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Structure of Nucleoside Analogues 3'-Fluoro-2',3'-dideoxyuridine, 3'-Fluoro-2',3'-dideoxy-5-bromouridine and 3'-Azido-2',3'-dideoxy-5-bromouridine*

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Abstract. (I) 1-(3-Fluoro-2,3-dideoxy-β-D-*erythro*-pentofuranosyl)uracil, $C_9H_{11}FN_2O_4$, $M_r = 230\cdot20$, monoclinic, $P2_1$, $a = 9\cdot046$ (5), $b = 6\cdot994$ (4), $c = 15\cdot826$ (8) Å, $\beta = 101\cdot19$ (4)°, $V = 982\cdot3$ (9) Å^3, $Z = 4$, $D_m = 1\cdot56$, $D_x = 1\cdot557$ Mg m^{-3}, λ(Mo $K\alpha$ radiation) = $0\cdot71073$ Å, $\mu = 0\cdot127$ mm^{-1}, $F(000) = 480$, $T = 290$ K, final $R = 0\cdot029$ for 1495 unique observed reflections. The asymmetric unit contains two molecules (*A* and *B*). For molecule *A*: the *N*-glycosidic torsion angle χ has a value of $-121\cdot1$ (2)° in the *anti* range; the sugar pucker is ^2E with $P = 165$ (1)° and $\psi_m = 35$ (1)° and the C4'—C5' conformation is $+sc$ (synclinal) with $\gamma = 51\cdot3$ (3)°. For molecule *B*: the *N*-glycosidic torsion angle χ has a value of $-150\cdot5$ (2)° in the *anti* range; the sugar pucker is ^2_3T with $P = 176$ (1)° and $\psi_m = 26$ (1)° and the C4'—C5' conformation is $+sc$ with $\gamma = 47\cdot4$ (3)°. (II) 1-(3-Fluoro-2,3-dideoxy-β-D-*erythro*-pentofuranosyl)-5-bromouracil, $C_9H_{10}BrFN_2O_4$, $M_r = 309\cdot09$, monoclinic, $P2_1$, $a = 5\cdot701$ (4), $b = 18\cdot192$ (9), $c = 10\cdot538$ (5) Å, $\beta = 95\cdot67$ (5)°, $V = 1088$ (1) Å^3, $Z = 4$, $D_m = 1\cdot89$, $D_x = 1\cdot888$ Mg m^{-3}, λ(Mo $K\alpha$) = $0\cdot71073$ Å, $\mu = 3\cdot759$ mm^{-1}, $F(000) = 616$, $T = 290$ K, final $R = 0\cdot034$ for 1597 unique observed reflections. The asymmetric unit contains two molecules (*A* and *B*). For molecule *A*: the *N*-glycosidic torsion angle χ has a value of $-168\cdot8$ (6)° in the *anti* range; the sugar pucker is ^2_3T with $P = 179$ (1)° and $\psi_m = 31$ (1)° and the C4'—C5' conformation is $+sc$ with $\gamma = 53\cdot9$ (9)°. For molecule *B*: the *N*-glycosidic torsion angle χ has a value of $-131\cdot8$ (7)° in the *anti* range; the sugar pucker is ^2E with $P = 161$ (1)° and $\psi_m = 35$ (1)° and the C4'—C5' conformation is $+sc$ with $\gamma = 51\cdot2$ (9)°. (III) 1-(3-Azido-2,3-dideoxy-β-D-*erythro*-pentofuranosyl)-5-bromouracil, $C_9H_{10}BrN_5O_4$, $M_r = 332\cdot11$, monoclinic, $P2_1$, $a = 5\cdot858$ (3), $b = 11\cdot813$ (6), $c = 17\cdot757$ (9) Å, $\beta = 92\cdot70$ (4)°, $V = 1227$ (1) Å^3, $Z = 4$, $D_m = 1\cdot80$, $D_x = 1\cdot797$ Mg m^{-3}, λ(Mo $K\alpha$) = $0\cdot71073$ Å, $\mu = 3\cdot332$ mm^{-1}, $F(000) = 664$, $T = 290$ K, final $R = 0\cdot027$ for 1713 unique observed reflections. The asymmetric unit contains two molecules (*A* and *B*). For molecule *A*: the *N*-glycosidic torsion angle χ has a value of $-168\cdot4$ (4)° in the *anti* range; the sugar pucker is $_3T^4$ with $P = 203$ (1)° and $\psi_m = 37$ (1)° and the C4'—C5' conformation is $+sc$ with $\gamma = 172\cdot1$ (5)°. For molecule *B*: the *N*-glycosidic torsion angle χ has a value of $-129\cdot8$ (5)° in the *anti* range; the sugar pucker is $^2T_3$ with $P = 173$ (1)° and $\psi_m = 33$ (1)° and the C4'—C5' conformation is *ap* (antiperiplanar) with $\gamma = 50\cdot5$ (7)°. All the conformational parameters are in accordance with the IUPAC–IUB Joint Commission on Biochemical Nomenclature [*Pure Appl. Chem.* (1983), **55**, 1273–

