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Structures of Two N-Bridgehead C-Nucleosides: 5,7-Dimethyl-3-β-D-ribofuranosyl[1,2,4]triazolo[4,3-*a*]pyrimidine, $C_{12}H_{16}N_4O_4$ (I), and 5,7-Dimethyl-2-β-D-ribofuranosyl[1,2,4]triazolo[1,5-*a*]pyrimidine–Methanol, $C_{12}H_{16}N_4O_4.CH_4O$ (II)

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Abstract. (I): $M_r = 280{\cdot}29$, monoclinic, $C2$, $a = 22{\cdot}152\ (6)$, $b = 7{\cdot}225\ (2)$, $c = 25{\cdot}530\ (5)$ Å, $\beta = 103{\cdot}7\ (2)^\circ$, $Z = 12$, $U = 3969{\cdot}02$ Å^3, $D_x = 1{\cdot}412$ Mg m^{-3}, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}920$ mm^{-1}, $F(000) = 1776$, room temperature. (II): $M_r = 312{\cdot}33$, orthorhombic, $P2_12_12_1$, $a = 23{\cdot}318\ (9)$, $b = 10{\cdot}109\ (4)$, $c = 6{\cdot}858\ (2)$ Å, $Z = 4$, $U = 1616{\cdot}58$ Å^3, $D_x = 1{\cdot}287$ Mg m^{-3}, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}852$ mm^{-1}, $F(000) = 664$, room temperature. Final $R = 0{\cdot}075$ for 3157 observed reflexions (I) and $R = 0{\cdot}064$ for 1352 observed reflexions (II) [$I > 2\sigma(I)$]. There are three asymmetric units (*A, B, C*) in the structure of (I) with different ribose puckers: an envelope $_2E$, $P = 340{\cdot}4^\circ$ (*A*), twisted $^2T_1$, $P = 145{\cdot}7^\circ$ (*B*) and $^3T_4$, $P = 27{\cdot}7^\circ$ (*C*). In (II) the ribose appears in a twisted $^2T_3$, $P = 181{\cdot}7^\circ$, conformation. Sugar conformations around C(4')–C(5') in (I) are *trans*, $\psi = 177{\cdot}6^\circ$ (*A*), *gauche*$^+$, $\psi = 56{\cdot}3^\circ$ (*B*), $\psi = 38{\cdot}0^\circ$ (*C*), and in (II) *trans*, $\psi = -177{\cdot}6^\circ$. The conformation about the C-glycosyl bond is high-*anti* [$\chi = 109{\cdot}6$ (*A*), $117{\cdot}0$ (*B*) and $107{\cdot}2^\circ$ (*C*)] in (I) and *anti* ($\chi = 72{\cdot}0^\circ$) in (II). The molecular packing is dominated by hydrogen bonds. A three-dimensional system of hydrogen bonds is formed by sugar–sugar interactions [O(2')–H$\cdots$O(3'), 2·892 (7), $A\cdots C$; O(3')–H$\cdots$O(5'), 2·814 (7), $B\cdots A$; O(5')–H$\cdots$O(2'), 2·861 (9) Å, $B\cdots B$] and sugar–base [O(3')–H$\cdots$N(2), 2·942 (8), $A\cdots C$; O(5')–H$\cdots$N(1), 2·837 (7), $A\cdots B$; 2·871 (11), $C\cdots A$; O(2')–H$\cdots$N(2), 2·842 (8), $B\cdots B$; O(2')–H$\cdots$N(1), 2·817 (10), $C\cdots C$; O(3')–H$\cdots$N(8), 2·868 (9) Å, $C\cdots A$] in (I). In (II) there are sugar–sugar [O(2')–H$\cdots$O(5'), 2·720 (7); O(5')–H$\cdots$O(3'), 2·695 (7) Å], sugar–solvent [O(3')–H$\cdots$O(1), 2·731 (8) Å], and solvent–base [O(1)–H$\cdots$N(1), 2·858 (7) Å] interactions. Base stacking does not occur in these structures.

Introduction. Our interest within the series of N-bridgehead nucleosides (Kojić-Prodić, Ružić-Toroš, Golič, Brdar & Kobe, 1982) is further extended to 3-β-D-ribofuranosyl[1,2,4]triazolo[4,3-*a*]pyrimidine (I) and 2-β-D-ribofuranosyl[1,2,4]triazolo[1,5-*a*]pyrimidine (II), basic heterocyclic systems considered as potential analogues of the antibiotics formycin A and B (Brdar, Japelj & Kobe, 1979).

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5,7-Dimethyl-3-β-D-ribofuranosyl[1,2,4]triazolo[4,3-*a*]pyrimidine (I) with a methyl group at position 5 and a ribofuranose moiety in a *peri* position lacks conformational flexibility about the glycosyl bond as compared to its isomer 5,7-dimethyl-2-β-D-ribofuranosyl[1,2,4]triazolo[1,5-*a*]pyrimidine (II) which can apparently adopt a necessary high-*anti* conformation (Miles, Miles & Eyring, 1978). ^{1}H and ^{13}C NMR measurements of (I) ($R_1 = R_2 = CH_3$) and (II) ($R_1 = R_2 = CH_3$) in solution (NOE, ^{1}H and ^{13}C spin-lattice-relaxation measurements) characterized (I) in a rigid high-*anti* conformation ($\chi = 90\pm20)^\circ$ and (II) predominantly as a flexible model in the *anti* conformation ($\chi = 60\pm30^\circ$) (Kobe & Pumpernik, 1983). The present X-ray structure determination of (I) has revealed three conformers appearing in the high-*anti* conformation. The molecule of (II) in the crystalline state is in the *anti* conformation. Both compounds maintain the same type of glycosyl conformation in solution and solid state. The testing of these compounds on herpes simplex and mengovirus has shown a moderate activity of the compound (II) in both cases (Brdar, Japelj & Kobe, 1979). Compound (I) has been found to be inactive.

