–C(5′)–O(5′)] = 50·8 (9) and O(4′)–C(4′)–C(5′)–O(5′) = −68·1 (9)°. The conformational parameters used follow the guidelines of IUPAC–IUB Joint Commission on Biochemical Nomenclature (1983). Table 2 shows relevant torsion angles.

Hydrogen bonding

The molecules are base-paired by the two hydrogen bonds N(7)···N(1)($-x$, $y+\frac{1}{2}$, $-z$) 2·86 (1), and O(6)···N(2)($-x$, $y+\frac{1}{2}$, $-z$) 2·94 (1) Å, as in the GD structure. Such base-pairing represents a model of Hoogsteen G–C pairing (Hoogsteen, 1959), with one of the TAG molecules mimicking the role of cytosine in this situation. However, the C(1′)···C(1′) separation of the coplanar base-pair is large, at 11·95 (2) Å. An additional hydrogen bond is present in the structure, O(5′1)···N(2)(x, $y+1$, z) 3·03 (1) Å. This hydrogen bond links the molecules together such that two chains of molecules stack along the *b* axis, cross-linked by base-pairing, with successive molecules of one chain linked by the O(5′1)···N(2) hydrogen bond (Fig. 2).

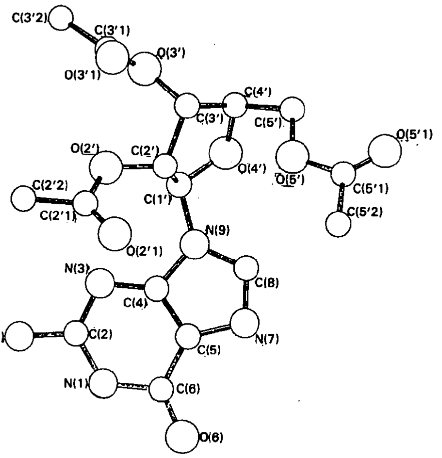

Fig. 1. Perspective view of the molecule showing the atomic numbering.

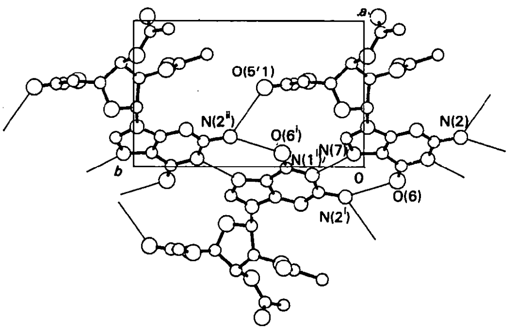

Fig. 2. View of the unit cell along **c** showing the hydrogen bonding and base-pairing and stacking along **b**. Symmetry code: (i) $-x$, $\frac{1}{2}+y$, $-z$; (ii) x, $1+y$, z.

Stacking

As we have observed in acetylated pyrimidines (Wilson, Low & Young, 1983; Low & Wilson, 1984; Wilson, Low, Tollin & Wilson, 1984; Wilson & Tollin, 1985), the acetyl groups play a major role in the stacking in acetyl-substituted nucleosides. The polar carbonyl group takes up important stacking positions in relation to neighbouring base rings. In the present structure a contact of O(2′1) with neighbouring base rings at ($x+1$, y, z), O(2′1) at 3·02 (2) Å from the plane of the ring (Table 2), overrides the strong tendency to base-stack in GD. This O atom is situated such that it also contacts the base of the molecule to which it belongs, at 3·15 (2) Å from this plane (Table 2). Thus the O atom sits between two base planes, which are both farther apart, at 6·17 (2) Å, and show less base overlap than in GD. Further investigations of this contact are in progress. Thus the stacking of acetyl O atoms has been observed to play an important part in the packing when in 5′ (Wilson *et al.*, 1983; Low & Wilson, 1984; Wilson & Tollin, 1985), 3′ (Wilson, Low, Tollin & Wilson, 1984), and now 2′ positions, and in both pyrimidine and purine nucleosides.

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