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1280] guidelines. Base-pair formation occurs in each of the three crystal structures.

Experimental. Details of data collection and refinement are listed in Table 1. Crystals were obtained at room temperature, (I) from amyl acetate–ethanol, (II) from ethanol–water and (III) from water. Density measured by flotation (I) in n-heptane/CCl_4 and (II and III) in $CHCl_3$/$CHBr_3$. Space group $P2_1$ from systematic absences $0k0$ for k odd. X-ray diffraction data collected on a STADI-4 computer-controlled four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. The standard reflections monitored after every 120 min showed no significant decrease in intensity per h. Lorentz–polarization corrections, absorption corrections by the method of North, Phillips & Mathews (1968) based on (II) three reflections ($\overline{301}$,$\overline{401}$,$\overline{622}$) and (III) four reflections ($0,\overline{10},9$, $1\overline{76}$, $04\overline{3}$, 022), no absorption corrections for (I). Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B) and Stewart, Davidson & Simpson (1965) (for H atoms).

Initial attempts to solve the structure of (I) with *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) failed. Modification of the default input parameters did not resolve the problem. The structure was solved using the 3'-fluoro-2',3'-dideoxyuridine skeleton from 3'-fluoro-3'-deoxythymidine (Everaert, Peeters, Blaton, De Ranter, van Aerschot & Herdewijn, 1990) as input model for the vector-search rotation-functions programs *ORIENT* (Beurskens, Beurskens, Strumpel & Nordman, 1987). The result of *ORIENT* was a well oriented skeleton which had to be positioned with respect to the space group symmetry elements by strengthened translation functions using the automated program *TRADIR* (Doesburg & Beurskens, 1983). The outcome of *TRADIR* was a well shifted and oriented skeleton which was used as input to *DIRDIF* (Beurskens, Bosman, Doesburg, van den Hark, Prick, Noordik, Beurskens, Gould & Parthasarathi, 1983) for further elucidation of the structure. *DIRDIF* revealed the positions of all non-H atoms of the second molecule in the asymmetric unit. A difference synthesis revealed the position of two H atoms (attached to atoms $O5'A$ and $O5'B$). All other H atoms were included at calculated positions (C—H and N—H distances 0·95 Å). For (II) and (III) the two Br positions were obtained from a sharpened Patterson synthesis. The positions of these atoms served as input for a Fourier synthesis which revealed the positions of 18 non-H atoms forming the two base moieties. A subsequent Fourier synthesis revealed all remaining non-H atoms. For (II) a difference synthesis revealed the positions of two H atoms (attached to atoms $O5'A$ and $O5'B$). All other

