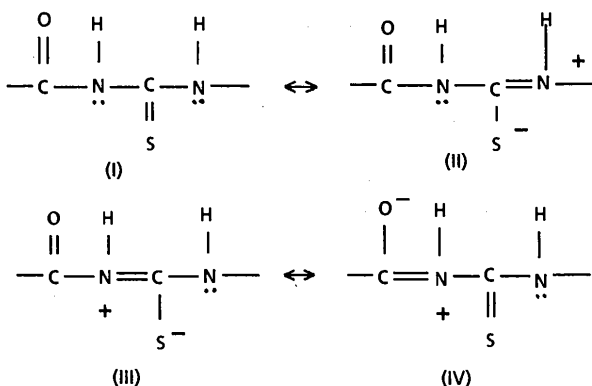


contributing since these two C—N distances are shorter than the others.



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## Structures of Two 8-(2,3-*O*-Isopropylidene- $\beta$ -D-ribofuranosylamino)pyrimido-[5,4-*d*]pyrimidines

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**Abstract.** 2,4,6-Trichloro-8-(2,3-*O*-isopropylidene- $\beta$ -D-ribofuranosylamino)pyrimido[5,4-*d*]pyrimidine (1) ethanol solvate,  $C_{14}H_{14}Cl_3N_5O_4 \cdot C_2H_5OH$ ,  $M_r = 468.72$ , triclinic,  $P1$ ,  $a = 5.1578$  (6),  $b = 9.3348$  (15),  $c = 11.115$  (2) Å,  $\alpha = 106.08$  (2),  $\beta = 96.713$  (9),  $\gamma = 93.731$  (12)°,  $V = 508.02$  (15) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.532$  g cm<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.54178$  Å,  $\mu = 45.244$  cm<sup>-1</sup>,  $F(000) = 242$ ,  $T = 295$  K,  $R = 0.0276$  for 2045 reflections ( $F \geq 4\sigma_F$ ). 4-Amino-6-chloro-8-(2,3-*O*-isopropylidene- $\beta$ -D-ribofuranosylamino)pyrimido[5,4-*d*]pyrimidine (2),  $C_{14}H_{17}ClN_6O_4$ ,  $M_r = 368.78$ , monoclinic,  $P2_1$ ,  $a = 5.0427$  (8),  $b = 9.994$  (2),  $c = 15.713$  (5) Å,  $\beta = 99.13$  (2)°,  $V = 781.8$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.566$  g cm<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.54178$  Å,  $\mu = 25.084$  cm<sup>-1</sup>,  $F(000) = 384$ ,  $T = 295$  K,  $R = 0.0365$  for 1413 reflections ( $F \geq 4\sigma_F$ ). The two structures are nearly identical despite the presence of ethanol in the lattice of (1). Each compound exhibits an intramolecular hydrogen bond from the bridging N atom

(N11) to O5' [ $d(H \cdots O) = 2.25$  (7),  $d(N \cdots O) = 2.841$  (4) Å,  $\angle(N-H \cdots O) = 133$  (6)° for (1);  $d(H \cdots O) = 2.37$  (5),  $d(N \cdots O) = 3.034$  (5) Å,  $\angle(N-H \cdots O) = 134$  (4)° for (2)]. The sugar conformations and puckering parameters are  ${}^4T_0$  ( $C_{4'}$ -endo),  $P = 243.1^\circ$  and  $\tau_m = 31.8^\circ$  for (1) and  ${}^3T$  ( $C_{4'}$ -endo- $C_{3'}$ -exo),  $P = 214.6^\circ$  and  $\tau_m = 30.2^\circ$  for (2). The pyrimidopyrimidine rings are nearly planar [r.m.s. deviations: 0.0180 (9) Å for (1) and 0.0215 (6) Å for (2)]. The dihedral angles between the fused pyrimidine rings are 1.58 (11)° for (1) and 2.09 (13)° for (2).

