

The carbonyl group of the acetyl substituent in (1) is disposed in a *transoid* sense with respect to the N(1)–C(2) double bond, which is not surprising in view of the preference of methyl vinyl ketone for such a *transoid* conformation (Liljefors & Allinger, 1976).

This structure determination definitively establishes that N(2) bears an H atom, *i.e.* that the structure is as shown in Fig. 3 and not one of the alternative tautomeric forms [4-hydroxyquinazoline or 4(1H)-quinazolinone]. The amide system indulges in intermolecular hydrogen bonding with a neighbouring molecule [N(2)···O(2) 2.889 Å] forming dimers. It is, perhaps, noteworthy that the position found for H(8) implies a considerable bond-angle distortion from ideality [C(7)–C(8)–H(8) 128 (2), C(9)–C(8)–H(8) 112 (2)°] in the sense that would relieve *ortho*-interactions between H(7) and H(8). Although this distortion may be an artefact of the limited data set available, it is significant that structures (4) and (5) display a similar pattern of distortion, though to a reduced extent.

Analysis of thermal vibrational ellipsoids for non-H atoms in terms of rigid-body motion (Cruickshank, 1956; Schomaker & Trueblood, 1968) leads to fair agreement between observed and calculated U_{ij} values ($\langle \Delta U_{ij}^2 \rangle^{1/2} = 34 \times 10^{-4} \text{ \AA}^2$), maximum discrepancies occurring for the carbonyl group in the acetyl substituent.

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Structure of 5-Bromo-2',3'-O-isopropylideneuridine, C₁₂H₁₅BrN₂O₆

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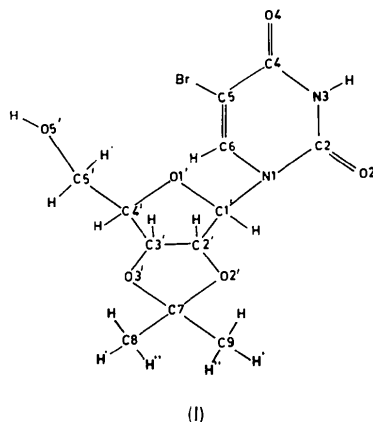
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Abstract. $M_r = 363.17$, orthorhombic, $P2_12_12_1$, $a = 5.251$ (4), $b = 14.962$ (5), $c = 19.112$ (5) Å, $U = 1501.41$ Å³, $Z = 4$, $D_x = 1.61$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 3.02$ mm⁻¹, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, final $R = 7.0\%$ for 1091 reflections with $F_o > 2\sigma(F_o)$. The glycosidic torsion angle χ_{CN} is 13.1 (12)°. The ribose has a C(3')-*exo*, C(4)-*endo* twist geometry. The dioxolane ring assumes an envelope conformation with O(3') displaced by 0.453 (10) Å from the plane of the other four atoms. The conformation about the C(4')–C(5') bond is *gauche-gauche*. The structure is stabilized by two hydrogen bonds between screw-axis-related molecules. The crystal packing and the conformation of the

molecule are very similar to those found in the structure of 2',3'-O-isopropylideneuridine which lacks the Br atom at the 5-position.

Introduction. We report here the structure of the title compound (I). This is part of a systematic study of nucleosides where the ribose is cyclized at O(2') and O(3') by an isopropylidene group. We have previously obtained the structures of 2',3'-O-isopropylideneuridine, (Katti, Seshadri & Viswamitra, 1981) and 5'-deoxy-5',6-epithio-5,6-dihydro-2',3'-O-isopropylidene-3-methyluridine (Gautham, Ramakrishnan, Seshadri, Viswamitra, Salisbury & Brown, 1982).



Experimental. Thin needle-like crystals grown from a solution of the compound in a water/acetone mixture by slow evaporation; unit-cell parameters refined from accurately measured 2θ values of 25 high-angle reflections; CAD-4 diffractometer, three-dimensional $\text{Cu } K\alpha$ intensity data, 1326 reflections measured ($\sin\theta/\lambda \leq 0.56 \text{ \AA}^{-1}$), ω - 2θ scan mode; background counts measured for $\frac{1}{6}$ th of the scan angle on either side of the Bragg peak; intensities of the 011 and the 033 reflections monitored throughout the data collection for instrument and crystal stability, variation in counts $< 5\%$; Lorentz and polarization corrections.