Experimental. Weissenberg photographs (Cu $K\alpha$ radiation) determined $P2_12_12_1$ uniquely for (II) and $C2$ or $C2/m$ for (I); the optically active molecule implies $C2$, which was confirmed by the structure analysis. Cell dimensions from diffractometer measurements [20 reflexions for (I) and 15 for (II)]. Crystals used: 0·39 × 0·29 × 0·34 mm (I) and 0·09 × 0·09 × 0·46 mm (II), Philips PW 1100 computer-controlled four-circle diffractometer, ω-scan mode [scan width = 0·6 (I), 1·5° θ (II), scan speed 1·8 (I), 0·05° θs^{-1} (II)], graphite-monochromated Cu $K\alpha$ radiation, 3157 (I) and 1352 (II) observed reflexions [$I > 2\sigma(I)$] in the range $3 < \theta < 70^\circ$, 21 (I) and 14 (II) unobserved; three standard reflexions.

*MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) gave the solution for (II) (based on 200 reflexions having $|E| \geq 1·30$) but in an initial step failed to solve the $C2$ structure. More appropriate origin- and enantiomorph-fixing reflexions were selected and five reflexions were added to the starting set. Two base fragments obtained in the E map (300 reflexions with $|E| \geq 1·5$) were used in the recycling procedure. In this step 40 atoms were located. A difference Fourier synthesis revealed the remaining 20 atoms. It did not locate the positions of H(O2′) (*A*), H(O5′) (*C*), and the H atoms of C(10) and C(11) in the units *B*,*C*.

Full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, with $w = w_1w_2$ where $w_1 = 1$ for $|F_o| \leq 35$ and $35/|F_o|$ for $|F_o| > 35$; $w_2 = 1$ for $\sin\theta \geq 0·40$ and $\sin\theta/0·40$ for $\sin\theta < 0·40$. For (II): $w_1 = 1$ for $|F_o| \leq 15$ and $15/|F_o|$ for $|F_o| > 15$; $w_2 = 1$ for $\sin\theta \geq 0·35$ and $\sin\theta/0·35$ for $\sin\theta < 0·35$. A scale factor, atomic coordinates, and anisotropic thermal parameters (539 variables) were refined for (I); H atoms included in structure-factor calculations only. For (II) a scale factor, atomic coordinates of non-H atoms and six H atoms [H(1′), H(2′), H(3′), H(4′), H(O2′), H(O3′)], anisotropic parameters of non-H atoms, and isotropic ones of the refined H atoms (223 variables) were refined. The H-atom positions are of low accuracy due to the poor ratio of observations to number of variables (~6). Anisotropic thermal parameters are in the usual range: the maximum values are U_{22} for O(5′*C*) (I) [0·139 (8) Å^2], U_{11} for O(5′) (II) [0·149 (4) Å^2], and U_{11} for C(12) (methanol, II) [0·238 (15) Å^2]. The final $R = 0·075$, $R_w = 0·090$ for 3157 (I) and $R = 0·064$, $R_w = 0·075$ for 1352 (II) observed reflexions [$S = 2·50$ (I), 0·96 (II); $\Delta/\sigma = 1·1698$ (I), 0·147 (II); $\Delta\rho = -0·18$–$0·25$ (I), $-0·15$–$0·10$ (II) e Å^{-3}].

Scattering factors from Cromer & Mann (1968) and (for H) Stewart, Davidson & Simpson (1965). Univac 1110 computer at the University Computing Centre in Zagreb with the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.*

The structural formulae with the atom numbering are given in Figs. 1 (I) and 2 (II). Interatomic distances and angles are listed in Tables 2 (I) and 3 (II). The molecular packing is illustrated in Figs. 3 (I) and 4 (II). The conformation about the C-glycosyl bond and sugar pucker are defined by torsion angles (Tables 4 and 5) and displacements from the best least-squares planes.*

Bases. 5,7-Dimethyl[1,2,4]triazolo[4,3-*a*]pyrimidine and 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine involve a bridgehead N at position 5 (classical numbering in purines) which introduces the major difference between the title compounds and formycin. If 5,7-dimethyl[1,2,4]triazolo[4,3-*a*]pyrimidine is compared with purine analogues, an interchange of N(9) and C(8) (purine numbering) is observed. These alterations mostly affect the electronic charge distribution and thus bond lengths and angles cannot be compared with those in formycin.