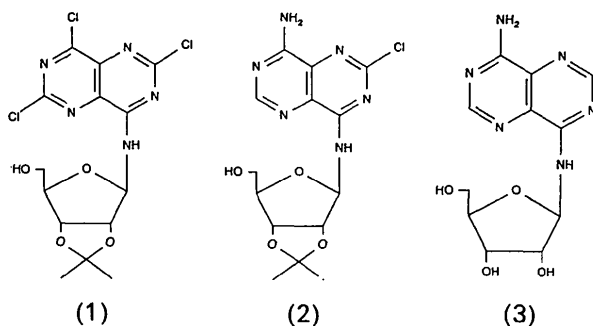
**Introduction.** The exocyclic aminonucleoside 4-amino-8-( $\beta$ -D-ribofuranosylamino)pyrimido[5,4-*d*]pyrimidine [ARPP (3)] was first reported as the product of the rearrangement of the purine ring in the aqueous ammonia adduct of 9-(2,3,5-tri-*O*-acetyl- $\beta$ -D-ribofuranosyl)purine-6-carbonitrile (Berman, Rousseau, Mancuso, Kreishman & Robins, 1973). ARPP possesses broad-spectrum antiviral activity (Westover *et al.*, 1981) and immunosuppressive activity and inhibits

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the growth of L1210 leukemia in mice (Robins & Revankar, 1985).



In order to continue biological evaluation of ARPP and certain of its derivatives, a direct synthesis of the nucleoside from the preformed pyrimidopyrimidine was studied (Sanghvi *et al.*, 1989), which resulted in a mixture of  $\alpha$  and  $\beta$  anomers. In addition, the deblocked nucleosides were observed to anomerize. The title compound (1) from which all the derivatives with  $\beta$ -anomeric configuration were synthesized was investigated by X-ray diffraction to verify the anomeric configuration. The title compound (2), derived from (1) *via* amination and selective dechlorination, was studied in order to identify the site of the dechlorination.

**Experimental.** Compound (1) was synthesized by the condensation of 2,3-*O*-isopropylidene- $\beta$ -ribofuranosylamine with 2,4,6,8-tetrachloropyrimido[5,4-*d*]pyrimidine. Compound (1) was derivatized by ammonolysis at the 4-position followed by selective dechlorination at the 2-position to give compound (2) (Sanghvi *et al.*, 1989). Table 1 summarizes data collection and refinement of both structures.

**Compound (1).** Crystals grew from ethanol as hexagonal needles. Crystallographic coordinates of all aglycon atoms (except for the ethanol solvate) were determined with *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). The positions of the remaining non-H atoms were revealed in two subsequent difference maps. H-atom positions were obtained from a difference map as peaks of density 0.21–0.46 e  $\text{\AA}^{-3}$  at  $R = 0.045$ . All non-H atoms were refined anisotropically. All positions and  $U$  values of the H atoms of the nucleoside and the hydroxyl H of the solvate were refined. The positions of the other H atoms of the solvate were idealized with  $d(\text{C-H}) = 1.00 \text{ \AA}$  and their  $U$  values were refined such that  $U(\text{H13A}) = U(\text{H13B})$  and  $U(\text{H14A}) = U(\text{H14B}) = U(\text{H14C})$ .

**Compound (2).** Crystals grew from ethanol as long, thin plates. Again, all aglycon atomic coordinates were determined from *MULTAN82* (Main *et al.*, 1982). The remaining non-H-atom positions were taken from a

Table 1. *Crystallographic summary for (1) and (2)*

(a) Data collection		
Mode		$\omega$ - $2\theta$ scan
Scan range ( $^\circ$ )		0.80 + 0.15 tan $\theta$
Background		Scan 0.25 times scan range before and after scan
Scan rate ( $^\circ \text{ min}^{-1}$ )		1.3–5.5
$2\theta$ range ( $^\circ$ )	(1)	(2)
Exposure time (h)	3–150	3–152
Stability correction range on $I$	22.2	30.1
Range in $hkl$ , min.	1.000–1.004	1.000–1.006
max.	0, –11, –13	0, 0, –20
Total reffs, measd, unique	6, 11, 13	6, 13, 20
Crystal dimensions (mm)	2085, 2085	1903, 1726
Crystal volume (mm <sup>3</sup> )	0.395 × 0.175 × 0.16 × 0.15	0.35 × 0.135 × 0.04
Crystal faces	0.00916	0.00191
Transmission factor range	{100}; {010}; {001}; {011}	{100}; {010}; {001}
	0.360–0.585	0.585–0.904
(b) Structure refinement		
Reflections used,	2045	1413
$m$ ( $F \geq 4\sigma_F$ )		
No. of variables, $n$	325	294
Extinction parameter	9.2 (5) × 10 <sup>-6</sup>	1.2 (3) × 10 <sup>-6</sup>
Goodness of fit, $S$	2.333	1.288
$R$ , $wR$	0.0276, 0.0429	0.0365, 0.0421
$R$ for all data	0.0286	0.0613
Max. $\Delta/\sigma$	0.029	0.006
Max., min. $\rho$ in $\Delta F$ map (e $\text{\AA}^{-3}$ )	0.23, –0.24	0.26, –0.23

