faiblesse des forces d'interactions intermoléculaires contraste donc avec la grande rigidité des rubans polymères assurée par la présence de liaisons hydrogène intramoléculaires fortes.

Nous remercions très vivement le Dr Pérez pour nous avoir communiqué le programme *CRYSP*, et le Dr Patel pour nous avoir fourni le composé.

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Structure of Clitocine at 173 K

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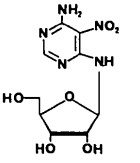
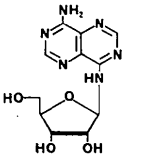
Abstract. 5-Nitro-4-(β-D-ribofuranosylamino)pyrimidine-6-amine, $C_9H_{13}N_5O_6$, $M_r = 287{\cdot}23$, monoclinic, $C2$, $a = 8{\cdot}162\,(2)$, $b = 6{\cdot}4803\,(15)$, $c = 21{\cdot}680\,(4)$ Å, $\beta = 90{\cdot}94\,(2)°$, $V = 1146{\cdot}5\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}664$ g cm^{-3}, Cu $K\alpha$ ($\lambda = 1{\cdot}54178$ Å), $\mu = 11{\cdot}704$ cm^{-1}, $F(000) = 600$, $T = 173$ K, $R = 0{\cdot}0374$ for 2300 reflections ($F \geq 4\sigma_F$); at $T = 295$ K, $a = 8{\cdot}210\,(3)$, $b = 6{\cdot}523\,(2)$, $c = 21{\cdot}736\,(6)$ Å, $\beta = 91{\cdot}09\,(2)°$, $V = 1163{\cdot}9\,(6)$ Å^3 and $D_x = 1{\cdot}639$ g cm^{-3}. The non-sugar portion is planar with each O atom of the nitro group intramolecularly hydrogen bonded to the H atoms of the two adjacent amino functions. The base is in the *anti* conformation, χ(O1′–C1′–N4–HN4) = 80· (2)°. The sugar moiety is disordered around the twofold axis. Conformer I is $C_{1'}$-*exo* of form $_1T^2$, $P = 134{\cdot}3°$ and $\tau_m = 42{\cdot}5°$; conformer II is $O_{4'}$-*endo*-$C_{1'}$-*exo* of form ^0_1T, $P = 108{\cdot}9°$ and $\tau_m = 38{\cdot}9°$.

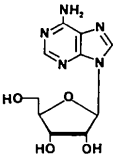
Introduction. Clitocine (1) was recently isolated from the mushroom *Clitocybe inversa*. The compound exhibits strong insecticidal activity against the pink bollworm *Pectinophora gossypiella*. Based on the NMR spectrum, Kubo, Kim, Wood & Naoki (1986) suggested that there exists an intramolecular hydrogen bond between the 4-amino hydrogen and the nitro group. The total synthesis of clitocine was initiated to investigate its antiparasitic, antitumor and antiviral



(1)



(2)



(3)

activity. Clitocine has been shown to be both a substrate and an inhibitor of adenosine kinase (Moss *et al.*, 1988). The exocyclic amino nucleoside, 4-amino-8-(β-D-ribofuranosylamino)pyrimido[5,4-*d*]pyrimidine (2), reported by Berman, Rousseau, Mancuso, Kreishman & Robins (1973), has been shown to be a substrate for adenosine kinase. Thus, the crystal

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Table 1. *Summary of data collection and structure solution for* (1)

(*A*) Data collection (173 K)*

Mode	ω–2θ scan
Scan range (°)	$1{\cdot}00 + 0{\cdot}15\tan\theta$
Background	Scan 0·25 times scan range before and after scan
Scan rate (° min $^{-1}$)	2·40–4·12
Exposure time (h)	32·5
Stability correction range on I:	0·988–1·000
2θ range (°)	3·0–152·0
Range in hkl, min.	0,−8,−27
max.	10,8,27
Total reflections measured, unique	2588, 2351
R_{int}	0·0309
Crystal dimensions (mm)	0·40 × 0·40 × 0·33 hexagon × 0·04 thick
Crystal volume (mm^3)	0·00575
Crystal shape	Thin hexagonal plate
Crystal faces	{1,1,0}; {0,1,0}; {0,0,1}
Transmission factor range	0·678–0·954

