74·0° for the 1,2-dioxane rings (Allen, Bellard & Kennard, 1986) and from 67·1 to 76·6° for the 1,2-oxazine rings (Riddell, Murray-Rust & Murray-Rust, 1974; Holzapfel, Kruger & Van Dyk, 1987*a,b,c*). In the case of compounds (2) and (3) this angle is even larger, namely 84·5° for both compounds. These large endocyclic torsion angles in 1,2-heteroatom cyclohexane rings has been ascribed to a reduction in O—O or O—N torsional strain with increasing angle (Riddell, Murray-Rust & Murray-Rust, 1974; Riddell, 1980). According to Allen, Bellard & Kennard (1986) this increased puckering also results in a decrease in the C—O—O (or C—O—N) valence angles, which would otherwise be unfavourably large. In the six chair-form 1,2-oxazine rings which have been reported (Riddell, Murray-Rust & Murray-Rust, 1974; Holzapfel, Kruger & Van Dyk, 1987*a,b,c*) the C—O—N angles range from 106·3 to 109·1° [mean value 107 (1)°; mean value for the 1,2-dioxanes and 1,2,4-trioxanes 107·2 (5)° (Allen, Bellard & Kennard, 1986)]. For (2) the C—O—N angle is 105·4 (3)°, while the C—O—O angle for (3) is 103·4 (1)°.

Another interesting feature of the *N*-cyclohexyl-3-cyano-1,2-oxazine systems is the orientation of the *N*-cyclohexyl ring with respect to the 1,2-oxazine ring. In compound (2) the O(1)—N(2)—C(10)—C(15) angle is 64 (1)°, while the C(10)—N(2)—C(3)—C(16) angle is 38 (1)°. In the naphthoxazines the equivalent angles range from 62 to 72° and from 49 to 62°, respectively. Since the range in the angles equivalent to C(10)—N(2)—C(3)—C(16) is considerably larger than the range in the angles equivalent to O(1)—N(2)—C(10)—C(15) it seems that the orientation of the *N*-cyclohexyl group is not critically dependent on the orientation of the cyano group. However, it is of interest to note that molecular-mechanics calculations on 1,1′-bipiperidines and *N*-cyclohexylpiperidines (Jaime & Ōsawa, 1983, 1984) showed that the orientation of α substituents has a direct influence on the orientation of such *N*-substituents.

The authors wish to thank the National Chemical Research Laboratory of the CSIR for intensity data collection and the Foundation for Research Development for financial support.

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Acta Cryst. (1987). C**43**, 1370–1372

Structure of 8-Bromo-2′,3′,5′-tri-*O*-acetyladenosine

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(*Received* 24 *November* 1986; *accepted* 2 *March* 1987)

Abstract. $C_{16}H_{18}BrN_5O_7$, $M_r = 472·3$, orthorhombic, $P2_12_12_1$, $a = 17·00$ (2), $b = 15·05$ (2), $c = 7·82$ (1) Å, $U = 2001$ Å^3, $Z = 4$, $D_x = 1·57$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 2·029$ mm^{-1}, $F(000) = 960$, $T = 293$ K. $R = 0·051$ for 1318 unique observed [$I > 3\sigma(I)$] reflections. Friedel pairs not merged. The molecule is *syn*, with χ(C4—N9—C1′—O4′) = 66 (1)°, has sugar pucker $^2T_3$, with $P = 181$ (1)°, and C4′—C5′ conformation of +*sc* (*gauche–gauche*). The only major conformational difference between this molecule and that of 2′,3′,5′-tri-*O*-acetyladenosine (TAA) [Wilson, Tollin & Howie (1986). *Acta Cryst.* C**42**, 697–700] is that around the C4′—C5′ bond which is *ap* in the case of TAA. The structure has base-paired symmetry-related molecules, with hydrogen bonds between the 6-amino and N1 and N7. This base pairing is similar to

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that found for TAA. The base-pair shows a propeller twist, defined as the angle between the base planes about a line joining them, of 29 (2)°.

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

Experimental. Crystals were obtained from aqueous solution. They had a prismatic habit bounded by {110}. Space group and initial cell dimensions were obtained from Weissenberg photographs mounted along all three axes. Data were collected on a Stoe–Stadi 2 two-circle diffractometer. The crystal used for data collection was of dimensions 0·38 × 0·32 × 1·48 mm and mounted along **c**.