Unit-cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections with  $48.9 < 2\theta < 59.4^\circ$  for (1) and  $41.7 < 2\theta < 57.2^\circ$  for (2).

Enraf-Nonius CAD-4 diffractometer with a graphite monochromator was used. Data reduction was accomplished with the *SDP-Plus* software (Frenz, 1985). Crystal and instrument stability were monitored by remeasurement of 3 check reflections. For (1), 13 $\bar{6}$ , 251 and 32 $\bar{2}$  were measured every 2 h. For (2), 13 $\bar{7}$ , 153 and 245 were measured every hour. A linear fit of the intensities of these reflections was used to correct the data.

Function minimized was  $\sum w(F_o - F_c)^2$ , where  $w^{-1} = (\sigma_F^2 + 0.0002F^2)$  for (1) and  $w^{-1} = (\sigma_F^2 + 0.0004F^2)$  for (2).  $\sigma_F = F\sigma_I/2I$ ;  $\sigma_I = [N_{pk} + N_{bg1} + N_{bg2}]^{1/2}$ .

difference map. All H-atom positions were located in a difference map as peaks of density 0.28–0.57 e  $\text{\AA}^{-3}$  at  $R = 0.074$ . All positional and thermal parameters were refined (only H atoms were treated isotropically). Both structures were refined with *SHELX76* (Sheldrick, 1976). Scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974) except those of H which were taken from Stewart, Davidson & Simpson (1965). Data were reduced with *SDP-Plus* (Frenz, 1985); least-squares planes program from Cordes (1983); figures were drawn with *ORTEPII* (Johnson, 1976).\*

\* Tables of anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H atoms, torsion angles, least-squares planes and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51818 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional and equivalent isotropic thermal parameters for non-hydrogen atoms in (1)

	x	y	z	U <sub>eq</sub> (Å <sup>2</sup> )*
Cl(1)	-0.0338 (2)	0.99324 (13)	0.64078 (12)	0.0585 (3)
Cl(2)	0.2991 (3)	0.7850 (2)	1.00902 (11)	0.0592 (3)
Cl(3)	0.9698	0.4126	0.7979	0.0569 (3)
N(1)	0.3120 (6)	0.8006 (3)	0.6131 (2)	0.0378 (7)
C(2)	0.1665 (6)	0.8742 (3)	0.6926 (3)	0.0398 (9)
N(3)	0.1493 (6)	0.8714 (3)	0.8119 (3)	0.0436 (8)
C(4)	0.3041 (6)	0.7863 (4)	0.8555 (3)	0.0402 (9)
N(5)	0.6254 (6)	0.6044 (3)	0.8280 (3)	0.0411 (8)
C(6)	0.7649 (6)	0.5298 (4)	0.7456 (3)	0.0393 (9)
N(7)	0.7764 (6)	0.5269 (3)	0.6252 (2)	0.0374 (8)
C(8)	0.6242 (6)	0.6141 (3)	0.5783 (3)	0.0338 (8)
C(9)	0.4618 (6)	0.7087 (3)	0.6590 (3)	0.0328 (8)
C(10)	0.4722 (6)	0.6962 (3)	0.7815 (3)	0.0364 (8)
N(11)	0.6136 (6)	0.6130 (3)	0.4586 (2)	0.0397 (8)
C(1')	0.7571 (6)	0.5165 (3)	0.3692 (3)	0.0353 (8)
C(2')	0.5897 (5)	0.4512 (3)	0.2385 (2)	0.0315 (8)
C(3')	0.7407 (6)	0.5125 (3)	0.1489 (3)	0.0330 (8)
C(4')	0.9363 (6)	0.6368 (3)	0.2350 (3)	0.0374 (9)
C(5')	0.8434 (7)	0.7915 (4)	0.2564 (4)	0.0485 (11)
C(6')	0.7085 (6)	0.2575 (3)	0.0798 (3)	0.0386 (9)
C(7')	0.8686 (10)	0.1275 (4)	0.0755 (5)	0.0624 (15)
C(8')	0.4942 (10)	0.2281 (6)	-0.0316 (4)	0.0621 (14)
O(2')	0.5961 (5)	0.2927 (2)	0.1964 (2)	0.0416 (7)
O(3')	0.8775 (4)	0.3881 (2)	0.0920 (2)	0.0387 (6)
O(4')	0.9863 (4)	0.5949 (3)	0.3501 (2)	0.0422 (7)
O(5')	0.5801 (5)	0.7867 (3)	0.2851 (2)	0.0436 (7)
O(12)	0.4705 (8)	1.0757 (3)	0.3276 (3)	0.0720 (13)
C(13)	0.4412 (9)	1.1542 (5)	0.4543 (5)	0.064 (2)
C(14)	0.2206 (11)	1.2484 (6)	0.4581 (6)	0.075 (2)

