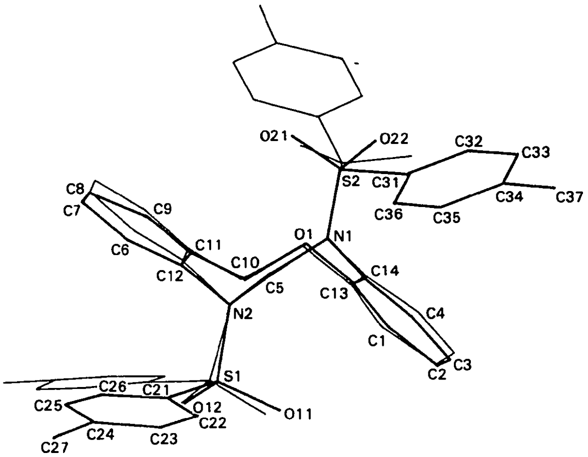

Fig. 1. Comparison of the structures of molecule 1 (bold line) and molecule 2 (fine line). The coincidence of the two molecules was obtained by fitting together the heterocyclic rings of the two molecules by least squares. The atomic numbering scheme is given for molecule 1.

symmetrical with respect to a pseudo-twofold axis running through C5 and the middle of the O1—C10 bond; the asymmetry parameters (Duax & Norton, 1975) $\Delta_2 = 23{\cdot}8\ (6)$ and $25{\cdot}0\ (5)°$ for molecules 1 and 2, respectively. The planes of the fused benzene rings form an angle of 24·5 (3)° in 1 and 25·1 (3)° in 2.

The N1 and N2 atoms show different behaviour in the two molecules. The tendency to form pyramidal bonds by the N2 atoms is more pronounced than for N1, particularly for N2 of the second molecule. The sums of the bond angles about the N atoms are: 359·1 (11)° for N1* and 359·7 (9)° for N1 and 356·8 (12)° for N2* and 353·7 (9)° for N2. The distance of N1 from the plane passing through C5, S2 and C14 is 0·082 (12) and 0·047 (14) Å, while that of N2 from the plane passing through C5, S1 and C12 is 0·156 (10) and 0·222 (12) Å, for molecules 1 and 2, respectively.

There are van der Waals molecular contacts only.

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Structure of 5-(Trifluoromethyl)-2′-deoxyuridine

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Abstract. $C_{10}H_{11}F_3N_2O_5$, $M_r = 296{\cdot}02$u, orthorhombic, $P2_12_12$, $a = 5{\cdot}618\ (4)$, $b = 23{\cdot}91\ (2)$, $c = 8{\cdot}897\ (5)$ Å, $U = 1195{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}65$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}15$ mm^{-1}, $F(000) = 608$, $T = 293$ K. $R = 0{\cdot}063$ for 615 unique observed $[F > 5\sigma(F)]$ reflections. The molecule is *anti*, $\chi = -143\ (1)°$. The sugar pucker is ${}^2_1T$ with $P = 161\ (1)°$ and $\psi_m = 42\ (1)°$. Atom O5′ is statistically disordered so that the conformation about the C4′—C5′ bond is either +*sc* or *ap*, with $\gamma = 67\ (1)$ and 158 (1)° respectively.

Introduction. We have determined the crystal and molecular structure of the title compound as part of our continuing program of investigation of modified nucleosides. Another crystal form of this compound has been reported by Tench (1972). This crystallized in space group $P2_1$ with cell dimensions $a = 8{\cdot}97$, $b = 5{\cdot}40$, $c = 12{\cdot}39$ Å, $\beta = 97{\cdot}0°$. The cell volume, 596 Å^3, is almost exactly half that of the present unit cell. No further information with regard to this structure is contained within the Cambridge Structural Database (Elder, Hull, Machin & Mills, 1981).