Range of indices: $-22 \le h \le 22$; $-19 \le k \le 19$; $0 \le l \le 6$. Absorption corrections applied, max. and min. transmission factors 0·52 and 0·36. Max. $(\sin\theta)/\lambda$ reached was 0·649 Å^{-1}. Standard reflections were measured every 100 reflections. No significant change in the intensities of these reflections was found throughout data collection. 5707 reflections measured, giving 2506 observed $[I > 3\sigma(I)]$; 1318 independent reflections used in the refinement, $R_{int} = 0{\cdot}016$. Friedel pairs not merged. The location of the Br atom was obtained from Harker sections, Fourier recycling completed the definition of the structure, and least-squares refinement on F was continued until the max. shift/e.s.d. was less than 0·1. *SHELX*76 (Sheldrick, 1976) was used for the Harker sections and refinement. *MITHRIL* (Gilmore, 1983) was used for Fourier recycling. H atoms were included at calculated positions with fixed isotropic temperature factors of approximately 1·5 times that of the parent atom. Anisotropic temperature factors were used for all non-hydrogen atoms, and the refinement converged at $R = 0{\cdot}051$, $wR = 0{\cdot}048$, $w = 2{\cdot}8559[\sigma^2(F) + 0{\cdot}000475F^2]$. 262 refined parameters; max. shift/e.s.d. $< 0{\cdot}04$; max. diff. peak, 0·75, min. diff. peak, $-0{\cdot}70$ e Å^{-3}. The inverse structure gave $R = 0{\cdot}070$, $wR = 0{\cdot}077$.

The largest of these peaks were associated with the Br atom. Scattering factors were 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 were carried out on the Dundee University DEC-10 computer. No corrections were made for secondary extinction.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3) *for non-hydrogen atoms with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
Br1	−80 (1)	5537 (1)	−3727 (1)	53 (1)
N1	1946 (5)	5986 (6)	2840 (12)	32 (3)
C2	1309 (7)	6465 (8)	3266 (13)	42 (5)
N3	667 (5)	6629 (7)	2341 (12)	41 (4)
C4	706 (6)	6213 (8)	846 (13)	32 (4)
C5	1300 (6)	5691 (8)	199 (13)	33 (4)
C6	1954 (6)	5570 (8)	1334 (17)	31 (4)
N6	2557 (5)	5048 (7)	956 (9)	42 (3)
N7	1143 (5)	5388 (6)	−1405 (10)	33 (3)
C8	447 (7)	5709 (8)	−1692 (14)	39 (4)
N9	144 (5)	6234 (6)	−418 (10)	33 (3)
C1′	−655 (5)	6594 (9)	−367 (13)	36 (4)
C2′	−1110 (5)	6327 (7)	1236 (16)	31 (4)
O2′	−1466 (4)	5482 (6)	866 (8)	52 (3)
C2′1	−1750 (6)	5042 (9)	2221 (17)	62 (5)
C2′2	−2134 (7)	4175 (8)	1749 (17)	84 (6)
O2′1	−1699 (5)	5307 (5)	3631 (9)	86 (4)
C3′	−1700 (5)	7075 (6)	1503 (14)	31 (4)
O3′	−2450 (4)	6807 (5)	749 (9)	52 (3)
C3′1	−3089 (7)	7058 (9)	1568 (18)	49 (5)
C3′2	−3812 (6)	6663 (8)	724 (14)	62 (5)
O3′1	−3091 (6)	7531 (8)	2751 (13)	112 (5)
C4′	−1360 (6)	7844 (8)	455 (14)	41 (4)
C5′	−1204 (6)	8638 (8)	1491 (18)	58 (5)
O5′	−883 (5)	8407 (6)	3074 (11)	64 (3)
C5′1	−223 (8)	8793 (9)	3535 (20)	61 (6)
C5′2	53 (8)	8440 (9)	5270 (14)	87 (6)
O5′1	110 (6)	9362 (7)	2720 (13)	107 (4)
O4′	−604 (4)	7523 (6)	−166 (9)	40 (3)

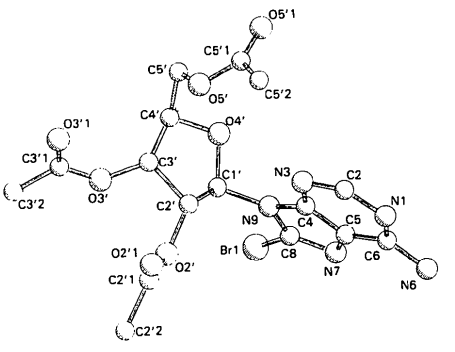

Fig. 1. Perspective drawing and atomic numbering of the molecule.

