6-Benzylamino-9-β-D-ribofuranosylpurine

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Abstract. $C_{17}H_{19}N_5O_4$, a cytokinin [Hashizume (1975). Private communication]. Triclinic, $P1$, $a = 8 \cdot 941$ (2), $b = 9 \cdot 779$ (2), $c = 5 \cdot 015$ (1) Å, $\alpha = 89 \cdot 63$ (2), $\beta = 91 \cdot 43$ (2), $\gamma = 68 \cdot 25$ (1)°, $U = 407 \cdot 1$ (2) Å^3, $Z = 1$, $D_x = 1 \cdot 46$, $D_m = 1 \cdot 48$ g cm^{-3}, μ(Mo $K\alpha$) = 1·26 cm^{-1}, χ_{CN} is $-11 \cdot 1°$ (*anti*), the sugar puckering C(2′)-*endo*-C(3′)-*exo* ($_3T^2$) and φ_{CO}–φ_{OO} *gauche–trans*. The torsional angle C[benzyl]–N[imino]–C(6)–N(1) is $-5 \cdot 2°$. Intermolecular hydrogen bonds are formed between O(3′) and N(7), O(5′) and N(1), and N(10) and O(2′). The intramolecular hydrogen bond [O(2′)–N(3)] also exists but the occupancy factor of the relevant hydrogen atom is 0·6.

Introduction. The *N*-alkylated adenine derivatives are known as minor components in tRNA and also as cytokinins of plants. The present work has been carried out to examine the effect of the substituent at C(6) on the molecular and crystal structure (Takeda, Ohashi, Sasada & Kakudo, 1975).

Crystals in the form of prisms were obtained by evaporating an acetonitrile solution at room temperature. Three-dimensional intensity data up to 60° (2θ)

were collected on a Rigaku four-circle automatic diffractometer with Zr-filtered Mo $K\alpha$ radiation (0·71069 Å), by the ω–2θ scan technique at a rate 2° (2θ) min^{-1}. Structure factors for 2861 reflexions were obtained, of which 639 with $|F_o| < 1 \cdot 5\sigma(|F_o|)$ were considered to be zero. Seven of the resolved peaks around the origin of a sharpened Patterson function were taken as those due to the purine moiety. Starting from 113 reliable phases ($|E_o| \geq 1 \cdot 5$) calculated with these seven atoms, tangent-formula refinement (Karle, 1968) gave the phases of 337 reflexions ($|E_o| \geq 1 \cdot 3$). The resulting E map revealed all the non-hydrogen atoms. When R became 0·11 by block-diagonal least-squares refinement, all the H atoms except that bonded to O(2′) were located on a difference map. After several cycles of refinement, two peaks around O(2′) were found on the difference map. These were considered to be due to a disordered H atom. From the peak height, its occupancy was assumed to be 0·6 for H(O2′A) and 0·4 for H(O2′B).

In the later stages of refinement the three strongest reflexions were excluded, because they seemed to suffer

Table 1. *Fractional atomic coordinates and thermal parameters* (*all* $\times 10^4$ *except for* H)