Table 1. *Details of data collection and structure refinement*

	(I)	(II)	(III)
Crystal dimensions (mm)	$0.10 \times 0.40 \times 0.20$	$0.60 \times 0.30 \times 0.25$	$0.35 \times 0.35 \times 0.30$
colour, shape	colourless, prismatic	yellowish, prismatic	colourless, prismatic
Lattice parameters			
Number of reflections	24	24	24
2θ range (°)	$21 < 2\theta < 30$	$22 < 2\theta < 26$	$21 < 2\theta < 25$
Scan technique	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Maximum $2\theta(°)$	50	50	50
hkl range	$-11 \leq h \leq 11$	$-7 \leq h \leq 0$	$-7 \leq h \leq 7$
	$-8 \leq k \leq 0$	$-22 \leq k \leq 22$	$-14 \leq k \leq 14$
	$-19 \leq l \leq 19$	$-13 \leq l \leq 13$	$-21 \leq l \leq 0$
Standard reflections	$33\overline{1}, 5\overline{32}, 1\overline{18}, 40\overline{6}$	$081, 055, 014, 06\overline{2}$	$140, 03\overline{6}, 01\overline{8}, 071$
No. of measured reflections	3778	4254	4446
No. of unique reflections	1891	1982	2261
No. of unique observed	1497	1597	1713
reflections ($F \geq 4\sigma F$)			
R_{int} (contributing reflections)	0·017	0·032	0·042
R, wR	0·029, 0·036	0·034, 0·042	0·027, 0·031
Goodness-of-fit S	1·008	1·325	1·111
Weighting scheme	$w = 1/[\sigma(F_o)]^2$	$w = 1/[\sigma(F_o)]^2$	$w = 1/[\sigma(F_o)]^2$
Max. shift/e.s.d.	0·03	0·03	0·03
Min. and max. residual electron density (e Å^{-3})	$-0.215, 0.131$	$-0.537, 0.233$	$-0.434, 0.537$
No. of refined parameters	289	306	402
No. of reflections per refined parameter	5·2	5·2	4·3

H atoms were included at calculated positions (C—H and N—H distances 0·95 Å); for (III) a difference synthesis revealed the positions of all H atoms.

For the three structures all non-H atoms were refined anisotropically on F by full-matrix least squares. Two reflections of (I) (002, 101), badly affected by extinction, were eliminated from the refinement. For (I) and (II) all H atoms were given fixed isotropic temperature factors 1·3 times that of the parent atom and allowed to ride on their parent atoms and for (III) all H atoms were refined with fixed isotropic temperature factors 1·3 times that of the parent atom. For compound (III) the peaks of minimum and maximum electron density (-0.434 and 0.537 e Å^{-3}) lie *ca* 1Å from the Br atom positions. Owing to absorption the C5A—Br5A distance is 1·840 (6) Å instead of a normal 1·883 Å distance for a Br—C_{sp^2} bond (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). All calculations were performed on a Digital PDP 11/73 and MicroVAX 2000 microcomputer using *SDP* (B. A. Frenz & Associates Inc. and Enraf–Nonius, 1985) and *PARST* (Nardelli, 1983).

A *PLUTO* (Motherwell & Clegg, 1978) plot of molecule A of each title compound with the atomic numbering scheme is shown in Fig. 1(a, b and c). The final fractional atomic coordinates are given in Table 2,* bond lengths, bond angles and some selected torsion angles are given in Table 3.