The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). An *E* map computed with the best set of phases (figure of merit = 3.0) revealed the positions of all atoms except those of the uracil base; these atoms were located from difference Fourier maps. Block-diagonal least-squares refinement (Shiono, 1968) with anisotropic temperature factors reduced *R* to 0.086. A difference map at this stage revealed the positions of all but four of the H atoms which were fixed using geometrical considerations. Further refinement with complex scattering factors (*International Tables for X-ray Crystallography*, 1974) for the Br atom and isotropic temperature factors for the H atoms gave a final *R* = 0.070 (*R_w* = 0.091) for the 1091 observed reflections; $F(000) = 736$. The function minimized was of the form $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$.

Discussion. The final positional parameters are given in Table 1* and molecular dimensions in Table 2. Fig. 1 shows a stereoview of the molecule.

Uracil base. The uracil base is *anti* with respect to the sugar ring. The glycosidic torsion angle, χ_{CN} , is $13.1 (12)^\circ$. This is significantly smaller than that found

* Lists of structure factors, anisotropic thermal parameters, least-squares-planes' data and a figure showing the geometry of the ribose ring have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38143 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in 5-bromouridine (56.0°) and 5-bromo-2'-deoxyuridine (47.2°) (Iball, Morgan & Wilson, 1966). In 2',3'-*O*-isopropylideneuridine (ISPU) χ_{CN} is 3.4° . The uracil ring is essentially planar. The maximum deviation from the mean plane is shown by C(2) [$0.051 (10) \text{ \AA}$]. The exocyclic atoms O(2) and Br show considerable deviations from the mean plane [$0.189 (7)$ and $0.160 (2) \text{ \AA}$], in contrast to the structures of 5-bromouridine and 5-bromo-2'-deoxyuridine where these two atoms lie essentially in the plane of the heterocycle (Iball *et al.*, 1966).

Table 1. Positional parameters ($\times 10^4$, for H $\times 10^3$) and isotropic thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B_{150}(\text{\AA}^2)$
For non-hydrogen atoms $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i a_j$.				
N(1)	7790 (18)	3107 (6)	6248 (4)	4.5 (2)
C(2)	6168 (21)	2779 (6)	5747 (5)	2.6 (3)
O(2)	6135 (15)	3043 (5)	5159 (3)	1.7 (2)
N(3)	4520 (20)	2118 (5)	5981 (4)	5.1 (3)
C(4)	4180 (26)	1847 (8)	6677 (6)	3.8 (3)
O(4)	2483 (19)	1299 (6)	6823 (5)	3.9 (3)
C(5)	5802 (26)	2288 (7)	7172 (5)	3.4 (3)
Br	5413 (4)	2035 (1)	8125 (1)	5.4 (1)
C(6)	7601 (24)	2881 (7)	6962 (5)	3.3 (3)
C(1')	9930 (20)	3704 (7)	5980 (5)	2.9 (3)
O(1')	11764 (15)	3784 (5)	6494 (4)	2.1 (2)
C(2')	9034 (22)	4630 (8)	5759 (6)	3.2 (3)
O(2')	9489 (18)	4773 (6)	5053 (4)	2.7 (2)
C(3')	10803 (26)	5269 (7)	6147 (6)	3.7 (3)
O(3')	12607 (18)	5490 (6)	5630 (4)	3.2 (2)
C(4')	12035 (23)	4706 (8)	6709 (6)	3.5 (3)
C(5')	10982 (27)	4816 (9)	7455 (5)	4.1 (4)
O(5')	8271 (20)	4778 (7)	7420 (4)	3.5 (3)
C(7)	11327 (28)	5459 (10)	4987 (6)	5.1 (4)
C(8)	13062 (41)	5155 (16)	4419 (8)	8.9 (7)
C(9)	9936 (33)	6359 (11)	4873 (9)	7.7 (6)
H(N3)	331 (35)	180 (10)	551 (7)	8.4 (44)
H(C6)	880 (18)	315 (5)	732 (4)	0.7 (18)
H(C1')	1072 (18)	349 (6)	543 (4)	1.6 (19)
H(C2')	726 (21)	475 (6)	590 (4)	3.5 (23)
H(C3')	1047 (19)	571 (6)	635 (4)	2.0 (19)
H(C4')	1371 (16)	480 (5)	678 (4)	0.1 (15)
H1(C5')	1147 (24)	536 (7)	754 (4)	3.6 (26)
H2 (C5')	1126 (18)	415 (5)	789 (4)	1.1 (17)
H(O5')	762 (21)	478 (6)	773 (5)	2.0 (19)
H1(C8)	1309 (16)	579 (5)	448 (3)	0.8 (17)
H2(C8)	1375 (30)	469 (9)	406 (6)	6.5 (33)
H3(C8)	1475 (19)	493 (6)	472 (5)	4.4 (19)
H1(C9)	838 (30)	632 (10)	444 (7)	0.0 (30)
H2(C9)	1087 (31)	674 (10)	454 (7)	9.5 (40)
H3(C9)	867 (32)	627 (9)	538 (7)	8.9 (37)