\*  $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ , where  $A_{ij}$  is the dot product of the  $i$ th and  $j$ th direct-space unit-cell vectors.

Table 3. Positional and equivalent isotropic thermal parameters for non-hydrogen atoms in (2)

	x	y	z	U <sub>eq</sub> (Å <sup>2</sup> )*
Cl	1.0144 (2)	0.8714	0.20942 (7)	0.0428 (3)
N(1)	0.1107 (8)	0.5372 (4)	0.0769 (2)	0.0346 (11)
C(2)	-0.0031 (11)	0.5653 (5)	-0.0018 (3)	0.0375 (13)
N(3)	0.0635 (8)	0.6605 (4)	-0.0559 (2)	0.0344 (11)
C(4)	0.2773 (8)	0.7373 (4)	-0.0267 (2)	0.0304 (12)
N(5)	0.6284 (8)	0.8009 (4)	0.0897 (2)	0.0316 (10)
C(6)	0.7421 (9)	0.7705 (5)	0.1679 (3)	0.0322 (12)
N(7)	0.6883 (7)	0.6737 (4)	0.2207 (2)	0.0297 (10)
C(8)	0.4794 (9)	0.5965 (4)	0.1919 (2)	0.0278 (12)
C(9)	0.3263 (9)	0.6185 (4)	0.1075 (2)	0.0290 (12)
C(10)	0.4167 (8)	0.7201 (4)	0.0597 (3)	0.0294 (12)
N(11)	0.4094 (8)	0.4951 (4)	0.2407 (2)	0.0301 (10)
N(12)	0.3682 (9)	0.8265 (4)	-0.0766 (2)	0.0375 (13)
C(1')	0.6017 (8)	0.4363 (4)	0.3090 (2)	0.0262 (11)
C(2')	0.4647 (8)	0.3635 (5)	0.3773 (2)	0.0272 (11)
C(3')	0.6088 (8)	0.2279 (4)	0.3858 (2)	0.0287 (11)
C(4')	0.7098 (8)	0.2064 (4)	0.3022 (2)	0.0285 (12)
C(5')	0.5161 (9)	0.1296 (4)	0.2363 (3)	0.0340 (13)
O(2')	0.5290 (7)	0.4230 (3)	0.4599 (2)	0.0352 (9)
O(3')	0.8289 (6)	0.2554 (3)	0.4528 (2)	0.0331 (9)
O(4')	0.7622 (6)	0.3396 (3)	0.2725 (2)	0.0301 (9)
O(5')	0.2672 (6)	0.2005 (4)	0.2216 (2)	0.0408 (11)
C(6')	0.7306 (8)	0.3433 (4)	0.5120 (2)	0.0311 (12)
C(7')	0.9535 (12)	0.4338 (7)	0.5524 (4)	0.053 (2)
C(8')	0.6060 (14)	0.2646 (6)	0.5775 (3)	0.048 (2)

\*  $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ , where  $A_{ij}$  is the dot product of the  $i$ th and  $j$ th direct-space unit-cell vectors.