The form of the anisotropic thermal factor is exp $(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	556	1750	−3000	90 (4)	76 (3)	353 (12)	−81 (5)	−39 (10)	77 (9)
C(2)	−886 (4)	1744 (4)	−2370 (8)	85 (4)	90 (4)	443 (16)	−72 (6)	−90 (13)	122 (12)
N(3)	−1252 (4)	915 (3)	−582 (6)	78 (3)	88 (3)	382 (12)	−70 (5)	−42 (10)	88 (10)
C(4)	81 (4)	22 (4)	753 (6)	75 (4)	68 (3)	280 (11)	−75 (5)	−12 (10)	23 (9)
C(5)	1645 (4)	−75 (4)	390 (7)	64 (3)	70 (3)	297 (11)	−65 (5)	−18 (10)	19 (9)
C(6)	1889 (4)	816 (4)	−1654 (6)	74 (3)	65 (3)	279 (11)	−70 (5)	0 (10)	−3 (9)
N(7)	2708 (4)	−1136 (3)	2113 (6)	65 (3)	81 (3)	350 (11)	−58 (5)	−24 (9)	58 (9)
C(8)	1774 (4)	−1642 (4)	3453 (7)	73 (4)	77 (3)	327 (12)	−58 (6)	−52 (11)	61 (10)
N(9)	174 (3)	−1000 (3)	2720 (6)	66 (3)	78 (3)	281 (9)	−85 (5)	−2 (8)	20 (8)
N(10)	3357 (3)	754 (3)	−2273 (6)	72 (3)	79 (3)	340 (11)	−62 (5)	3 (9)	71 (9)
C(1′)	−1209 (4)	−1304 (4)	3751 (6)	68 (3)	80 (3)	245 (10)	−75 (5)	29 (9)	9 (9)
O(1′)	−569 (3)	−2606 (3)	5330 (5)	108 (3)	96 (3)	293 (9)	−117 (5)	−70 (8)	91 (8)
C(2′)	−2239 (4)	−1597 (4)	1489 (6)	67 (3)	73 (3)	227 (10)	−69 (5)	11 (9)	10 (9)
O(2′)	−3545 (3)	−314 (3)	659 (6)	71 (3)	95 (3)	373 (10)	−64 (5)	−32 (8)	94 (8)
C(3′)	−2799 (4)	−2737 (4)	2825 (6)	68 (3)	69 (3)	272 (11)	−69 (5)	16 (9)	15 (9)
O(3′)	−4083 (3)	−2076 (3)	4568 (5)	74 (3)	110 (3)	367 (10)	−79 (5)	88 (9)	11 (9)
C(4′)	−1305 (4)	−3640 (4)	4478 (7)	81 (4)	77 (3)	268 (11)	−69 (6)	22 (10)	52 (9)
C(5′)	−55 (5)	−4888 (4)	2985 (8)	106 (5)	88 (4)	394 (15)	−30 (7)	34 (13)	45 (12)
O(5′)	−557 (4)	−6087 (3)	2646 (7)	214 (6)	84 (3)	484 (14)	−87 (7)	−51 (14)	33 (10)
C(11)	3699 (4)	1547 (4)	−4497 (7)	97 (4)	80 (3)	313 (12)	−88 (6)	98 (11)	−8 (10)
C(12)	4006 (4)	2914 (4)	−3698 (7)	72 (4)	71 (3)	309 (12)	−57 (5)	−31 (10)	71 (10)
C(13)	5072 (5)	3333 (4)	−5161 (8)	100 (5)	102 (4)	431 (16)	−82 (7)	39 (14)	104 (13)
C(14)	5316 (5)	4628 (5)	−4531 (10)	128 (6)	118 (5)	652 (24)	−161 (9)	−82 (18)	190 (18)
C(15)	4528 (6)	5485 (5)	−2482 (9)	160 (6)	95 (4)	566 (21)	−146 (9)	−224 (18)	113 (15)
C(16)	3460 (6)	5069 (5)	−1006 (9)	211 (8)	97 (4)	443 (18)	−132 (10)	−44 (19)	−21 (14)
C(17)	3206 (5)	3791 (5)	−1635 (9)	153 (6)	104 (5)	417 (17)	−137 (9)	90 (16)	2 (13)

Table 1 (cont.)

	$x \times 10^3$	$y \times 10^3$	$z \times 10^3$	$B(\text{Å}^2)$
H(C2)	−185 (5)	248 (5)	−322 (8)	3·2 (8)
H(C8)	211 (4)	−247 (4)	489 (7)	2·6 (7)
H(N10)	412 (4)	25 (4)	−128 (7)	1·8 (6)
H(C1′)	−189 (4)	−44 (4)	487 (6)	1·5 (5)
H(C2′)	−152 (4)	−204 (3)	0 (6)	1·0 (5)
H(O2′A)*	−306 (7)	23 (7)	−14 (12)	2·7 (12)
H(O2′B)	−360 (11)	−50 (10)	−90 (17)	2·8 (18)
H(C3′)	−304 (4)	−336 (4)	147 (7)	2·1 (6)
H(O3′)	−489 (5)	−172 (5)	385 (9)	4·3 (9)
H(C4′)	−166 (4)	−407 (4)	601 (7)	2·0 (6)
H(C5′1)	87 (5)	−512 (5)	413 (8)	3·7 (9)
H(C5′2)	6 (4)	−453 (4)	114 (7)	2·2 (6)
H(O5′)	−20 (6)	−665 (6)	376 (10)	6·2 (12)
H(C111)	463 (4)	87 (4)	−540 (7)	2·0 (7)
H(C112)	275 (5)	184 (5)	−581 (8)	3·4 (8)
H(C13)	559 (5)	269 (5)	−671 (8)	3·4 (8)
H(C14)	608 (6)	490 (6)	−559 (10)	5·9 (12)
H(C15)	459 (6)	641 (5)	−201 (9)	4·7 (10)
H(C16)	284 (6)	572 (5)	39 (9)	5·3 (11)
H(C17)	257 (5)	344 (5)	−54 (9)	4·2 (9)

* Populations: H(O2′A) 0·6, H(O2′B) 0·4.