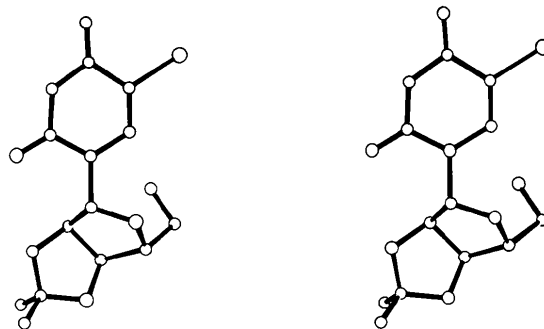


Fig. 1. A stereoview of a molecule of the title compound.

Table 2. Bond distances (Å), bond angles (°) and torsion angles (°)

N(1)—C(2)	1.372 (14)	C(2')—O(2')	1.386 (13)
N(1)—C(1')	1.525 (14)	C(2')—C(3')	1.525 (17)
N(1)—C(6)	1.408 (13)	O(2')—C(7')	1.414 (17)
C(2)—O(2)	1.192 (12)	C(3')—O(3')	1.409 (15)
C(2)—N(3)	1.389 (14)	C(3')—C(4')	1.511 (17)
N(3)—C(4)	1.403 (14)	O(3')—C(7')	1.402 (15)
C(4)—O(4)	1.243 (16)	C(4')—O(1')	1.447 (14)
C(4)—C(5)	1.434 (17)	C(4')—C(5')	1.537 (16)
C(5)—Br	1.870 (10)	C(5')—O(5')	1.426 (18)
C(5)—C(6)	1.357 (17)	C(7)—C(8)	1.488 (23)
C(1')—O(1')	1.382 (13)	C(7)—C(9)	1.548 (22)
C(1')—C(2')	1.523 (16)		
C(6)—N(1)—C(2)	123.1 (9)	C(1')—C(2')—O(2')	110.9 (9)
C(6)—N(1)—C(1')	121.2 (8)	C(1')—C(2')—C(3')	104.3 (9)
C(2)—N(1)—C(1')	115.6 (8)	O(2')—C(2')—C(3')	105.8 (9)
N(1)—C(2)—O(2)	123.3 (10)	C(2')—O(2')—C(7')	108.5 (9)
O(2)—C(2)—N(3)	122.0 (10)	C(2')—C(3')—O(3')	102.4 (9)
C(2)—N(3)—C(4)	126.2 (9)	C(2')—C(3')—C(4')	104.9 (9)
N(3)—C(4)—O(4)	119.6 (11)	O(3')—C(3')—C(4')	110.0 (10)
O(4)—C(4)—C(5)	125.6 (11)	C(3')—O(3')—C(7')	106.5 (10)
N(3)—C(4)—C(5)	114.7 (10)	C(3')—C(4')—O(1')	106.7 (9)
C(4)—C(5)—Br	118.9 (9)	C(3')—C(4')—C(5')	116.5 (10)
C(4)—C(5)—C(6)	121.2 (11)	O(1')—C(4')—C(5')	109.3 (9)
Br—C(5)—C(6)	119.8 (9)	C(4')—C(5')—O(5')	108.1 (10)
C(5)—C(6)—N(1)	115.6 (10)	O(2')—C(7')—O(3')	105.8 (10)
N(1)—C(2)—N(3)	114.6 (9)	O(2')—C(7')—C(8)	105.2 (12)
C(1')—O(1')—C(4')	110.7 (8)	O(2')—C(7')—C(9)	108.8 (11)
N(1)—C(1')—O(1')	108.9 (8)	O(3')—C(7')—C(8)	110.0 (13)
N(1)—C(1')—C(2')	113.5 (8)	O(3')—C(7')—C(9)	108.7 (12)
O(1')—C(1')—C(2')	109.5 (9)		
C(6)—N(1)—C(1')—O(1')	13.1 (12)	O(1')—C(4')—C(5')—O(5')	-73.7 (11)
C(1')—C(2')—C(3')—C(4')	-16.0 (11)	C(2')—O(2')—C(7')—O(3')	21.0 (13)
C(2')—C(3')—C(4')—O(1')	-20.0 (12)	O(2')—C(7')—O(3')—C(3')	-33.4 (12)
C(3')—C(4')—O(1')—C(1')	-16.7 (12)	C(7')—O(3')—C(3')—C(2')	31.2 (12)
C(4')—O(1')—C(1')—C(2')	6.3 (11)	O(3')—C(3')—C(2')—O(2')	-18.1 (11)
O(1')—C(1')—C(2')—C(3')	6.6 (11)	C(3')—C(2')—O(2')—C(7')	-1.5 (12)
C(3')—C(4')—C(5')—O(5')	47.3 (14)		