Table 4. Bond lengths (Å) in (1) and (2)

	(1)	(2)
N(1)—C(2)	1.305 (4)	1.308 (6)
C(2)—N(3)	1.347 (5)	1.354 (6)
N(3)—C(4)	1.307 (5)	1.343 (6)
N(5)—C(6)	1.307 (4)	1.308 (5)
C(6)—N(7)	1.339 (4)	1.330 (6)
N(7)—C(8)	1.332 (4)	1.326 (5)
C(9)—C(8)	1.456 (4)	1.441 (5)
C(9)—N(1)	1.352 (4)	1.381 (6)
C(10)—C(4)	1.419 (4)	1.437 (5)
C(10)—N(5)	1.365 (5)	1.362 (6)
C(10)—C(9)	1.394 (4)	1.383 (6)
N(11)—C(8)	1.322 (4)	1.351 (6)
Cl(1)—C(2)	1.732 (4)	—
Cl(2)[N(12)]—C(4)	1.713 (4)	1.317 (6)
Cl(3)[Cl]—C(6)	1.735 (4)	1.744 (4)
C(1')—N(11)	1.453 (4)	1.451 (5)
C(2')—C(1')	1.542 (4)	1.547 (6)
O(4')—C(1')	1.419 (4)	1.437 (5)
C(3')—C(2')	1.537 (4)	1.533 (6)
O(2')—C(2')	1.427 (3)	1.418 (5)
C(4')—C(3')	1.512 (4)	1.498 (6)
O(3')—C(3')	1.432 (4)	1.430 (5)
C(5')—C(4')	1.516 (5)	1.515 (6)
O(4')—C(4')	1.438 (4)	1.449 (5)
O(5')—C(5')	1.432 (5)	1.427 (6)
C(7')—C(6')	1.505 (6)	1.503 (7)
C(8')—C(6')	1.510 (5)	1.509 (8)
O(2')—C(6')	1.445 (4)	1.441 (5)
O(3')—C(6')	1.417 (4)	1.425 (5)
C(14)—C(13)	1.480 (8)	—
C(13)—O(12)	1.427 (6)	—

sponding bond angles in (1) and (2) are within 3 e.s.d.'s except those involving C(4), in which the differences result from the aforementioned conjugation of the amino group with the ring in (2).

**Discussion.** The atomic coordinates are listed in Tables 2 and 3; bond lengths and bond angles are listed in Tables 4 and 5, respectively. The atom labeling is shown in Figs. 1 and 2 for compounds (1) and (2), respectively.

*The aglycon moiety.* As observed in ARPP (3) (Narayanan & Berman, 1975), the two fused pyrimidine rings in each structure are essentially planar (r.m.s. deviation less than 0.012 Å for each ring) and are only slightly less coplanar than found in ARPP [dihedral angles: 1.58 (11)° for (1); 2.09 (13)° for (2); and 0.59° for (3)]. In (1), the C(4)—Cl(2) bond length is significantly shorter than the C(2)—Cl(1) and C(6)—Cl(3) bond lengths. The C(4) position of (1) is most susceptible to nucleophilic substitution (Sanghvi *et al.*, 1989). The C(6)—Cl bond in (2) is slightly longer than all the C—Cl bonds in (1). The pyrimidopyrimidine ring systems in (1), (2) and (3) as well as in 2,6-bis(diethanolamino)-4,8-dipiperidinopyrimido[5,4-*d*]pyrimidine (Luger, 1982) have a bonding pattern of alternating long and short bonds as sketched in structures (1), (2) and (3) above. Despite this similarity, there are some drastic differences in certain bond lengths; hence, C(2)—N(3) and C(6)—N(7) in (1) and (2) are substantially shorter than the corresponding bonds in (3). The amino functions in each are conjugated with the heterocycle, distorting in various degrees the double-bond character of the adjacent C—N bonds. Corre-

Table 5. Bond angles ( $^{\circ}$ ) in (1) and (2)