(*B*) Structure refinement†

Reflections used, m ($F \geq 4\sigma_F$)	2300
No. of variables, n	264
Extinction parameter	5·8 (16) × 10^{-7}
Goodness of fit, S	2·15
R, wR	0·0374, 0·0519
R for all data	0·0386
Max. shift/e.s.d.	0·03
Max., min. density in ΔF map (e Å^{-3})	0·60, −0·34

* Unit-cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections with $45{\cdot}5 < 2\theta < 58{\cdot}5°$. Enraf–Nonius CAD-4 diffractometer with a graphite monochromator was used. Intensities were corrected for Lorentz and polarization effects, absorption and decay. Crystal and instrument stability were monitored by re-measurement of 3 check reflections (1,1,10, 13$\bar{9}$, $\bar{3}$18) 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 $w^{-1} = (\sigma_F^2 + 0{\cdot}0004F^2)$. $\sigma_F = F\sigma_I/2I$; $\sigma_I = [N_{pk} + N_{bg1} + N_{bg2}]^{1/2}$.

structure of clitocine was investigated in order to compare it with adenosine (3) and the pyrimidopyrimidine (2) and to investigate its intramolecular hydrogen bonding.

Experimental. The title compound was synthesized by a direct glycosylation of 4,6-diamino-5-nitropyrimidine followed by deblocking (Moss *et al.*, 1988). Clitocine crystallizes from absolute ethanol as nucleated clusters of very thin colorless plates (see Table 1 for summary of data collection and refinement). The structure was solved by direct methods (*MULTAN*82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) with data collected at room temperature. Following isotropic refinement of the non-hydrogen atoms, it was obvious that O3′ and O5′ are disordered. The structure refined to $R = 0{\cdot}051$ with these data. A set of data was collected at 173 K with which the disorder was resolved. The refinement was accomplished with a full-matrix least-squares routine (*SHELX*76; Sheldrick, 1976). All non-hydrogen atoms were refined anisotropically. The disordered atoms, C3′, C5′, O3′ and O5′ (referred to as conformers I and II with unique atoms of conformer II designated by *D* appended to the atom label) were constrained in the following ways: equivalent pairs of distances were equated [*e.g.* d(C2′–C3′)=d(C2′–C3′*D*); d(C3′–O3′)=d(C3′*D*–O3′*D*)]; U_{11}, U_{22} and U_{33} were equated for pairs C3′ and C3′*D* and for pairs C5′ and C5′*D*. The site occupation refined to 0·504:0·496 (I:II) before H atoms were added and was subsequently fixed at 0·50 for all disordered atoms for the remainder of the refinement. All H atoms on non-disordered non-hydrogen atoms were taken from a difference map (0·45–0·82 e Å^{-3}) and refined isotropically. Although peaks at positions for H atoms on C3′ and C5′ were observed in the ΔF map, positions for these H atoms were idealized. The temperature factors were equated but varied for H5′ atoms. Peaks (0·29–0·33 e Å^{-3}) near the disordered O atoms suggested positions for H atoms on these atoms although the geometry was not ideal. In order to establish directionality to the hydrogen-bonding scheme, these positions were input at 50% occupancy and refined under the geometrical constraints: d(O–H) $\simeq$0·90 (2) Å for all 3′- and 5′-hydroxy hydrogens; d(C···H) $\simeq$1·92 (2) Å for 3′-hydroxy and $\simeq$1·96 (2) Å for 5′-hydroxy hydrogens. 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 *ORTEP*II (Johnson, 1976).

Discussion. The atomic coordinates are listed in Table 2 and bond lengths and bond angles are given in Table 3.* The atom labeling is detailed in Fig. 1.