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53592 (58 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters with e.s.d.'s of the refined parameters in parentheses*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
(I)				
N1A	4434 (2)	−40*	3367 (1)	2·42 (4)
C2A	5624 (3)	−603 (4)	3009 (2)	2·62 (5)
O2A	6214 (2)	−2157 (3)	3151 (1)	3·81 (4)
N3A	6082 (2)	687 (3)	2474 (1)	2·78 (4)
C4A	5500 (3)	2479 (4)	2274 (2)	2·63 (5)
O4A	5967 (2)	3444 (3)	1740 (1)	3·61 (4)
C5A	4334 (3)	3015 (4)	2724 (2)	2·80 (5)
C6A	3831 (3)	1754 (4)	3228 (1)	2·69 (5)
C1'A	3795 (3)	−1380 (4)	3903 (1)	2·59 (5)
C2'A	3819 (3)	−700 (5)	4809 (2)	3·11 (5)
C3'A	2498 (3)	−1711 (5)	5029 (2)	3·29 (6)
F3'A	2945 (2)	−3565 (3)	5288 (1)	4·99 (4)
C4'A	1385 (3)	−1810 (4)	4198 (2)	2·94 (5)
O4'A	2264 (2)	−1639 (3)	3533 (1)	3·17 (4)
C5'A	188 (3)	−306 (5)	4081 (2)	3·75 (6)
O5'A	847 (2)	1513 (4)	4237 (1)	4·44 (5)
N1B	−104 (2)	2119 (3)	8587 (1)	2·35 (4)
C2B	1025 (3)	2732 (4)	8192 (2)	2·59 (5)
O2B	1598 (2)	4302 (3)	8332 (1)	4·00 (4)
N3B	1431 (2)	1500 (4)	7614 (1)	2·78 (4)
C4B	784 (3)	−234 (4)	7365 (2)	2·70 (4)
O4B	1173 (2)	−1122 (3)	6779 (1)	3·73 (4)
C5B	−339 (3)	−786 (4)	7827 (2)	3·24 (5)
C6B	−743 (3)	373 (4)	8402 (2)	3·13 (5)
C1'B	−603 (3)	3419 (4)	9205 (1)	2·57 (5)
C2'B	−1879 (3)	4694 (5)	8794 (2)	3·66 (6)
C3'B	−2854 (3)	4840 (4)	9448 (2)	3·01 (5)
F3'B	−2420 (2)	6414 (3)	9979 (1)	4·78 (4)
C4'B	−2552 (3)	3037 (4)	9963 (2)	2·81 (5)
O4'B	−1126 (2)	2340 (3)	9825 (1)	2·84 (3)
C5'B	−3746 (3)	1562 (6)	9712 (2)	4·17 (6)
O5'B	−4053 (2)	1405 (4)	8809 (1)	5·29 (5)
(II)				
N1A	2040 (10)	3080*	7681 (6)	2·5 (1)
C2A	3780 (10)	2596 (4)	8126 (7)	2·7 (2)
O2A	5520 (10)	2809 (3)	8772 (5)	3·7 (1)
N3A	3430 (10)	1900 (4)	7758 (6)	2·8 (1)
C4A	1660 (10)	1617 (4)	6921 (7)	2·5 (1)
O4A	1660 (10)	985 (3)	6589 (6)	3·6 (1)
C5A	−100 (10)	2170 (4)	6522 (7)	2·7 (2)
Br5A	−2664 (1)	1853·7 (6)	5408·5 (8)	3·36 (2)
C6A	160 (10)	2859 (4)	6894 (7)	2·5 (1)
C1'A	2370 (10)	3859 (4)	8086 (7)	2·9 (2)
C2'A	4340 (10)	4229 (4)	7450 (8)	3·4 (2)
C3'A	3420 (20)	5001 (5)	7327 (8)	3·9 (2)
F3'A	4070 (10)	5375 (3)	8452 (5)	5·7 (1)
C4'A	800 (10)	4915 (4)	7161 (8)	3·1 (2)
O4'A	335 (9)	4230 (3)	7769 (6)	3·4 (1)
C5'A	−300 (20)	4924 (5)	5809 (8)	4·1 (2)
O5'A	820 (10)	4390 (4)	5105 (6)	4·8 (2)
N1B	6740 (10)	−1197 (3)	7575 (6)	2·6 (1)
C2B	5030 (10)	−738 (4)	7056 (7)	2·8 (2)
O2B	3290 (10)	−958 (3)	6413 (6)	4·2 (1)
N3B	5390 (10)	−19 (4)	7322 (6)	3·0 (1)
C4B	7180 (10)	293 (4)	8096 (7)	2·8 (2)
O4B	7210 (10)	941 (3)	8360 (6)	3·5 (1)
C5B	8950 (10)	−231 (4)	8566 (7)	2·5 (1)
Br5B	11572 (1)	92·3 (6)	9604·1 (7)	3·16 (1)
C6B	8690 (10)	−930 (4)	8305 (7)	2·5 (1)
C1'B	6440 (10)	−1979 (4)	7408 (7)	2·8 (2)
C2'B	8220 (10)	−2321 (4)	6604 (7)	2·9 (2)
C3'B	8490 (10)	−3072 (5)	7143 (7)	3·2 (2)
F3'B	6750 (10)	−3537 (3)	6575 (5)	5·2 (1)
C4'B	8180 (10)	−2986 (4)	8516 (7)	2·7 (2)
O4'B	6945 (9)	−2313 (3)	8607 (5)	3·0 (2)
C5'B	10460 (10)	−2937 (5)	9358 (8)	3·7 (2)
O5'B	11870 (10)	−2396 (4)	8859 (6)	4·2 (1)