Bond distances and angles are in agreement with the given atom type, hybridization and corresponding conjugation (Tables 2,3). Their values in the base

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* Lists of structure factors, anisotropic thermal parameters, displacements from the best least-squares planes, hydrogen-bond distances, H-atom coordinates and bond lengths and angles involving H atoms, and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38591 (53 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates* (×10⁴) *and isotropic thermal parameters* (×10²) *for non-hydrogen atoms*

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

	x	*y*	*z*	U_{eq} (Å²)
Structure (I), units *A*, *B*, *C*				
N(1*A*)	335 (2)	5454	7954 (2)	5·7 (3)
N(2*A*)	934 (2)	5431 (10)	7885 (2)	5·4 (3)
C(3*A*)	918 (2)	5687 (10)	7374 (2)	3·6 (3)
N(4*A*)	306 (2)	5520 (9)	7078 (2)	3·4 (3)
C(5*A*)	5 (2)	5553 (11)	6532 (2)	3·7 (3)
C(6*A*)	−627 (2)	5408 (12)	6425 (2)	4·2 (4)
C(7*A*)	−948 (2)	5262 (11)	6842 (2)	4·1 (4)
N(8*A*)	−664 (2)	5142 (10)	7348 (2)	4·5 (3)
C(9*A*)	−28 (2)	5296 (12)	7471 (2)	4·4 (4)
C(10*A*)	364 (3)	5746 (14)	6117 (2)	5·2 (4)
C(11*A*)	−1648 (2)	5184 (15)	6711 (3)	5·6 (5)
O(4′*A*)	1572 (2)	4341 (7)	6841 (1)	3·8 (3)
C(1′*A*)	1481 (2)	5937 (10)	7148 (2)	3·5 (4)
C(2′*A*)	2070 (2)	6060 (10)	7602 (2)	3·6 (4)
O(2′*A*)	2526 (2)	7033 (7)	7387 (1)	4·3 (3)
C(3′*A*)	2238 (2)	4073 (10)	7711 (2)	3·3 (3)
O(3′*A*)	2886 (1)	3724 (8)	7928 (1)	4·4 (3)
C(4′*A*)	2025 (2)	3132 (10)	7164 (2)	3·2 (3)
C(5′*A*)	1754 (3)	1237 (11)	7181 (2)	4·4 (4)
O(5′*A*)	1541 (2)	454 (8)	6661 (1)	4·6 (3)
N(1*B*)	5223 (2)	5545 (11)	6408 (2)	5·0 (3)
N(2*B*)	4886 (2)	5448 (11)	5881 (2)	4·8 (3)
C(3*B*)	4293 (2)	5305 (11)	5874 (2)	3·6 (3)
N(4*B*)	4226 (2)	5288 (9)	6397 (1)	3·4 (3)
C(5*B*)	3720 (2)	5206 (11)	6645 (2)	4·0 (4)
C(6*B*)	3872 (3)	5123 (13)	7181 (2)	4·9 (4)
C(7*B*)	4503 (3)	5107 (12)	7483 (2)	4·6 (4)
N(8*B*)	4977 (2)	5307 (11)	7257 (2)	4·9 (4)
C(9*B*)	4830 (2)	5392 (11)	6719 (2)	4·1 (3)
C(10*B*)	3071 (2)	5371 (14)	6294 (2)	5·0 (4)
C(11*B*)	4645 (4)	4828 (17)	8096 (3)	7·1 (5)
O(4′*B*)	3508 (2)	3237 (8)	5438 (1)	4·3 (3)
C(1′*B*)	3792 (2)	4961 (11)	5380 (2)	3·7 (4)
C(2′*B*)	4034 (3)	4700 (11)	4868 (2)	3·9 (4)
O(2′*B*)	4182 (2)	6406 (7)	4668 (2)	5·0 (3)
C(3′*B*)	3467 (3)	3664 (13)	4507 (2)	4·6 (4)
O(3′*B*)	2994 (2)	4938 (10)	4263 (1)	6·1 (3)
C(4′*B*)	3227 (3)	2483 (12)	4910 (2)	4·4 (4)
C(5′*B*)	3360 (3)	452 (14)	4908 (3)	5·7 (5)
O(5′*B*)	4006 (2)	119 (10)	4992 (2)	6·2 (3)
N(1*C*)	6932 (3)	5171 (13)	615 (2)	6·4 (4)
N(2*C*)	6910 (2)	3563 (10)	891 (2)	5·1 (4)
C(3*C*)	6774 (3)	2156 (13)	549 (2)	4·8 (5)
N(4*C*)	6690 (2)	2857 (11)	35 (2)	5·4 (4)
C(5*C*)	6522 (3)	2047 (16)	−482 (3)	6·1 (5)
C(6*C*)	6465 (4)	3234 (18)	−894 (3)	6·9 (6)
C(7*C*)	6593 (4)	5131 (19)	−809 (3)	7·4 (6)
N(8*C*)	6768 (3)	5906 (13)	−322 (2)	7·2 (5)
C(9*C*)	6802 (3)	4684 (13)	94 (3)	5·2 (5)
C(10*C*)	6426 (5)	49 (21)	−554 (4)	8·8 (7)
C(11*C*)	6521 (6)	6352 (20)	−1305 (3)	9·7 (7)
O(4′*C*)	6048 (2)	−246 (12)	534 (2)	7·3 (4)
C(1′*C*)	6703 (3)	218 (16)	688 (2)	5·4 (5)
C(2′*C*)	6927 (3)	−244 (13)	1293 (2)	4·8 (5)
O(2′*C*)	7248 (2)	−1954 (9)	1376 (2)	5·7 (3)
C(3′*C*)	6312 (3)	−343 (14)	1470 (2)	5·2 (4)
O(3′*C*)	6354 (2)	−1408 (9)	1938 (2)	5·9 (3)
C(4′*C*)	5866 (3)	−1137 (14)	974 (2)	5·3 (4)
C(5′*C*)	5186 (4)	−762 (18)	900 (4)	8·0 (6)
O(5′*C*)	5038 (3)	1042 (15)	1056 (3)	11·2 (6)
Structure (II)				
N(1)	1548 (1)	4172 (4)	4666 (7)	4·0 (3)
C(2)	1389 (2)	5455 (5)	4661 (8)	3·7 (3)
N(3)	1813 (1)	6335 (4)	4631 (7)	4·0 (3)
N(4)	2284 (1)	5535 (4)	4625 (7)	3·8 (3)
C(5)	2855 (2)	5905 (6)	4591 (9)	4·5 (4)
C(6)	3232 (2)	4906 (6)	4575 (9)	5·0 (4)
C(7)	3044 (2)	3581 (7)	4598 (9)	4·9 (4)
N(8)	2497 (1)	3223 (4)	4624 (7)	4·5 (3)
C(9)	2124 (2)	4235 (5)	4629 (8)	4·0 (3)
C(10)	2984 (2)	7344 (6)	4588 (12)	6·3 (4)
C(11)	3472 (2)	2467 (7)	4598 (12)	6·6 (5)
O(4′)	557 (1)	5640 (4)	6629 (5)	4·3 (2)
C(1′)	779 (2)	5891 (6)	4714 (8)	3·7 (3)
C(2′)	385 (2)	5140 (6)	3317 (8)	3·8 (3)
O(2′)	367 (1)	5811 (5)	1519 (6)	5·2 (3)
C(3′)	−186 (2)	5111 (5)	4403 (8)	3·7 (3)
O(3′)	−498 (1)	6296 (4)	4190 (6)	4·9 (2)
C(4′)	7 (2)	4998 (5)	6527 (8)	3·7 (3)
C(5′)	55 (3)	3592 (6)	7235 (9)	5·5 (4)
O(5′)	214 (2)	3645 (4)	9224 (6)	8·0 (4)
O(1)	1041 (2)	1609 (4)	4309 (9)	8·2 (4)
C(12)	1404 (7)	457 (14)	4859 (29)	20 (1)