The pyrimidine ring and functional groups. The nitro group is hydrogen bonded to the 4-amino H atom, HN4, postulated by Kubo *et al.* (1986) and to the 6-amino H atom, HN61 (Table 4). As a result, the entire aglycon (non-sugar) moiety resembles a planar tricyclic ring system. Although there are no 2,4-diamino-5-nitropyrimidine structures reported, similar intramolecular hydrogen bonding has been observed in 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965), 1,3-diamino-2,4,6-trinitrobenzene (Holden, 1967) and its 5-hydroxy (Bhattacharjee & Ammon, 1981), 5-fluoro (Ammon, Bhattacharjee & Holden, 1982), 5-carboxamide (Ammon & Bhattacharjee, 1982) and 5-carboxylic acid (Ammon & Prasad, 1985)

* Lists of anisotropic thermal 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 44774 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional and thermal parameters for atoms in clitocine*

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

	x	y	z	U_{eq}
N1	0·0002 (2)	0·290586	0·41836 (7)	0·0222 (4)
C2	−0·0635 (2)	0·3515 (3)	0·36501 (8)	0·0226 (5)
N3	0·0122 (2)	0·4149 (3)	0·31462 (6)	0·0233 (4)
C4	0·1782 (2)	0·4173 (4)	0·31670 (7)	0·0225 (4)
C5	0·2628 (2)	0·3471 (4)	0·37145 (8)	0·0211 (4)
C6	0·1674 (2)	0·2901 (3)	0·42312 (8)	0·0210 (4)
N4	0·2543 (2)	0·4905 (4)	0·26705 (7)	0·0295 (5)
N5	0·4366 (2)	0·3452 (3)	0·37512 (7)	0·0226 (4)
O5*A*	0·5186 (2)	0·4002 (3)	0·33015 (6)	0·0275 (4)
O5*B*	0·5065 (2)	0·2869 (3)	0·42345 (6)	0·0291 (4)
N6	0·2263 (2)	0·2370 (4)	0·47802 (7)	0·0268 (4)
C1′	0·1718 (2)	0·5942 (4)	0·21636 (8)	0·0270 (5)
C2′	0·2783 (2)	0·7648 (4)	0·18959 (9)	0·0315 (5)
C3′	0·1910 (5)	0·7953 (5)	0·12646 (14)	0·0314 (8)
C4′	0·1205 (2)	0·5797 (4)	0·11259 (9)	0·0296 (5)
C5′	0·189 (2)	0·480 (2)	0·0553 (6)	0·0495 (14)
O4′	0·1451 (2)	0·4553 (3)	0·16685 (6)	0·0321 (4)
O2′	0·2701 (2)	0·9509 (4)	0·22179 (7)	0·0381 (4)
O3′	0·0541 (5)	0·9329 (7)	0·1249 (2)	0·0407 (11)
O5′	0·1468 (6)	0·2576 (6)	0·0547 (2)	0·0442 (12)
C3′*D*	0·2234 (5)	0·7769 (5)	0·12113 (13)	0·0316 (8)
C5′*D*	0·189 (2)	0·449 (2)	0·0612 (6)	0·0492 (14)
O3′*D*	0·1346 (6)	0·9670 (7)	0·1186 (2)	0·0481 (13)
O5′*D*	0·0647 (5)	0·2964 (7)	0·0404 (2)	0·0430 (11)
H2	−0·175 (4)	0·359 (5)	0·3648 (13)	0·046 (8)
HN4	0·364 (4)	0·468 (5)	0·2669 (11)	0·040 (7)
HN61	0·329 (5)	0·246 (7)	0·485 (2)	0·063 (10)
HN62	0·152 (3)	0·237 (4)	0·5082 (11)	0·021 (5)
H1′	0·077 (3)	0·652 (4)	0·2263 (10)	0·024 (6)
H2′	0·394 (3)	0·708 (4)	0·1853 (11)	0·033 (7)
H3′	0·2716 (5)	0·8557 (5)	0·09730 (14)	0·040 (15)
H4′	−0·011 (4)	0·612 (5)	0·1095 (13)	0·046 (8)
H5′1	0·310 (2)	0·497 (2)	0·0552 (6)	0·058 (10)
H5′2	0·140 (2)	0·548 (2)	0·0178 (6)	0·058 (10)
HO2′	0·363 (6)	0·952 (8)	0·247 (2)	0·093 (14)
HO3′	0·056 (12)	1·00 (2)	0·089 (3)	0·179†
HO5′	0·16 (2)	0·212 (7)	0·015 (2)	0·179†
H3′*D*	0·3071 (5)	0·7797 (5)	0·08798 (13)	0·029 (12)
H5′*D*1	0·289 (2)	0·375 (2)	0·0767 (6)	0·058 (10)
H5′*D*2	0·219 (2)	0·540 (2)	0·0258 (6)	0·058 (10)
HO3′*D*	0·15 (2)	1·029 (12)	0·157 (3)	0·179†
HO5′*D*	0·088 (10)	0·171 (5)	0·057 (5)	0·179†