Table 2 *(cont.)*

	x	y	z	$B_{eq}(\text{Å}^2)$
(III)				
N1A	1328 (8)	6390*	1139 (2)	2·2 (1)
C2A	10 (10)	6080 (5)	1713 (3)	2·3 (1)
O2A	−1648 (7)	5454 (4)	1608 (2)	3·06 (9)
N3A	685 (8)	6494 (4)	2402 (3)	2·5 (1)
C4A	2470 (10)	7208 (5)	2583 (3)	2·6 (1)
O4A	2921 (9)	7505 (4)	3230 (2)	3·7 (1)
C5A	3734 (9)	7518 (5)	1929 (3)	2·4 (1)
Br5A	6219 (1)	8462·8 (8)	2062·6 (4)	3·64 (1)
C6A	3138 (9)	7104 (6)	1248 (3)	2·6 (1)
C1'A	800 (10)	5795 (5)	395 (3)	2·4 (1)
C2'A	−1420 (10)	6228 (7)	12 (4)	3·7 (2)
C3'A	−830 (10)	6311 (6)	−814 (3)	3·3 (1)
N3'A	−1160 (10)	5170 (5)	−1147 (3)	4·2 (1)
N4'A	−831 (9)	5111 (5)	−1819 (3)	3·4 (1)
N5'A	−560 (10)	4945 (6)	−2435 (3)	4·5 (1)
C4'A	1690 (10)	6648 (5)	−741 (3)	2·6 (1)
O4'A	2565 (6)	6035 (4)	−82 (2)	2·50 (8)
C5'A	1980 (10)	7905 (7)	−637 (3)	3·6 (1)
O5'A	4348 (9)	8168 (4)	−468 (3)	5·1 (1)
N1B	4538 (8)	4757 (4)	3917 (2)	2·4 (1)
C2B	5970 (10)	5122 (5)	3374 (3)	2·3 (1)
O2B	7693 (7)	5686 (4)	3523 (2)	3·18 (9)
N3B	5369 (8)	4796 (4)	2656 (2)	2·4 (1)
C4B	3542 (9)	4115 (5)	2422 (3)	2·3 (1)
O4B	3243 (7)	3885 (4)	1745 (2)	3·3 (1)
C5B	2203 (9)	3766 (5)	3031 (3)	2·3 (1)
Br5B	−311 (1)	2777·2 (7)	2798·1 (3)	3·17 (1)
C6B	2710 (10)	4081 (5)	3730 (3)	2·3 (1)
C1'B	4960 (10)	5116 (6)	4702 (3)	2·6 (1)
C2'B	3180 (10)	5895 (6)	4982 (3)	3·3 (1)
C3'B	3130 (10)	5606 (6)	5804 (3)	3·1 (1)
N3'B	4960 (10)	6271 (6)	6203 (3)	4·3 (1)
N4'B	4864 (9)	6305 (5)	6904 (3)	3·1 (1)
N5'B	4930 (10)	6438 (6)	7522 (3)	3·9 (1)
C4'B	3670 (10)	4339 (6)	5822 (3)	2·9 (1)
O4'B	4933 (7)	4126 (4)	5160 (2)	2·70 (8)
C5'B	1590 (10)	3574 (7)	5829 (3)	3·6 (1)
O5'B	−38 (8)	3869 (5)	5251 (3)	4·5 (1)

* Parameter kept fixed for origin definition.

Table 3. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

	A	B
(I)		
N1—C2	1·369 (3)	1·365 (3)
N1—C6	1·366 (3)	1·358 (4)
N1—C1'	1·459 (4)	1·470 (3)
C2—O2	1·212 (3)	1·217 (3)
C2—N3	1·358 (3)	1·359 (3)
N3—C4	1·372 (4)	1·370 (4)
C4—O4	1·219 (3)	1·223 (3)
C4—C5	1·433 (4)	1·417 (4)
C5—C6	1·327 (4)	1·322 (4)
C1'—C2'	1·507 (3)	1·503 (4)
C1'—O4'	1·406 (3)	1·391 (3)
C2'—C3'	1·486 (4)	1·487 (4)
C3'—F3'	1·396 (4)	1·394 (3)
C3'—C4'	1·496 (3)	1·499 (5)
C4'—O4'	1·441 (3)	1·436 (3)
C4'—C5'	1·495 (5)	1·490 (4)
C5'—O5'	1·406 (5)	1·406 (3)
C2—N1—C6	121·4 (2)	120·6 (2)
C2—N1—C1'	119·1 (2)	117·6 (3)
C6—N1—C1'	119·6 (2)	121·7 (2)
N1—C2—O2	122·5 (2)	122·1 (2)
N1—C2—N3	115·2 (2)	115·6 (2)
O2—C2—N3	122·3 (2)	122·3 (2)
C2—N3—C4	127·0 (2)	126·8 (2)
N3—C4—O4	119·7 (2)	119·9 (2)