Table 2. *Bond distances* (Å) *and angles* (°) *for non-hydrogen atoms, structure* (I)

	A	*B*	*C*
N(1)–N(2)	1·380 (8)	1·379 (7)	1·366 (12)
N(1)–C(9)	1·307 (8)	1·314 (9)	1·340 (11)
N(2)–C(3)	1·310 (9)	1·314 (8)	1·327 (11)
C(3)–N(4)	1·392 (7)	1·376 (8)	1·379 (10)
C(3)–C(1′)	1·502 (9)	1·490 (8)	1·462 (15)
N(4)–C(5)	1·395 (8)	1·416 (9)	1·413 (11)
N(4)–C(9)	1·391 (9)	1·395 (7)	1·345 (13)
C(5)–C(6)	1·367 (9)	1·329 (9)	1·340 (14)
C(5)–C(10)	1·475 (10)	1·508 (8)	1·462 (19)
C(6)–C(7)	1·417 (10)	1·429 (9)	1·407 (19)
C(7)–N(8)	1·298 (8)	1·321 (10)	1·332 (12)
C(7) C(11)	1·508 (9)	1·534 (10)	1·521 (16)
N(8)–C(9)	1·374 (8)	1·335 (8)	1·372 (12)
O(4′)–C(1′)	1·437 (9)	1·418 (10)	1·450 (10)
O(4′)–C(4′)	1·434 (7)	1·450 (8)	1·434 (11)
C(1′)–C(2′)	1·527 (8)	1·536 (10)	1·541 (10)
C(2′)–O(2′)	1·442 (9)	1·403 (10)	1·416 (11)
C(2′)–C(3′)	1·492 (10)	1·561 (10)	1·537 (12)
C(3′)–O(3′)	1·433 (7)	1·422 (10)	1·404 (10)
C(3′)–C(4′)	1·524 (9)	1·527 (12)	1·521 (10)
C(4′)–C(5′)	1·500 (11)	1·497 (14)	1·497 (13)
C(5′)–O(5′)	1·417 (8)	1·416 (9)	1·424 (17)
N(2)–N(1)–C(9)	105·9 (5)	107·6 (5)	105·3 (8)
N(1)–N(2)–C(3)	109·0 (5)	108·9 (5)	110·1 (6)
N(2)–C(3)–N(4)	108·6 (5)	109·0 (5)	107·7 (8)
N(2)–C(3)–C(1′)	124·7 (5)	124·3 (6)	126·5 (7)
N(4)–C(3)–C(1′)	126·4 (5)	126·1 (6)	125·8 (7)
C(3)–N(4)–C(5)	135·4 (6)	135·5 (5)	133·3 (9)
C(3)–N(4)–C(9)	103·7 (5)	105·2 (5)	105·9 (7)
C(5)–N(4)–C(9)	120·9 (5)	119·3 (5)	120·8 (7)
N(4)–C(5)–C(6)	114·9 (6)	115·4 (5)	115 (1)
N(4)–C(5)–C(10)	120·6 (5)	118·3 (5)	120·6 (8)
C(6)–C(5)–C(10)	124·4 (6)	126·1 (6)	124·3 (9)
C(5)–C(6)–C(7)	121·9 (6)	122·1 (7)	121·6 (9)
C(6)–C(7)–N(8)	122·8 (5)	122·7 (6)	124 (1)
C(6)–C(7)–C(11)	120·6 (6)	119·2 (7)	117·2 (9)
N(8)–C(7)–C(11)	116·5 (6)	118·0 (6)	119 (1)
C(7)–N(8)–C(9)	116·8 (6)	115·5 (5)	114 (1)
N(1)–C(9)–N(4)	110·8 (5)	109·2 (5)	111·1 (8)
N(1)–C(9)–N(8)	126·4 (6)	126·1 (5)	124·1 (9)
N(4)–C(9)–N(8)	122·5 (5)	124·7 (6)	124·7 (7)
C(1′)–O(4′)–C(4′)	110·1 (4)	109·6 (5)	109·9 (5)
C(3)–C(1′)–O(4′)	110·5 (5)	108·5 (6)	108·4 (7)
C(3)–C(1′)–C(2′)	110·7 (5)	113·6 (5)	115·0 (7)
O(4′)–C(1′)–C(2′)	104·8 (5)	103·5 (6)	106·6 (7)
C(1′)–C(2′)–O(2′)	106·9 (5)	111·2 (6)	111·8 (7)
C(1′)–C(2′)–C(3′)	102·5 (5)	99·7 (5)	102·0 (6)
O(2′)–C(2′)–C(3′)	111·9 (5)	115·5 (5)	111·3 (7)
C(2′)–C(3′)–O(3′)	115·1 (6)	110·7 (7)	113·1 (6)
C(2′)–C(3′)–C(4′)	104·4 (5)	103·2 (5)	102·5 (6)
O(3′)–C(3′)–C(4′)	109·9 (5)	108·5 (6)	113·6 (8)
O(4′)–C(4′)–C(3′)	106·1 (5)	106·0 (6)	103·7 (7)
O(4′)–C(4′)–C(5′)	110·0 (5)	109·3 (6)	106·3 (7)
C(3′)–C(4′)–C(5′)	114·8 (6)	116·4 (7)	118·1 (8)
C(4′)–C(5′)–O(5′)	112·6 (6)	111·0 (7)	115·0 (9)