Experimental. Crystals were obtained from aqueous solution. Space group and initial cell dimensions were obtained from Weissenberg photographs. Data were collected on a Nicolet $P3$ (four-circle) diffractometer in Aberdeen by RAH. The crystal had dimensions 0·24 × 0·14 × 0·14 mm. Cell parameters were measured on the diffractometer using 14 reflections in the 2θ range 15–23°. Range of indices: $0 \leq h \leq 8$; $0 \leq k \leq 12$; $0 \leq l \leq 30$. Data measured using $\omega/2\theta$ scans in the range $0 < 2\theta < 50°$. Standard reflections, 027 and 108, were measured every 50 reflections. The intensities of these reflections did not vary by more than 2σ from their means throughout the data collection. Lorentz and polarization factors were applied. No corrections were made for absorption or secondary extinction. 1087 independent reflections measured, giving 615 observed [$F > 5\sigma(F)$] reflections used in the refinement. The structure was solved using the *SHELXS*86 program, (Sheldrick, 1986).

The E map revealed all atomic positions except that of O5′. There were several peaks close to atom C5′ which were possible atomic positions. An electron density calculation subsequent to a structure-factor calculation based on the located atoms showed an extended area of electron density in the region in which atom O5′ might be expected to be found. A difference electron density synthesis after several cycles of isotropic least squares showed two main peaks in this region. Two oxygen atoms with assumed site occupancies of 0·5 at sites based on the positions of these peaks but with C—O bond lengths constrained at the nearly 'ideal' length of 1·4 Å were then included in the refinement. Hydrogen atoms were included at calculated positions (C—H and N—H 1·08 Å), including 'half' hydrogens on C5′ corresponding to the positions of the two O5′ 'half' atoms. These H atoms were given fixed isotropic temperature factors, approximately 1·5 times that of their parent atom on which they were allowed to ride. No positions were obtained for the H atoms attached to atoms O3′ and O5′, which were, therefore, refined isotropically as was atom C5′. All other non-hydrogen atoms were refined anisotropically. Blocked full-matrix refinement (on F) was carried out using the program *SHELX*76 (Sheldrick, 1976). The constrained refinement converged at $R = 0{\cdot}063$, $wR = 0{\cdot}049$, $w = 1{\cdot}7074\,[\sigma^2]^{-1}$. Results summarized in Tables 1 and 2.* 170 refined parameters; max. shift/e.s.d. < 0·01; max. difference peak, 0·29; min. −0·34 e Å^{-3}.

A refinement with the constraints on atoms C5′ and O5′ removed now gave R 0·062. In this refinement the only bond length which differed at a significance level greater than 3σ from those in Table 2 was C5′—O5′, 1·31 (2) Å.

Table 1. *Coordinates* (× 10^4) *for non-hydrogen atoms with e.s.d.'s in parentheses*

	x	y	z	U_{eq}(Å^2 × 10^3)
N1	1774 (17)	1623 (4)	10104 (9)	30 (3)
C2	2007 (24)	2044 (5)	9055 (13)	34 (4)
O2	3245 (13)	2438 (3)	9185 (8)	38 (3)
N3	564 (18)	1971 (3)	7767 (10)	32 (3)
C4	−1054 (26)	1546 (5)	7533 (14)	43 (5)
O4	−2187 (16)	1527 (3)	6360 (8)	58 (3)
C5	−1124 (21)	1124 (5)	8683 (14)	37 (4)
C7	−2733 (25)	624 (6)	8536 (17)	54 (5)
F7*A*	−4997 (14)	787 (3)	8361 (8)	65 (3)
F7*B*	−2224 (15)	342 (3)	7280 (8)	74 (3)
F7*C*	−2610 (16)	288 (3)	9696 (8)	77 (3)
C6	264 (19)	1172 (5)	9913 (12)	33 (4)
C1′	3246 (21)	1678 (5)	11489 (11)	31 (4)
C2′	1788 (21)	1893 (4)	12820 (11)	35 (4)
C3′	3364 (24)	1698 (5)	14104 (12)	45 (5)
O3′	5363 (15)	2079 (3)	14244 (8)	43 (2)
C4′	4128 (20)	1135 (5)	13554 (11)	38 (4)
C5′	2653 (28)	660 (6)	14204 (15)	79 (5)
O5′*A*	283 (32)	669 (7)	13713 (18)	74 (6)
O5′*B*	2750 (39)	181 (7)	13314 (18)	114 (8)
O4′	4013 (15)	1143 (3)	11918 (8)	51 (3)