* U values for HO3′, HO5′, HO3′*D* and HO5′*D* were varied as a single parameter until the last cycles after which that value was fixed.

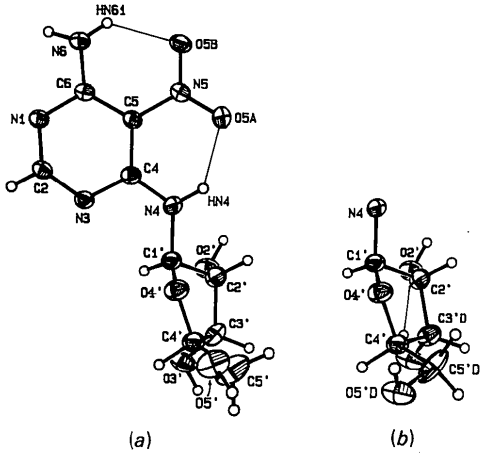

Fig. 1. Thermal ellipsoid plots of the two conformers [(*a*) conformer I; (*b*) conformer II] illustrating atom labeling and intramolecular hydrogen bonding. The aglycon is identical for the two conformers. The ellipsoids are drawn at the 50% probability level.

Table 3. *Bond lengths* (Å) *and bond angles* (°) *in clitocine*

1	2	3	1–2	1–2–3
C2	N1	C6	1·321 (2)	116·45 (14)
N3	C2	N1	1·329 (2)	129·1 (2)
C4	N3	C2	1·355 (2)	117·04 (15)
C5	C4	N4	1·437 (2)	123·6 (2)
C5	C4	N3		119·4 (2)
N4	C4	N3	1·339 (2)	117·0 (2)
C6	C5	N5	1·423 (2)	120·8 (2)
C6	C5	C4		118·1 (2)
N5	C5	C4	1·419 (2)	121·0 (2)
N6	C6	N1	1·322 (2)	114·6 (2)
N6	C6	C5		125·5 (2)
N1	C6	C5	1·367 (2)	119·87 (15)
C1′	N4	C4	1·445 (3)	124·0 (2)
O5*A*	N5	O5*B*	1·244 (2)	120·14 (14)
O5*A*	N5	C5		120·24 (15)
O5*B*	N5	C5	1·244 (2)	119·61 (15)
C2′	C1′	O4′	1·527 (3)	104·7 (2)
C2′	C1′	N4		111·4 (2)
O4′	C1′	N4	1·415 (3)	110·2 (2)
O2′	C2′	C1′	1·396 (3)	113·8 (2)
C4′	O4′	C1′	1·438 (3)	106·3 (2)
C3′	C2′	O2′	1·545 (4)	107·9 (2)
C3′*D*	C2′	O2′	1·545 (3)	114·9 (2)
C3′	C2′	C1′		99·9 (2)
C3′*D*	C2′	C1′		104·1 (2)
C4′	C3′	C2′	1·538 (4)	102·8 (2)
C4′	C3′*D*	C2′	1·539 (5)	102·8 (2)
C4′	C3′	O3′		105·8 (3)
C4′	C3′*D*	O3′*D*		115·8 (4)
O3′	C3′	C2′	1·429 (6)	116·8 (3)
O3′*D*	C3′*D*	C2′	1·429 (6)	102·7 (3)
C5′	C4′	O4′	1·514 (12)	112·6 (5)
C5′*D*	C4′	O4′	1·514 (13)	103·9 (5)
C5′	C4′	C3′		114·0 (5)
C5′*D*	C4′	C3′*D*		110·2 (5)
C3′	C4′	O4′		107·6 (2)
C3′*D*	C4′	O4′		107·4 (2)
O5′	C5′	C4′	1·482 (12)	109·4 (8)
O5′*D*	C5′*D*	C4′	1·482 (13)	109·7 (9)