moieties of three asymmetric units (I) are within 3σ. The base conformations are defined by the mean torsion angles of the five- and six-membered rings: 9·2 (7), 2·3 (1·0) (*A*); 1·9 (9), 3 (1) (*B*); 1·3 (8), 1·5 (1·0) (*C*) and 0·5 (6), 0·3 (8)° in (II).* Deviations of the atoms from the best least-squares planes through the all atoms of the five- and six-membered rings are in the range (I): 0·001 (10)

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* See deposition footnote.

Table 3. *Bond distances* (Å) *and angles* (°) *for non-hydrogen atoms, structure* (II)

N(1)–C(2)	1·349 (7)	N(8)–C(9)	1·342 (7)
N(1)–C(9)	1·344 (7)	O(4′)–C(1′)	1·434 (7)
C(2)–N(3)	1·329 (7)	O(4′)–C(4′)	1·440 (7)
C(2)–C(1′)	1·490 (7)	C(1′)–C(2′)	1·530 (8)
N(3)–N(4)	1·365 (6)	C(2′)–O(2′)	1·408 (7)
N(4)–C(5)	1·382 (7)	C(2′)–C(3′)	1·528 (8)
N(4)–C(9)	1·367 (7)	C(3′)–O(3′)	1·408 (7)
C(5)–C(6)	1·340 (9)	C(3′)–C(4′)	1·530 (8)
C(5)–C(10)	1·485 (9)	C(4′)–C(5′)	1·506 (9)
C(6)–C(7)	1·409 (10)	C(5′)–O(5′)	1·414 (8)
C(7)–N(8)	1·326 (7)	O(1)–C(12)	1·488 (17)
C(7)–C(11)	1·505 (10)		
C(9)–N(1)–C(2)	103·2 (4)	N(1)–C(9)–N(8)	127·6 (5)
N(1)–C(2)–N(3)	116·0 (4)	N(4)–C(9)–N(8)	123·8 (5)
N(1)–C(2)–C(1′)	123·2 (5)	C(1′)–O(4′)–C(4′)	110·9 (4)
N(3)–C(2)–C(1′)	120·7 (5)	C(2)–C(1′)–O(4′)	108·3 (4)
C(2)–N(3)–N(4)	101·7 (4)	C(2)–C(1′)–C(2′)	114·3 (5)
N(3)–N(4)–C(5)	128·0 (5)	O(4′)–C(1′)–C(2′)	105·6 (4)
N(3)–N(4)–C(9)	110·4 (4)	C(1′)–C(2′)–O(2′)	109·1 (5)
C(5)–N(4)–C(9)	121·6 (5)	C(1′)–C(2′)–C(3′)	103·2 (4)
N(4)–C(5)–C(6)	115·4 (5)	O(2′)–C(2′)–C(3′)	114·2 (4)
N(4)–C(5)–C(10)	117·4 (5)	C(2′)–C(3′)–O(3′)	112·5 (5)
C(6)–C(5)–C(10)	127·2 (5)	C(2′)–C(3′)–C(4′)	102·0 (4)
C(5)–C(6)–C(7)	120·7 (5)	O(3′)–C(3′)–C(4′)	108·3 (5)
C(6)–C(7)–N(8)	124·0 (6)	O(4′)–C(4′)–C(3′)	106·0 (4)
C(6)–C(7)–C(11)	120·3 (5)	O(4′)–C(4′)–C(5′)	110·0 (5)
N(8)–C(7)–C(11)	115·7 (6)	C(3′)–C(4′)–C(5′)	113·5 (5)
C(7)–N(8)–C(9)	114·5 (5)	C(4′)–C(5′)–O(5′)	107·1 (5)
N(1)–C(9)–N(4)	108·6 (5)		