	(1)	(2)
C(9)–N(1)–C(2)	114.0 (3)	114.0 (4)
N(1)–C(2)–Cl(1)	117.0 (3)	–
N(1)–C(2)–N(3)	128.9 (3)	129.0 (4)
Cl(1)–C(2)–N(3)	114.2 (3)	–
C(2)–N(3)–C(4)	115.8 (3)	116.9 (3)
N(3)–C(4)–C(10)	123.0 (3)	120.1 (4)
Cl(2)[N(12)]–C(4)–N(3)	117.5 (3)	121.3 (4)
C(10)–C(4)–Cl(2)[N(12)]	119.5 (3)	118.7 (4)
C(10)–N(5)–C(6)	112.8 (3)	112.9 (4)
N(5)–C(6)–Cl(3)[Cl]	115.8 (3)	114.8 (3)
N(5)–C(6)–N(7)	130.9 (3)	130.8 (4)
Cl(3)[Cl]–C(6)–N(7)	113.3 (2)	114.5 (3)
C(6)–N(7)–C(8)	116.8 (3)	116.1 (3)
N(7)–C(8)–C(9)	119.5 (3)	120.4 (4)
C(9)–C(8)–N(11)	119.6 (3)	119.1 (4)
N(11)–C(8)–N(7)	120.9 (3)	120.5 (3)
C(10)–C(9)–C(8)	115.9 (3)	115.9 (4)
C(10)–C(9)–N(1)	124.2 (3)	123.5 (3)
C(8)–C(9)–N(1)	119.9 (3)	120.6 (4)
N(5)–C(10)–C(4)	121.8 (3)	119.6 (4)
N(5)–C(10)–C(9)	124.1 (3)	123.8 (3)
C(4)–C(10)–C(9)	114.1 (3)	116.6 (4)
C(1')–N(11)–C(8)	123.5 (3)	121.3 (4)
C(2')–C(1')–O(4')	106.8 (2)	107.6 (3)
C(2')–C(1')–N(11)	111.7 (3)	112.6 (3)
O(4')–C(1')–N(11)	111.8 (2)	109.3 (3)
C(3')–C(2')–O(2')	105.0 (2)	104.7 (3)
C(3')–C(2')–C(1')	104.3 (2)	102.7 (3)
O(2')–C(2')–C(1')	110.1 (2)	112.0 (3)
C(4')–C(3')–O(3')	109.2 (2)	109.9 (3)
C(4')–C(3')–C(2')	104.9 (2)	105.8 (3)
O(3')–C(3')–C(2')	102.3 (2)	101.4 (3)
C(5')–C(4')–O(4')	112.7 (3)	112.1 (3)
C(5')–C(4')–C(3')	113.9 (3)	113.6 (4)
O(4')–C(4')–C(3')	104.6 (3)	104.8 (3)
O(5')–C(5')–C(4')	109.4 (3)	108.3 (4)
C(7')–C(6')–C(8')	113.3 (3)	113.0 (4)
C(7')–C(6')–O(2')	108.5 (3)	108.7 (4)
C(8')–C(6')–O(2')	110.0 (3)	110.1 (4)
C(8')–C(6')–O(3')	111.7 (3)	110.4 (4)
O(2')–C(6')–O(3')	103.4 (2)	104.9 (3)
O(3')–C(6')–C(7')	109.4 (3)	109.4 (4)
C(1')–O(4')–C(4')	109.7 (2)	110.3 (3)
C(2')–O(2')–C(6')	107.8 (2)	109.0 (3)
C(3')–O(3')–C(6')	106.2 (2)	106.8 (3)
C(14)–C(13)–O(12)	111.6 (4)	–

*The sugar moiety.* The  $\beta$ -anomeric configuration was confirmed for both (1) and (2). The conformational parameters [according to Altona & Sundaralingam (1972)] of the ribose moieties are given in Table 6. The conformations in (1) and (2) are very distinct in comparison to ARPP, which is to be expected in light of the isopropylidene blocking groups and the N(11)···O(5') intramolecular hydrogen bonds in the former. The pseudorotation angle of (1) is very similar to those observed in the compounds 6,5'-anhydro-5-bromo-6-hydroxy-2',3'-*O*-isopropylidene-tubercidin (Asahi, Anzai, Suzuki & Iwasaki, 1973) and 2,5'-anhydro-2',3'-*O*-isopropylidene-cyclouridine (Manor, Saenger,