Table 4. *Hydrogen bonding in* (1)

	D–H···*A*		Symmetry of *A* relative to *D*			*d*(*D*···*A*) (Å)	*d*(H···*A*) (Å)	*D*–H···*A* (°)
N4	HN4	O5*A*	*x*,	*y*,	*z*	2·602 (2)	1·90 (3)	133· (2)
N6	HN61	O5*B*	*x*,	*y*,	*z*	2·612 (2)	2·00 (4)	127· (3)
N6	HN61	O5*B*	1−*x*,	*y*,	1−*z*	3·045 (2)	2·39 (3)	134· (3)
N6	HN62	N1	−*x*,	*y*,	1−*z*	2·954 (2)	2·07 (2)	169· (2)
O2′	HO2′	N3	0·5+*x*,	0·5+*y*,	*z*	2·808 (2)	1·91 (4)	164· (4)
O3′	HO3′	O5′	*x*,	1+*y*,	*z*	2·712 (6)	1·95 (11)	140· (8)
O3′*D*	HO3′*D*	O2′	*x*,	*y*,	*z*	2·482 (5)	1·79 (7)	130· (7)
O5′*D*	HO5′*D*	O3′*D*	*x*,	*y*−1,	*z*	2·780 (6)	1·92 (5)	159· (6)
O5′	HO5′	O5′*D*	−*x*,	*y*,	−*z*	2·680 (6)	2·23 (6)	109· (6)
Other interoxygen distances								
Across twofold axis								
O5′*D*		O5′*D*	−*x*,	*y*,	−*z*	2·031 (6):	impossible!	
O5′		O5′	−*x*,	*y*,	−*z*	3·345 (6)		
Along chains parallel to *b* axis								
O3′		O5′*D*	*x*,	1+*y*,	*z*	2·986 (6)		
O3′*D*		O5′	*x*,	1+*y*,	*z*	2·341 (6):	very improbable!	

derivatives. The range of H···O distances is 1·70–2·28 Å.

The slightly pyramidal amino N atoms, N4 and N6, are conjugated with the pyrimidine ring as suggested by the short C–N distances [N4, 1·339 (2) and N6, 1·322 (2) Å] which are comparable to the shortest C–N distances in the pyrimidine ring. The range of C–N(amino) distances in the trinitrobenzenes is 1·310–1·327 Å.

The pyrimidine ring has a slight boat conformation; the largest deviation from planarity is 0·023 (2) Å for

Table 5. *Sugar conformational parameters in conformers* I *and* II *of* (1) *and in* (2)

Parameter		I	II	(2)
		Sugar conformation		
τ_0 (°)	C4′–O4′–C1′–C2′	−39·5 (2)	−39·5 (2)	−44·0
τ_1 (°)	O4′–C1′–C2′–C3′	43·0 (2)	31·9 (2)	27·1
τ_2 (°)	C1′–C2′–C3′–C4′	−29·7 (3)	−12·6 (3)	1·1
τ_3 (°)	C2′–C3′–C4′–O4′	8·1 (3)	−10·3 (3)	−25·4
τ_4 (°)	C3′–C4′–O4′–C1′	19·2 (2)	31·5 (2)	43·9
τ_m (°)	Amplitude of pucker	42·5	38·9	45·0
P (°)	Pseudorotation angle	134·3	108·9	88·6
Conformation		$C_{1'}$-*exo* $_1T^2$	$O_{1'}$-*endo*–$C_{1'}$-*exo* ^0_1T	$O_{4'}$-*endo* O_1
Glycosidic linkage				
χ (°)	O4′–C1′–N4–HN4	80· (2)	80· (2)	95· (7)
χ' (°)	O4′–C1′–N4–C4	−99·2 (2)	−99·2 (2)	−99·2 (5)
χ'' (°)	C1′–N4–C4–N3	9·8 (3)	9·8 (3)	14·0 (7)
Side-chain conformation				
$\omega_{(0)}$ (°)	O4′–C4′–C5′–O5′	42·8 (9)	82·4 (7)	−174·7
$\omega_{(t)}$ (°)	C3′–C4′–C5′–O5′	165·8 (6)	−162·8 (5)	−58·3