Table 4. *Torsion angles* (°) *involving the glycosyl bond and ribose moiety, structure* (I)

Greek letters correspond to Sundaralingam's (1969) notation.

		A	*B*	*C*
χ	O(4′)–C(1′)–C(3)–N(2)	109·6 (7)	117·0 (8)	107·2 (8)
τ_0	C(4′)–O(4′)–C(1′)–C(2′)	21·7 (7)	−34·5 (6)	−6 (1)
τ_1	O(4′)–C(1′)–C(2′)–C(3′)	−33·6 (7)	42·0 (6)	−18 (1)
τ_2	C(1′)–C(2′)–C(3′)–C(4′)	32·6 (7)	−34·4 (7)	34·3 (9)
τ_3	C(2′)–C(3′)–C(4′)–O(4′)	−20·5 (7)	15·7 (8)	−39·0 (9)
τ_4	C(3′)–C(4′)–O(4′)–C(1′)	−1·0 (7)	11·5 (7)	28 (1)
	O(2′)–C(2′)–C(3′)–O(3′)	38·9 (7)	−37·6 (9)	37·7 (9)
	O(5′)–C(5′)–C(4′)–O(4′)	58·0 (8)	−63·6 (8)	−78 (1)
ψ	O(5′)–C(5′)–C(4′)–C(3′)	177·6 (5)	56·3 (8)	38 (1)

Table 5. *Torsion angles* (°) *involving the glycosyl bond and ribose moiety, structure* (II)

O(4′)–C(1′)–C(2)–N(3)	−107·1 (6)	C(3′)–C(4′)–O(4′)–C(1′)	−12·2 (6)
C(4′)–O(4′)–C(1′)–C(2′)	−10·1 (6)	O(2′)–C(2′)–C(3′)–O(3′)	−37·0 (7)
O(4′)–C(1′)–C(2′)–C(3′)	28·3 (6)	O(5′)–C(5′)–C(4′)–O(4′)	63·7 (7)
C(1′)–C(2′)–C(3′)–C(4′)	−34·5 (5)	O(5′)–C(5′)–C(4′)–C(3′)	−177·6 (5)
C(2′)–C(3′)–C(4′)–O(4′)	29·2 (6)		

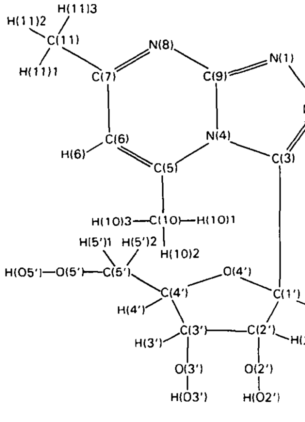

Fig. 1. Structural formula of (I) and atom numbering.

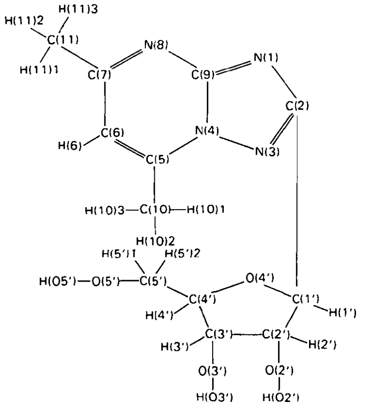

Fig. 2. Structural formula of (II) and atom numbering.

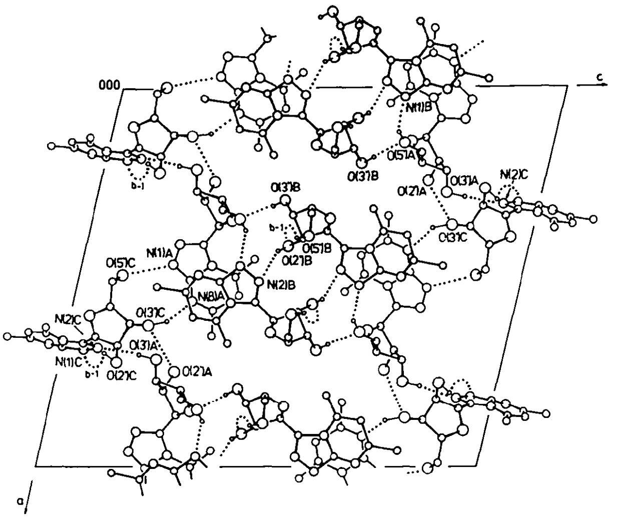

Fig. 3. Molecular packing of (I) along **b**. The system of three-dimensional hydrogen bonds between sugar–sugar and sugar–base moieties is marked by dotted lines. For clarity, only the H atoms involved in hydrogen bonds are shown. The positions of H(O2′) (*A*) and H(O5′) (*C*) were not determined. The positive direction of **b** is away from the viewer.