from secondary extinction. The final R was 0·049. The weighting scheme was: $w = 0·1$ if $|F_o| < 1·0$, $w = 1$ if $1·0 \le |F_o| \le 20·0$, and $w = 20·0/|F_o|$ if $|F_o| > 20·0$. Atomic scattering factors of C, N and O were taken from *International Tables for X-ray Crystallography* (1974) and that of H from Stewart, Davidson & Simpson (1965). Atomic coordinates and thermal parameters are given in Table 1.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31409 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
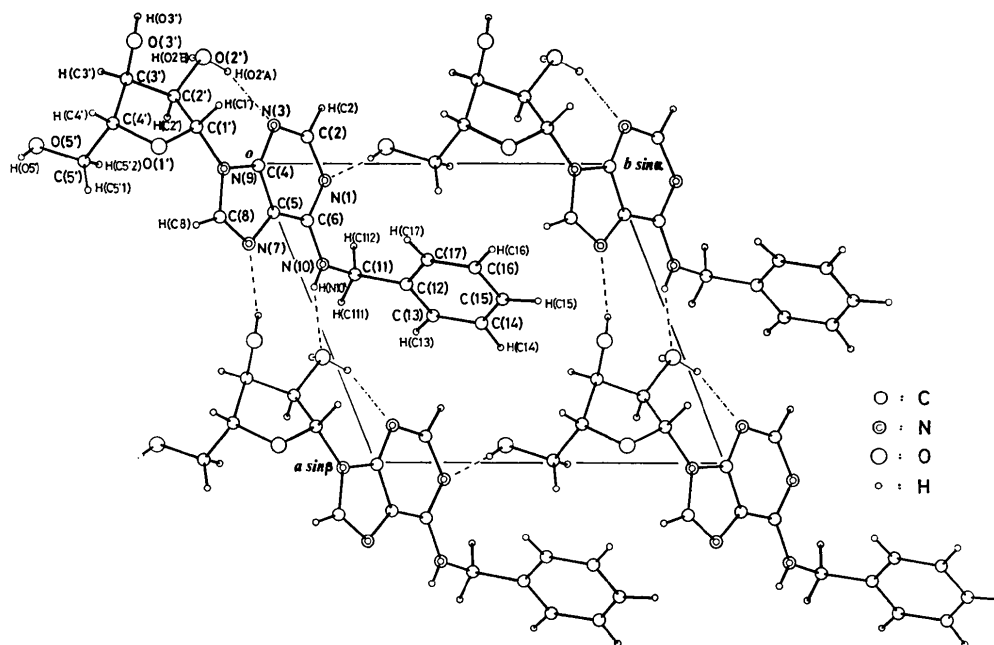
Discussion. Fig. 1 shows the crystal structure viewed along the c axis. Three intermolecular hydrogen bonds, given in Table 2, connect the molecules to form a two-dimensional sheet and an intramolecular hydrogen bond is partly formed between O(2′) and N(3) through H(O2′A). However, there is no hydrogen bond between the sugar hydroxy groups; this is a unique situation since all the nucleoside crystal structures so far reported have more than one hydrogen bond between the sugars. The distances between non-bonded atoms are not significantly shorter than the normal van der Waals contacts. The bond lengths and angles are shown in Fig. 2.

In the purine moiety, the bond lengths excepting N(1)–C(6) coincide with those of adenosine (Lai & Marsh, 1972). The difference between N(1)–C(6)–N(10) and C(5)–C(6)–N(10), 1·6°, is smaller than in adenosine (6·4°), probably owing to a steric hindrance of the bulky benzyl group. The purine ring is planar within 0·024 Å, as seen in Table 3. Closer examination shows, however, that the purine base is bent slightly and the dihedral angle between the five- and six-membered rings is 1·5°. The purine rings are stacked at a spacing of 3·45 Å. The overlapping area between five- and six-membered rings is a little larger than that of adenosine, in spite of the bulky substituent at N(10). This seems to have some connexion with the stabilization of the anticodon loop by the alkylated nucleosides on the 3′ side in the Fuller & Hodgson (1967) model.

In the sugar moiety, C(2′)–O(2′) is shorter than C(3′)–O(3′), as observed in the other nucleosides. The sugar puckering referred to the plane of C(1′), O(1′) and C(4′) is described as C(2′)-*endo*–C(3′)-*exo*, $_3T^2$, (Sundaralingam, 1971). The torsional angles are given

Fig. 1. The crystal structure viewed along the c axis. The broken lines represent intermolecular hydrogen bonds and the dot-dashed line represents an intramolecular hydrogen bond.