Table 3 *(cont.)*

	A	B
N3—C4—C5	114·3 (2)	113·7 (2)
O4—C4—C5	126·0 (3)	126·4 (3)
C4—C5—C6	119·7 (3)	120·7 (3)
N1—C6—C5	122·2 (2)	122·5 (3)
N1—C1'—C2'	114·6 (2)	112·9 (2)
N1—C1'—O4'	108·1 (2)	109·0 (2)
C2'—C1'—O4'	105·5 (2)	106·9 (3)
C1'—C2'—C3'	102·1 (2)	104·4 (2)
C2'—C3'—F3'	108·1 (2)	109·8 (2)
C2'—C3'—C4'	104·6 (2)	104·6 (2)
F3'—C3'—C4'	108·8 (2)	109·6 (2)
C3'—C4'—O4'	105·4 (2)	106·0 (3)
C3'—C4'—C5'	115·1 (2)	113·0 (3)
O4'—C4'—C5'	109·9 (2)	110·5 (2)
C1'—O4'—C4'	110·2 (2)	111·3 (2)
C4'—C5'—O5'	110·1 (2)	108·4 (3)
C2—N1—C1'—O4'	−121·1 (2)	−150·5 (2)
C2'—C1'—O4'—C4'	−19·5 (3)	−10·3 (3)
O4'—C1'—C2'—C3'	32·9 (3)	22·9 (3)
C1'—C2'—C3'—C4'	−33·8 (3)	−26·2 (3)
C2'—C3'—C4'—O4'	23·0 (3)	20·6 (3)
C3'—C4'—O4'—C1'	−2·1 (3)	−6·5 (3)
C3'—C4'—C5'—O5'	51·3 (3)	47·4 (3)

(II)

	A	B
N1—C2	1·371 (9)	1·356 (9)
N1—C6	1·349 (9)	1·38 (1)
N1—C1'	1·490 (8)	1·44 (1)
C2—O2	1·210 (9)	1·212 (9)
C2—N3	1·33 (1)	1·35 (1)
N3—C4	1·371 (9)	1·367 (9)
C4—O4	1·202 (9)	1·212 (9)
C4—C5	1·45 (1)	1·44 (1)
C5—C6	1·32 (1)	1·31 (1)
C5—Br5	1·874 (7)	1·858 (7)
C1'—C2'	1·52 (1)	1·52 (1)
C1'—O4'	1·35 (1)	1·41 (1)
C2'—C3'	1·50 (1)	1·48 (1)
C3'—F3'	1·39 (1)	1·39 (1)
C3'—C4'	1·50 (1)	1·48 (1)
C4'—O4'	1·44 (1)	1·419 (9)
C4'—C5'	1·50 (1)	1·51 (1)
C5'—O5'	1·41 (1)	1·41 (1)
C2—N1—C6	121·6 (5)	121·2 (6)
C2—N1—C1'	116·6 (6)	119·1 (6)
C6—N1—C1'	121·8 (5)	119·7 (6)
N1—C2—O2	120·7 (7)	122·5 (8)
N1—C2—N3	115·2 (6)	115·2 (6)
O2—C2—N3	124·0 (8)	122·3 (7)
C2—N3—C4	128·5 (6)	128·0 (6)
N3—C4—O4	121·8 (7)	122·3 (7)
N3—C4—C5	111·6 (6)	112·8 (7)
O4—C4—C5	126·5 (7)	124·9 (7)
C4—C5—C6	121·2 (7)	120·6 (7)
C4—C5—Br5	116·3 (5)	119·2 (6)
Br5—C5—C6	122·5 (6)	120·1 (6)
N1—C6—C5	121·5 (6)	122·2 (7)
N1—C1'—C2'	111·8 (6)	113·3 (6)
N1—C1'—O4'	109·0 (6)	107·8 (6)
C2'—C1'—O4'	108·9 (6)	103·7 (7)
C1'—C2'—C3'	100·4 (6)	102·4 (7)
C2'—C3'—F3'	108·9 (7)	110·7 (6)
C2'—C3'—C4'	104·6 (7)	105·0 (6)
F3'—C3'—C4'	109·4 (7)	109·7 (6)
C3'—C4'—O4'	105·5 (7)	105·4 (6)
C3'—C4'—C5'	115·4 (7)	113·7 (7)
O4'—C4'—C5'	110·8 (6)	108·3 (7)
C1'—O4'—C4'	110·6 (6)	111·7 (6)
C4'—C5'—O5'	108·9 (7)	108·3 (6)
C2—N1—C1'—O4'	−168·8 (6)	−131·8 (7)
C2'—C1'—O4'—C4'	−11·2 (8)	−21·2 (8)
O4'—C1'—C2'—C3'	26·7 (8)	32·8 (7)
C1'—C2'—C3'—C4'	−31·2 (8)	−32·7 (8)