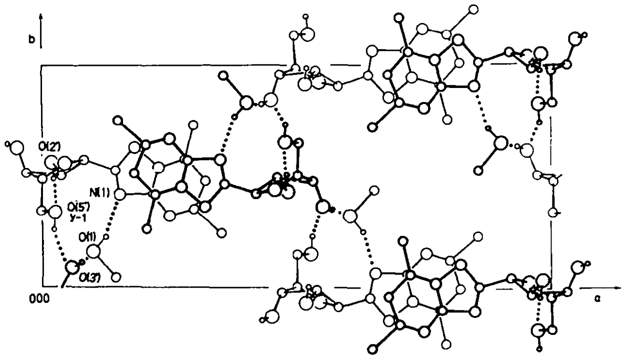

Fig. 4. A view of the crystal structure of (II) along **c** showing hydrogen bonds (dotted lines). Only the H atoms involved in hydrogen bonds are shown.

[C(6)]–0·081 (11) [N(1)] (*A*); 0·003 (9) [N(8)]–0·058 (10) [C(7)] (*B*); 0·012 (10)[C(5)]–0·033 (10) [C(6)] (*C*), and (II): 0·000 (6) [C(2), N(8)]–0·004 (6) Å [N(4), C(9)].* The base of (I)*A* deviates considerably from planarity; the puckering of the five-membered ring at the N(1), N(2), C(3) side is obvious (Table 4). The departures of N(1) [0·081 (11)] and N(2) [−0·067 (11) Å] from the best least-squares plane in (I) *A* are considerably larger than in (I) *B* [0·049 (9), −0·026 (9)] and *C* [−0·020 (11), −0·027 (7) Å]. N(1), N(2) [and N(8)] are available as proton-acceptor sites for hydrogen bonds. All available sites are involved in hydrogen bonding but N(2) of (I)*A* does not exhibit any intermolecular contact less than 3·5 Å. The existing hydrogen-bonding system may cause the puckering of the triazole ring in molecule *A*.

Ribose moieties. Interatomic distances in the ribose residues of the three units *A,B,C* in (I) and in those in (II) are within 4σ (Tables 2,3). Bond angles are influenced by the mode of puckering (or conformation) more than bond distances. Four different ribose conformations appear in these structures and thus the bond angles are more scattered than the bond lengths. The shortening of the endocyclic bond length C(1′)—O(4′) relative to the normal C—O single bond (1·428 Å, Sundaralingam, 1969), common for N-glycosyl derivatives, is not observed; the smallest value is in (I) *B*, 1·418 (10) Å, but the difference from the single C—O bond is within 3σ. The asymmetry in C(1′)—O(4′) and C(4′)—O(4′) is not pronounced; the differences between these two bonds in all molecules are within 3σ. Bond angles C(1′)—O(4′)—C(4′) are close to 109·9° [(I): 110·1 (4) (*A*), 109·6 (5) (*B*), 109·9 (5) (*C*); (II): 110·9 (4)°]. The endocyclic O(4′)—C(1′)—C(2′) in (I) *B* is 103·5 (6)° which is smaller than in (I) *A* and *C* and in (II). In formycin (Prusiner, Brennan & Sundaralingam, 1973) the value 103·4 (3)° has been observed. In (I)*B* and formycin the ribose is in the ${}^2T_1$ conformation.

The puckering of the ribose moiety is described by means of the torsional angles τ_0–τ_4 (Tables 4,5) and a pseudorotation angle *P* (Altona & Sundaralingam, 1972). Both general modes of puckering, C(3′)-*endo* and C(2′)-*endo*, occur in these structures. The C(2′)-*exo*, envelope ${}_2E$, appearing in (I)*A* is a variant of C(3′)-*endo* (Sundaralingam, 1975*b*). The C(3′)-*endo*—C(4′)-*exo*, ${}^3T_4$, is observed in (I)*C*. The C(2′)-*endo* mode of puckering occurs in (I)*B* [C(2′)-*endo*—C(1′)-*exo*, ${}^2T_1$] and in (II) [C(2′)-*endo*—C(3′)-*exo*, ${}^2T_3$]. The values of the pseudorotation angle *P* are given in the *Abstract*.

The conformation about the exocyclic bond C(4′)—C(5′) is defined by the value of the torsion angle ψ along C(3′)—C(4′)—C(5′)—O(5′) (Sundaralingam, 1969; 1975*a*). The conformation *gauche*$^+$ is observed in (I)*B* (ψ = 56·5) and *C* (ψ = 38·0°). The *trans* conformation is found in (I)*A* (ψ = 177·6) and in (II) (ψ = −177·6°).