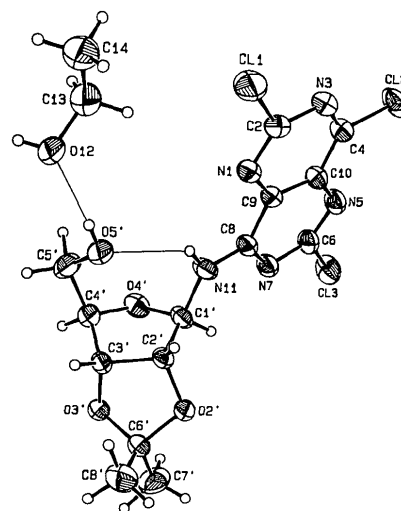


Fig. 1. Thermal-ellipsoid plot of (1) illustrating atom labeling and intramolecular hydrogen bonding. The ellipsoids are drawn at the 50% probability level.

Table 6. Sugar conformational parameters in (1), (2) and (3)

	(1)	(2)	(3)	
<b>Sugar conformation</b>				
$\tau_0(^{\circ})$	C(4')–O(4')–C(1')–C(2')	22.9 (3)	8.4 (4)	–44.0
$\tau_1(^{\circ})$	O(4')–C(1')–C(2')–C(3')	–4.3 (3)	10.5 (4)	27.1
$\tau_2(^{\circ})$	C(1')–C(2')–C(3')–C(4')	–14.4 (3)	–24.9 (4)	1.1
$\tau_3(^{\circ})$	C(2')–C(3')–C(4')–O(4')	27.9 (3)	30.5 (4)	–25.4
$\tau_4(^{\circ})$	C(3')–C(4')–O(4')–C(1')	–32.3 (3)	–24.4 (4)	43.9
$\tau_m(^{\circ})$	Amplitude of pucker	31.8	30.2	45.0
$P(^{\circ})$	Pseudorotation angle	243.1	214.6	88.6
	Conformation	$C_{4'}$ -endo	$C_{3'}$ -exo	$O_{1'}$ -endo
		$^4T_0$	$^3T$	$O_E$
<b>Glycosidic linkage</b>				
$\chi_{CN}^{\circ}$	O(4')–C(1')–N(11)–H(11)	66. (6)	66. (4)	95. (7)
$\chi'_{CN}^{\circ}$	O(4')–C(1')–N(11)–C(8)	–101.2 (4)	–82.3 (4)	–99.2 (5)
$\chi''_{CN}^{\circ}$	C(1')–N(11)–C(8)–N(7)	1.7 (5)	–22.2 (6)	14.0 (7)
<b>Side chain conformation</b>				
$\varphi_{O_5}^{\circ}$	O(4')–C(4')–C(5')–O(5')	–72.2 (4)	–61.1 (5)	–174.7
$\varphi_{C_6}^{\circ}$	C(3')–C(4')–C(5')–O(5')	46.8 (4)	57.4 (5)	–58.3

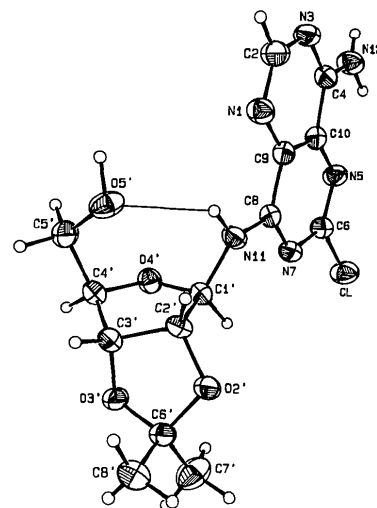


Fig. 2. Thermal-ellipsoid plot of (2) illustrating atom labeling and intramolecular hydrogen bonding. The ellipsoids are drawn at the 50% probability level.