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

O3′, C5′, O5′*A* and O5′*B* isotropic.

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

C2—N1	1·379 (12)	C6—N1	1·382 (12)
O1′—N1	1·490 (11)	O2—C2	1·177 (12)
N3—C2	1·414 (13)	C4—N3	1·380 (13)
O4—C4	1·223 (13)	C5—C4	1·438 (14)
C7—C5	1·504 (16)	C6—C5	1·348 (14)
F7*A*—C7	1·339 (14)	F7*B*—C7	1·336 (14)
F7*C*—C7	1·310 (15)	C2′—C1′	1·529 (12)
O4′—C1′	1·403 (12)	C3′—C2′	1·518 (13)
O3′—C3′	1·451 (13)	C4′—C3′	1·496 (14)
C5′—C4′	1·519 (16)	O4′—C4′	1·457 (10)
O5′*A*—C5′	1·401 (12)*	O5′*B*—C5′	1·394 (12)*

C6—N1—C2	123·0 (10)	C1′—N1—C2	116·2 (9)
C1′—N1—C6	120·8 (9)	O2—C2—N1	125·0 (13)
N3—C2—N1	113·9 (10)	N3—C2—O2	121·1 (11)
C4—N3—C2	126·2 (10)	O4—C4—N3	119·9 (12)
C5—C4—N3	115·3 (12)	C5—C4—O4	124·6 (13)
C7—C5—C4	120·8 (12)	C6—C5—C4	120·1 (12)
C6—C5—C7	119·1 (12)	F7*A*—C7—C5	110·6 (12)
F7*B*—C7—C5	110·2 (12)	F7*B*—C7—F7*A*	104·6 (11)
F7*C*—C7—C5	112·7 (11)	F7*C*—C7—F7*A*	108·6 (13)
F7*C*—C7—F7*B*	109·7 (13)	C5—C6—N1	121·4 (11)
C2′—C1′—N1	111·9 (9)	O4′—C1′—N1	108·3 (8)
O4′—C1′—C2′	105·1 (8)	C3′—C2′—C1′	99·6 (8)
O3′—C3′—C2′	108·9 (9)	C4′—C3′—C2′	101·4 (9)
C4′—C3′—O3′	111·8 (10)	C5′—C4′—C3′	113·0 (11)
O4′—C4′—C3′	107·6 (9)	O4′—C4′—C5′	111·5 (10)
O5′*A*—C5′—C4′	112·9 (14)	O5′*B*—C5′—C4′	112·1 (14)
O5′*B*—C5′—O5′*A*	82·7 (14)	C4′—O4′—C1′	107·3 (9)

* Constrained bond lengths.

Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The program packages *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978) were also used. All

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51349 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

calculations were carried out on the Dundee University PRIME computer. The absolute configuration of the molecule was known and was thus not determined.