The glycosyl bond and molecular packing. The title nucleosides possess a C-glycosyl bond with the values (I): 1·502 (9) (*A*), 1·490 (8) (*B*), 1·462 (15) (*C*), and (II): 1·490 (7) Å. These values are in the range found in formycin derivatives: formycin A, 1·501 (5) (Prusiner, Brennan & Sundaralingam, 1973), formycin A.H$^+$, 1·492 (17) (Koyama, Umezawa & Iitaka, 1974), formycin B, 1·493 (4), oxoformycin B, 1·501 (6) (Koyama, Nakamura, Umezawa & Iitaka, 1976), 8-methylformycin, 1·494 (2) (Abola, Sims, Abraham, Lewis & Townsend, 1974). The shortening of the C—C glycosyl bond is observed in 8-aza-9-deazapurine nucleosides but also in C—N bonds of other nucleosides containing N in the *ortho* position to the glycosyl bond (Singh & Hodgson, 1977*a*).

The orientation of the base relative to the sugar ring, described in terms of rotation about the C(1′)—C(3) glycosyl bond for the sequence O(4′)—C(1′)—C(3)—N(2), in (I) is high-*anti* [109·6 (7) (*A*), 117·0 (8) (*B*), 107·2 (8)° (*C*)] (Sundaralingam, 1969, 1975*a,b*). In (II) the conformation about the C(1′)—C(2) glycosyl bond, defined by the torsion angle O(4′)—C(1′)—C(2)—N(1) = 72·0 (7)°, is *anti.* The nucleosides involving a C-glycosyl bond mostly prefer the *syn* conformation (Sundaralingam, 1975*a,b*). The χ angles in oxoformycin B (−164·1) (Koyama, Nakamura, Umezawa & Iitaka, 1976), formycin hydrobromide monohydrate (−149·3) (Koyama, Umezawa & Iitaka, 1974), and formycin B hydrochloride (−140·1°) (Singh & Hodgson, 1977*b*) are in the *syn* range. The molecules of formycin monohydrate (χ = 109·8) (Prusiner, Brennan & Sundaralingam, 1973) and 8-azaadenosine (χ = 103·7°) (Singh & Hodgson, 1977*a*) adopt the high-*anti* conformation. Of all the formycin derivatives, only formycin B is in the *anti* conformation (χ = 30·4°) (Koyama, Nakamura, Umezawa & Iitaka, 1976). The 8-azapurines are mostly characterized by higher *anti* glycosyl angles (Sundaralingam, 1975*a*) in which the repulsion between the base and the 5′-hydroxyl oxygen is alleviated. The methyl group at position 5 and the ribofuranose moiety in a *peri* position considerably reduce the flexibility about the glycosyl bond. The high-*anti* conformation is maintained in solution (Kobe & Pumpernik, 1983) and the solid state. Probably hydrogen bonds do not affect the conformation about the glycosyl bond. (II) is more flexible and adopts the more common *anti* conformation.

The crystal packing is realized through three-dimensional hydrogen bonds (Figs. 3,4). Sugar–sugar interactions occur in both structures and are detailed in the *Abstract*. Sugar–base interactions occur in (I) only and in (II) both the base and the sugar are involved in hydrogen bonds, to the solvent (see *Abstract*). In both

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* See deposition footnote.

bases only the acceptor sites for protons are available. Thus, base–base interaction is not possible. In (I) *B* and *C*, N(1) and N(2), but not N(8), are involved in hydrogen bonds. However, in (I)*A*, N(1) and N(8) are hydrogen bonded whereas N(2) is free and does not make any contact $< 3{\cdot}50$ Å. The ring O(4′) atom of the ribose is not involved in a hydrogen bond. Base stacking does not occur in these structures.

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(*E*)-3-Hexenedinitrile, $C_6H_6N_2$

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Abstract. $M_r = 106{\cdot}13$, $P2_1/c$, $a = 4{\cdot}033\ (2)$, $b = 14{\cdot}201\ (8)$, $c = 5{\cdot}331\ (6)$ Å, $\beta = 103{\cdot}04\ (6)°$, $V = 297{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}185$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}82$ cm^{-1}, $F(000) = 112$, $T = 296\ (2)$ K, $R = 0{\cdot}079$ for 524 reflections. The molecule lies on a center of symmetry; it is close to planar with the cyano groups eclipsing the double bond. Bond lengths and angles are normal. The short contacts in the packing are from the nitrogen atom to the cyano carbon atom, 3·38 (1) and 3·65 (1) Å, and from the nitrogen atom to the α-carbon atom, 3·39 (1) Å, all of types found in the packing of other nitriles.

Introduction. As part of a study of Lewis-acid–Lewis-base interactions in the solid state we have determined the structure of the title compound. This structure is the third in a series where we are examining the environment of the nitrile group attached to otherwise aliphatic hydrocarbons. See also Britton & Gleason (1982–fumaronitrile) and Gleason & Britton (1982–tetramethylsuccinonitrile).

Experimental. Sample obtained from the organic chemical collection of the Department of Chemistry of the University of Minnesota, recrystallized from ethanol, crystal roughly equant, $0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}3$ mm, lattice parameters determined from accurate measurement of positions of eight reflections with $10 < \theta < 18°$, Hilger & Watts four-circle automatic diffractometer, systematic absences $0k0$ $k = 2n + 1$, $h0l$ $l = 2n + 1$, no absorption corrections, one quadrant of data, $0 < \theta < 26°$, h 0–4, k 0–18, l −6–6, 569 independent reflections, 524 with $I_{\rm obs} > 0$ used; two check reflections, measured every 25 data measurements, showed no significant variation with time; trial structure found

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