Davies, Jankowski & Rabczenko, 1974) in which the 5'-anhydro linkage with the aglycon is similar in effect to the intramolecular hydrogen bonding found in the present study. The side chains of both (1) and (2) are *gg*, the juxtaposition required for the hydrogen bonding to occur. The bond lengths in the ribose moieties of (1) and (2) are equal within 3 e.s.d.'s except for O(4')—C(1'). The dioxolane rings are C<sub>6'</sub>-*endo*-O<sub>3'</sub>-*exo* and O<sub>3'</sub>-*exo*-C<sub>3'</sub>-*endo* for (1) and (2), respectively, similar to the conformations observed in the 5'-anhydro structures (Asahi *et al.*, 1973; Manor *et al.*, 1974).

**Packing.** The hydrogen bonding in the two structures is detailed in Table 7 and illustrated in the packing diagrams of Figs. 3 and 4. The N(11)···O(5') intramolecular hydrogen bonds in each structure are not

particularly strong in light of their geometrical parameters. Molecules of (1) are linked along the *b* axis through moderately strong intermolecular hydrogen bonds from O(5') to the ethanol solvate and from the ethanol to the ether O atom O(2'). Compound (2) crystallizes in hydrogen-bonded layers parallel to the *ab* plane with the hydrophobic isopropylidene groups above and below the layers. Beside the more common hydrogen bond O(5')···N(3), the amino group is involved in less frequently observed interactions; *i.e.*, H(12*B*) weakly interacts with the furan O atom O(4') and H(12*A*) appears to interact with the  $\pi$  cloud around N(1) of the pyrimidopyrimidine system. The H(12*A*)···N(1) vector is approximately perpendicular to the ring plane. The sum of the van der Waals radii of H (1.2 Å) and the half-thickness of an aromatic ring (1.7 Å) is 2.9 Å (Pauling, 1960), which is considerably longer than the observed H(12*A*)···plane distance of 2.40 (6) Å.

Table 7. Hydrogen bonding in (1) and (2)

D—H···A	Symmetry of A relative to D	d(D···A) (Å)	d(H···A) (Å)	$\angle$ (D—H···A) (°)
Compound (1)				
N(11)—H(11)···O(5')	<i>x,y,z</i>	2.841 (4)	2.25 (7)	133. (6)
O(5')—H(O5')···O(12)	<i>x,y,z</i>	2.716 (4)	2.00 (5)	176. (6)
O(12)—H(O12)···O(2')	<i>x,1+y,z</i>	2.887 (4)	2.11 (6)	167. (6)
Compound (2)				
N(11)—H(11)···O(5')	<i>x,y,z</i>	3.034 (5)	2.37 (5)	134. (4)
O(5')—H(O5')···N(3)	$-x,y-0.5,-z$	2.888 (5)	1.90 (6)	167. (5)
N(12)—H(12 <i>B</i> )···O(4')	$1-x,y+0.5,-z$	3.048 (4)	2.32 (4)	165. (5)
N(12)—H(12 <i>A</i> )···N(1)	$1-x,y+0.5,-z$	3.204 (6)	2.50 (6)	151. (4)
N(12)—H(12 <i>A</i> )···plane	$1-x,y+0.5,-z$	3.112 (4)	2.40 (6)	

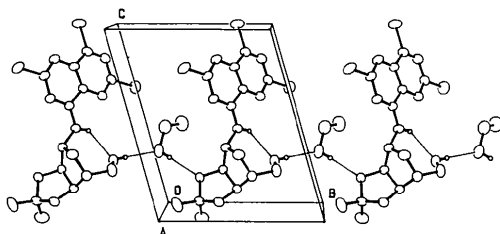


Fig. 3. Crystal packing diagram of (1), viewed along the *a* axis, illustrating the hydrogen-bonding chain along the *b* axis.

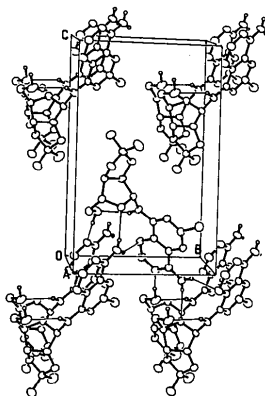


Fig. 4. Crystal packing diagram of (2), viewed along the *a* axis, illustrating the hydrogen-bonded layer parallel to the *ab* plane and the hydrophobic region between the layers.

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