Table 3 *(cont.)*

	A	B
C2'—C3'—C4'—O4'	26·4 (8)	20·8 (8)
C3'—C4'—O4'—C1'	−9·6 (8)	0·7 (8)
C3'—C4'—C5'—O5'	53·9 (9)	51·2 (9)

(III)

	A	B
N1—C2	1·355 (8)	1·376 (7)
N1—C6	1·364 (7)	1·366 (7)
N1—C1'	1·513 (7)	1·467 (7)
C2—O2	1·230 (7)	1·228 (8)
C2—N3	1·358 (7)	1·364 (7)
N3—C4	1·371 (8)	1·386 (7)
C4—O4	1·219 (7)	1·236 (6)
C4—C5	1·452 (9)	1·428 (8)
C5—C6	1·336 (8)	1·316 (7)
C5—Br5	1·840 (6)	1·910 (5)
C1'—C2'	1·529 (9)	1·492 (9)
C1'—O4'	1·394 (7)	1·425 (7)
C2'—C3'	1·526 (9)	1·501 (8)
C3'—N3'	1·481 (9)	1·483 (9)
C3'—C4'	1·530 (9)	1·53 (1)
N3'—N4'	1·219 (7)	1·249 (7)
N4'—N5'	1·130 (8)	1·107 (7)
C4'—O4'	1·449 (7)	1·440 (7)
C4'—C5'	1·51 (1)	1·520 (9)
C5'—O5'	1·439 (8)	1·409 (7)
C2—N1—C6	121·6 (4)	120·7 (4)
C2—N1—C1'	115·7 (4)	119·7 (5)
C6—N1—C1'	122·4 (5)	119·6 (4)
N1—C2—O2	121·3 (5)	122·7 (5)
N1—C2—N3	115·5 (5)	115·3 (5)
O2—C2—N3	123·1 (6)	121·9 (6)
C2—N3—C4	128·2 (5)	127·4 (5)
N3—C4—O4	121·8 (5)	119·4 (5)
N3—C4—C5	112·3 (5)	112·6 (4)
O4—C4—C5	125·8 (5)	128·0 (5)
C4—C5—Br5	118·7 (5)	117·3 (4)
C4—C5—C6	120·6 (5)	121·9 (5)
Br5—C5—C6	120·7 (4)	120·9 (4)
N1—C6—C5	121·7 (5)	122·1 (5)
N1—C1'—C2'	111·5 (5)	114·0 (5)
N1—C1'—O4'	108·1 (4)	107·4 (5)
C2'—C1'—O4'	107·5 (5)	106·9 (5)
C1'—C2'—C3'	102·8 (5)	103·2 (5)
C2'—C3'—N3'	107·1 (6)	107·4 (5)
C2'—C3'—C4'	101·4 (5)	103·3 (6)
N3'—C3'—C4'	112·2 (5)	111·3 (6)
C3'—N3'—N4'	114·8 (6)	115·4 (5)
N3'—N4'—N5'	173·4 (7)	172·3 (7)
C3'—C4'—O4'	103·9 (5)	105·5 (5)
C3'—C4'—C5'	111·6 (5)	114·6 (5)
O4'—C4'—C5'	111·2 (5)	110·2 (5)
C1'—O4'—C4'	110·5 (4)	110·0 (5)
C4'—C5'—O5'	109·8 (5)	111·3 (5)
C2—N1—C1'—O4'	−168·4 (4)	−129·8 (5)
C2'—C1'—O4'—C4'	2·8 (6)	−14·2 (6)
O4'—C1'—C2'—C3'	20·4 (7)	29·7 (6)
C1'—C2'—C3'—C4'	−33·9 (7)	−32·9 (6)
C2'—C3'—C4'—O4'	36·1 (6)	25·1 (6)
C3'—C4'—O4'—C1'	−24·9 (6)	−7·0 (6)
C3'—C4'—C5'—O5'	172·1 (5)	50·5 (7)