Table 2. *Hydrogen-bond lengths and angles*

D	A				D···A	H···A		
O(3')····N(7)	(−1+x,	y,	z)		2·903 (4) Å	2·16 (3) Å	O(3')–H(O3') —N(7)	167 (3)°
O(5')····N(1)	(	x, −1+y,	1+z)		2·915 (4)	2·16 (4)	O(5')- H(O5')—N(1)	174 (4)
N(10)···O(2')	(	1+z,	y,	z)	2·923 (4)	2·15 (3)	N(10)-H(N10)—O(2')	154 (3)
O(2')····N(3)	(	x,	y,	z)	2·811 (4)	1·98 (4)	O(2')–H(O2'A)-N(3)	153 (4)

Table 3. *Deviations of the atoms from the least-squares planes*

X, Y, Z in Å referred to orthogonal a, normal to ac^* and c^*, respectively.

(I) Ribose plane: $0·4967X−0·3705Y−0·7849Z+1·9004=0$
(II) Ribose plane: $0·6429X−0·3990Y−0·6539Z+1·7982=0$
(III) Purine plane: $−0·1490X−0·7170Y−0·6810Z+0·2781=0$
(IV) Phenyl plane: $−0·5822X+0·5084Y−0·6345Z+0·2191=0$

	I	II		III			IV	
C(1')	0·057* Å	0·000* Å	N(1)	0·008* Å	N(7)	−0·013* Å	C(11)	0·061 Å
O(1')	−0·092*	0·000*	C(2)	−0·013*	C(8)	0·006*	C(12)	−0·001*
C(2')	0·588	0·214	N(3)	0·001*	N(9)	0·019*	C(13)	−0·002*
C(3')	−0·052*	−0·414	C(4)	−0·009*	N(10)	0·086	C(14)	0·003*
C(4')	0·087*	0·000*	C(5)	−0·023*	C(1')	0·061	C(15)	−0·001*
C(5')	1·438	1·386	C(6)	0·024*	C(11)	0·250	C(16)	−0·002*
							C(17)	0·003*

* Atoms included in the calculation of the least-squares plane.

in Table 4. The conformation about the glycosidic bond is *anti* (Sundaralingam, 1969). The conformation about

Table 4. *Torsional angles*

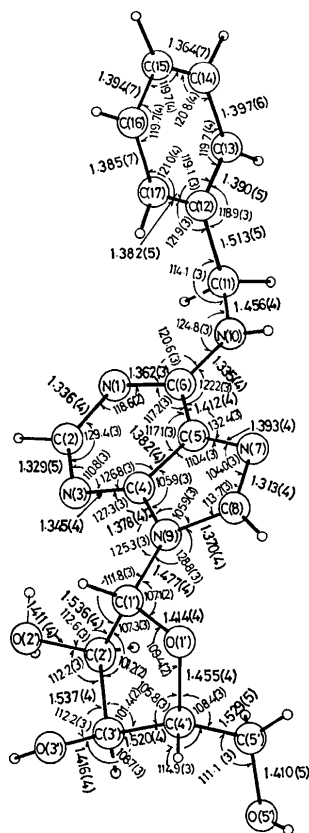|		
C(8)—N(9)—C(1')–O(1')	$[\chi_{CN}]$	−11·1°
C(3')–C(4')–C(5')–O(5')	$[\varphi_{co}]$	−75·5
O(1')–C(4')–C(5')–O(5')	$[\varphi_{oo}]$	166·5
N(1)—C(6)—N(10)—C(11)		−5·2
C(6)—N(10)-C(11)—C(12)		102·0
N(10)-C(11)—C(12)—C(13)		148·1
N(10)-C(11)—C(12)—C(17)		−34·8

Fig. 2. Bond lengths (Å) and bond angles (°). The estimated standard deviations are in parentheses. The bond lengths involving hydrogen atoms are 0·95–1·03 Å for C–H, 0·75–0·76 Å for O–H and 0·83 Å for N–H. The estimated deviations are 0·03–0·05 Å. The bond lengths of O(2')–H(O2'A) and O(2')–O(H2'B) are 0·91 (4) and 0·81 (9) Å, respectively.

C(4')-C(5'), φ_{CO}–φ_{OO}, is *gauche–trans* (Shefter & True-blood, 1965). The orientation of the alkyl group is the same as those of other *N*-alkylated adenine derivatives and the dihedral angle between the phenyl and purine planes is 98·9°, which is similar to that between the C=C plane and the purine plane in N^2-(Δ^2-isopentenyl)-2-methylthioadenine (McMullan & Sundaralingam, 1971).

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