Table 2. *Interatomic distances* (Å)

C8–Br1	1·845 (11)	C3′–C2′	1·523 (13)
C2–N1	1·344 (15)	C2′1–O2′	1·339 (15)
C6–N1	1·333 (16)	C2′2–C2′1	1·505 (18)
N3–C2	1·332 (15)	O2′1–C2′1	1·176 (15)
C4–N3	1·329 (14)	O3′–C3′	1·462 (11)
C5–C4	1·376 (15)	C4′–C3′	1·531 (15)
N9–C4	1·375 (13)	C3′1–O3′	1·317 (15)
C6–C5	1·433 (15)	C3′2–C3′1	1·517 (17)
N7–C5	1·361 (13)	O3′1–C3′1	1·167 (18)
N6–C6	1·326 (14)	C5′–C4′	1·467 (17)
C8–N7	1·297 (14)	O4′–C4′	1·456 (13)
N9–C8	1·372 (14)	O5′–C5′	1·397 (16)
C1′–N9	1·463 (13)	C5′1–O5′	1·313 (16)
C2′–C1′	1·526 (15)	C5′2–C5′1	1·532 (19)
O4′–C1′	1·411 (16)	O5′1–C5′1	1·208 (18)
O2′–C2′	1·439 (13)		

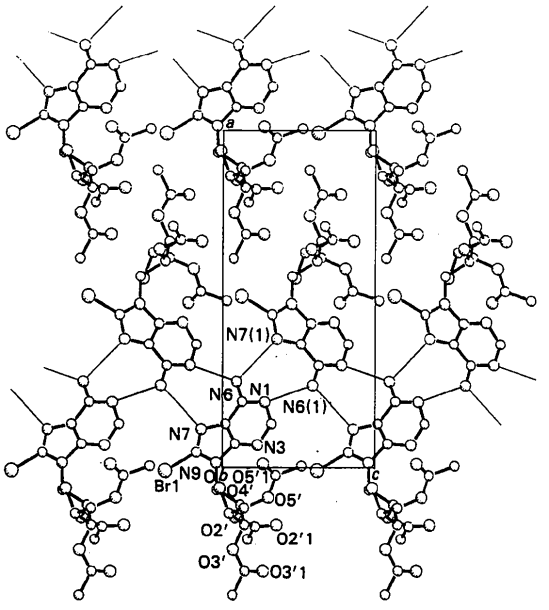

Fig. 2. View of unit cell along **b** showing hydrogen bonding. Symmetry code (i) denotes the equivalent position $\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$.

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

The bond lengths and angles are in good agreement with those for TAA (Wilson, Tollin & Howie, 1986). The N-glycosidic torsion angle χ is 66 (1)°, in the *syn* range. The sugar pucker is $^2T_3$ (C2'-*endo*–C3'-*exo*), with $P = 181$ (1)°, and $\psi_m = 19$ (1)°. The C4'—C5' conformation, with $\gamma = 40$ (1)° and $\gamma' = -75$ (1)°, is +*sc* (*gauche–gauche*). The conformational parameters used follow the guidelines of the IUPAC-IUB Commission on Biochemical Nomenclature (1983). There are two hydrogen bonds present in the structure: N1···N6 3·01 (2) ($\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$) and N6···N7 3·09 (2) Å ($\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$). Thus each molecule is involved in four hydrogen bonds (Fig. 2), two with each of two translationally related bases, forming a chain of paired bases along **c**, similar to the situation in TAA. There is a propeller twist (Dickerson, 1983) of 29 (2)°, between the planes of the two paired bases. This represents one of the largest propeller twists observed in nucleoside structures. Such twists are reviewed by Wilson & Tollin (1987).

The authors thank Dr C. C. Wilson for very helpful discussions.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43846 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1987). C**43**, 1372–1375

(±)-14β-Hydroxy-1β,4β-methano-5β,8α,9β-androstane-7,17-dione

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(*Received* 6 *November* 1986; *accepted* 30 *January* 1987)

Abstract. $C_{20}H_{28}O_3$, $M_r = 316{\cdot}4$, triclinic, $P\bar{1}$, $a = 7{\cdot}408$ (2), $b = 10{\cdot}758$ (2), $c = 11{\cdot}687$ (2) Å, $\alpha = 66{\cdot}02$ (1), $\beta = 86{\cdot}72$ (2), $\gamma = 74{\cdot}85$ (2)°, $U = 820$ Å^3, $Z = 2$, $D_x = 1{\cdot}28$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 0{\cdot}079$ mm^{-1}, $F(000) = 344$, $T = 298$ K, $R = 0{\cdot}0408$ ($wR = 0{\cdot}0518$) for 2800 observed [$I > 3\sigma(I)$] reflections. In the title compound the 1β,4β-methano bridge forces rings *A* and *B* into boat conformations. Ring *C*,

0108-2701/87/071372-04$01.50