Each structure contains two molecules in the asymmetric unit. This is a remarkable fact. To justify that no higher symmetry has been overlooked and that the two molecules in the asymmetric unit are crystallographically independent the following arguments can be used. Weissenberg photographs have been taken to give a view of the entire reciprocal-lattice level. From this, the cell parameters and space

group have been deduced and no higher symmetry has been noticed. Density measurements confirm the calculated density. In each structure, the conformation of the two independent molecules is significantly different (see *i.e.* γ, χ and the sugar puckering), and, at last, the chemical synthesis excludes racemic mixtures. The presence of the two independent molecules, which are linked by a hydrogen bonding

network, is probably due to the small differences in energy for changing the pseudorotation phase angle *P*. Indeed, the variation of the total energy when the pseudorotation phase angle *P* changes between 130 and 200°, *i.e.* the range of possible C2'-*endo* conformations, is within $8·37 \times 10^3$ J mol⁻¹ (Saenger, 1984).

Related literature. The method of preparation for (I) has been described by Herdewijn, Van Aerschot & Kerremans (1989) and for (II) by Van Aerschot, Herdewijn, Balzarini, Pauwels & De Clercq (1989). Compound (III) has been synthesized according to Lin, Chen, McLaren, Gao, Ghazzouli & Prusoff (1987).

Fig. 1. Atomic numbering scheme of molecule *A* of (*a*) compound (I), (*b*) compound II and (*c*) compound III.

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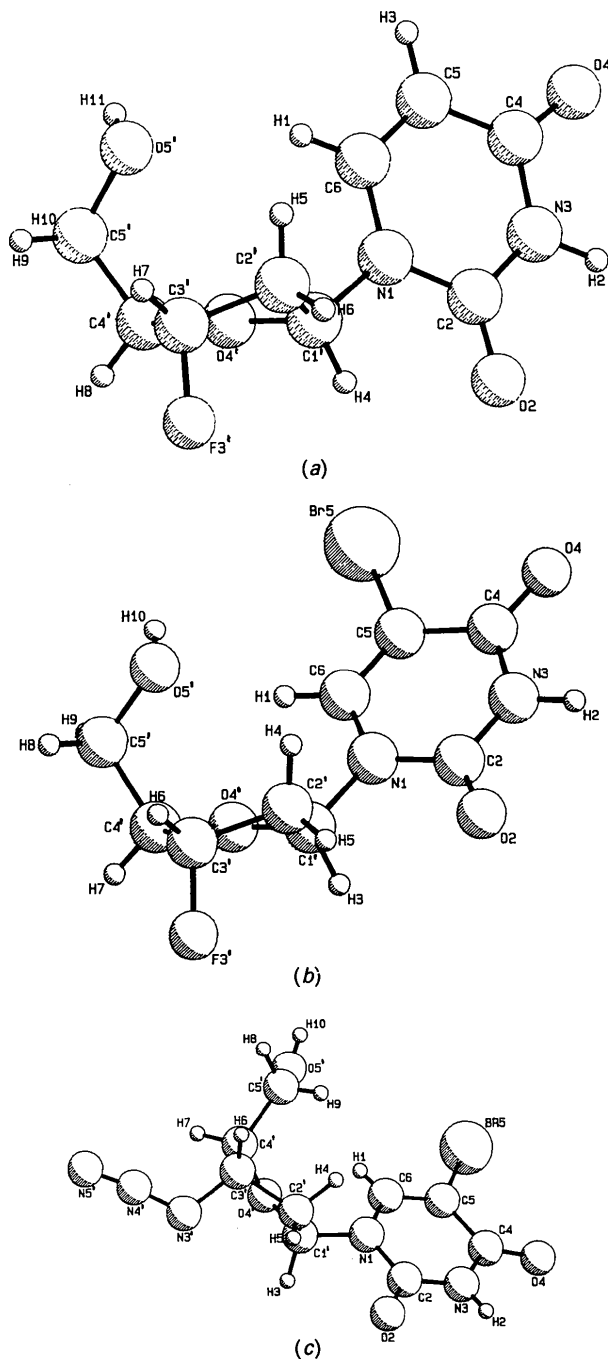VAN AERSCHOT, A., HERDEWIJN, P., BALZARINI, J., PAUWELS, R. & DE CLERCQ, E. (1989). *J. Med. Chem.* 32, 1743–1749.