Discussion. The atomic numbering is given in the perspective drawing (Fig. 1). The bonds and angles are normal with the exception of those involving the disordered O5′ atom. A similar statistical disordering of an O5′ atom is reported by Narayanan & Berman (1977) in the structure of 5-[*N*-(L-leucyl)amino]uridine. In this latter structure the C5′–O5′ bonds were short, 1·19 and 1·315 Å, as were the bonds in the unconstrained refinement of the present compound, C5′–O5′*A*, 1·35 (2) and C5′–O5′*B*, 1·31 (2) Å. The conformations about the C4′–C5′ bond, the sugar ring pucker $P = 167°$ and $\chi = -130°$, are also similar to those of the present compound. The sugar ring pucker and the glycosyl torsion angle are similar to those found for the thymidine molecules in thymidine-(5′,3′)-thymidylate-5′ (Camerman, Fawcett & Camerman, 1976), $P = 164$ and 173°, $\chi = -147$ and −139°. However, in thymidine itself (Young, Tollin & Wilson, 1969), the sugar ring pucker, $P = 187°$, is markedly different although the value of χ is similar, −139°. The present conformation is close to the theoretical minimum obtained from conformational energy calculations (Saran, Perahia & Pullman, 1973).

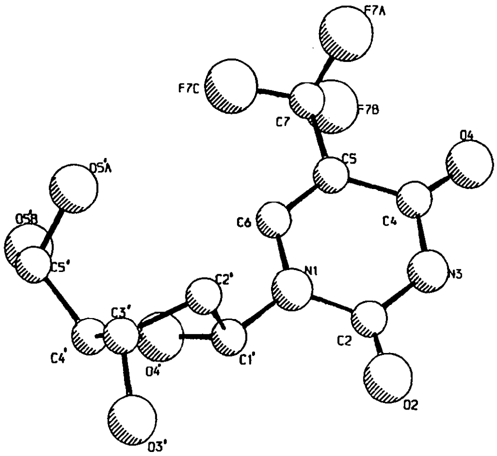

Fig. 1. Perspective drawing of the molecule with atomic numbering. Atoms O5′*A* and O5′*B* have site occupancies of 0·5.

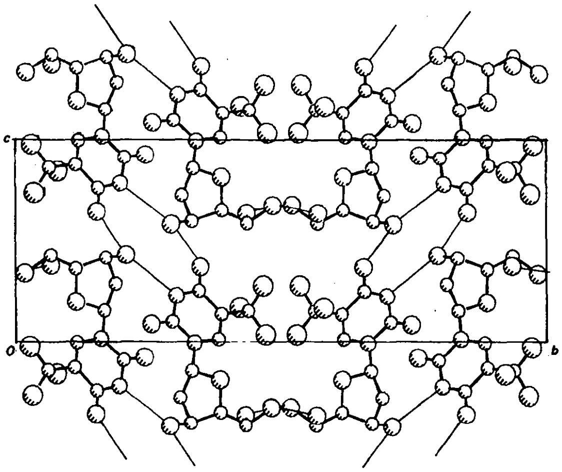

Fig. 2. View of the contents of the unit cell, viewed down **a**, showing the molecular packing.

The following short contacts between symmetry-related molecules are observed: N3···O3′ $(-\frac{1}{2}-x, \frac{1}{2}-y, 2-z)$, 2·89 (2), O3′···O4 $(1-x, -y, 1+z)$, 2·68 (2), O5′*A*···O5′*A* $(-x, -y, z)$, 3·21 (2), O5′*B*···O5′*A* $(-x, -y, z)$, 2·67 (2) and O5′*B*···O5′*B* $(1-x, -y, -z)$, 2·67 (2) Å. These almost certainly indicate hydrogen bonding. If this is the case then this hydrogen-bonding scheme is the same as that found in the crystal structure of thymidine (Young, Tollin & Wilson, 1969), although the O5′···O5′ hydrogen bonding for the present structure is complicated by the disorder. Since the hydrogen-bonding schemes are essentially the same in both compounds presumably the changed sugar ring pucker helps to accommodate the larger volume of the trifluoromethyl group. There are no contacts between the F atoms and the O3′ and O5′ atoms which would suggest any potential hydrogen bonding. However the F atoms are involved in several short contacts with F atoms in symmetry-related molecules. These contacts have distances lying in the range 2·98 (2) to 3·26 (2) Å. Fig. 2 shows the molecular packing.

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