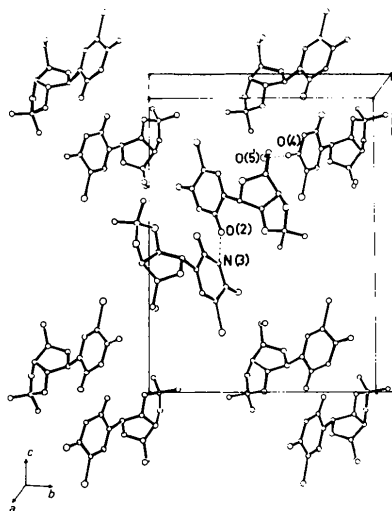


Fig. 2. Crystal packing.

Ribose. The sugar pucker is C(3')-*exo*, C(4')-*endo*, corresponding to a ${}_3T^4$ twist conformation. The phase angle P of pseudorotation (Altona & Sundaralingam,

1972) is 216.6 (3)°, the same as that found in ISPU ($P = 216.3^\circ$). The deviations of C(3') and C(4') from the C(1')—C(2')—O(1') three-atom plane are 0.169 (13) and 0.148 (12) Å, respectively (0.188 and 0.159 Å in ISPU). The maximum amplitude of pucker ($\zeta_{m,\max}$), is 19.9 (15)°, comparable with that (23.7°) found in ISPU. The ribose ring shows considerable flattening compared to normal *S* or *N* type ribose rings (Altona & Sundaralingam, 1972).

Dioxolane ring. In the five-membered dioxolane ring, C(3'), C(2'), O(2') and C(7) are nearly coplanar, as indicated by the torsion angle of -1.5 (12)°. O(3') is considerably out of this plane [0.453 (10) Å], as was also found in the structure of ISPU (0.457 Å). The pseudorotation parameters for the dioxolane ring are $P = 123.4$ (1)° and $\lambda_{m,\max} = 33.6$ (22)°. These values are 124 and 33.9° in ISPU and 147.8 and 35.1° in 2',3'-*O*-isopropylideneadenosine (Sprang, Rohrer & Sundaralingam, 1978).

The geometry about the exocyclic C(4')—C(5') bond is the commonly observed *gauche-gauche* conformation with the torsion angles O(5')—C(5')—C(4')—O(1') and O(5')—C(5')—C(4')—C(3') -73.7 (11) and 47.3 (14)° respectively.

Molecular packing. The crystal structure is stabilized by two hydrogen bonds. A bond, N—H...O [2.821 (13) Å], is formed between O(2) of one molecule and N(3) of another related by the symmetry operation $(x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1)$. Molecules related by $(-x + 1, y - \frac{1}{2}, -z + \frac{1}{2})$ also form a hydrogen bond between O(5') and O(4) [2.726 (16) Å]. Fig. 2 shows the crystal packing. The hydrogen-bonding scheme is identical with that observed in ISPU. There is no self-base-pairing of the uracil base.

The brominated analogue is thus virtually identical in both molecular conformation as well as crystal structure to 2',3'-*O*-isopropylideneuridine.

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