C5. The three unsubstituted pyrimidine rings contained in the Cambridge Structural Database (1987) have a maximum deviation of 0·004 Å. The rings in the trinitrobenzene (TNBZ) structures have maximum deviations ranging from 0·016 to 0·090 Å. The average C–C bond distance [1·430 (10) Å] is 0·057 Å greater than the average found in the pyrimidines; this lengthening effected by the nitro and amino substituents is seen in the TNBZ structures as well (average: 1·440 Å).

The C5–N5 bond [1·419 (2) Å] is substantially shorter than C–N bonds for aliphatic nitro groups [1·534 (18) Å average for 49 bonds in CSD] but is consistent with nitro groups flanked on both sides by amino groups in the trinitrobenzenes [average: 1·423 (8) Å]. The dihedral angle between the ring and the C5, N5, O5*A*, O5*B* plane in (1) is 0·34 (8)°. The range is 0·72–16·74° in these TNBZ structures; for nitro groups not flanked by two amino groups in these TNBZ compounds, the range is 4·75–53·47° with an average C–N(nitro) distance of 1·45 (3) Å. Despite the attractive forces of the intramolecular hydrogen bonding, steric effects may be present in (1). This is suggested by the bond angles, C5–C4–N4 [123·6 (2)°] and C5–C6–N6 [125·5 (2)°], which are larger than the expected 120°. Therefore, the increased double-bond character of the C5–N5 bond in (1) appears to result from coplanarity of the pyrimidine ring and the nitro group which is a consequence of the hydrogen bonding and minimal steric hindrance produced by subtle changes in bond lengths, angles and planarity.

The sugar moiety. The β-anomeric configuration is confirmed. The conformational parameters of the sugar are listed in Table 5. Neither conformer has a pseudorotation angle P that falls into the normal ranges for either β-purines or β-pyrimidines (Altona & Sundaralingam, 1972). The puckering of conformer II is midway between that of conformer I and the related nitrogen-bridged nucleoside, 4-amino-8-(β-D-ribofuranosylamino)pyrimido[5,4-*d*]pyrimidine, (2) (Narayanan & Berman, 1975). Thus, conformer II appears to have an O3′*D*···O2′ intramolecular hydrogen bond [d(O···O) = 2·482 (5) Å] similar to that observed in (2). The relationship of the base to the sugar as described by the torsion angles χ, χ' and χ'' in (1) and (2) is remarkably similar. As an adenosine analog, clitocine can be described in the crystalline state as having the *anti* conformation with HN4 replacing C8 of adenosine [torsion angle O4′–C1′–N4–HN4 = 80· (2)° in (1) compared with 9·9° in (3)].

Crystal packing and intermolecular hydrogen bonding. Crystal packing is illustrated in Fig. 2 with hydrogen bonds indicated by thin lines; hydrogen-bonding data are listed in Table 4. In addition to the HN61···O5*B* intramolecular hydrogen bond, HN61 is weakly bound to O5*B* related by twofold symmetry (1−x, y, 1−z) resulting in bifurcation, which is also observed in the TNBZ structures. The only intermolecular hydrogen bonding between the aglycon and the sugar occurs through HO2′···N3. The distances listed at the bottom of Table 4 suggest that certain conformer interactions are impossible: first, conformer II cannot hydrogen bond to conformer I *via* O3′*D*···O5′ interactions along the *b* axis; second, conformer II cannot interact with itself across the twofold axis. The first anomaly implies that no mixed-conformer interactions exist along the *b* axis. Thus, the crystal structure is composed of chains of a single conformer linked

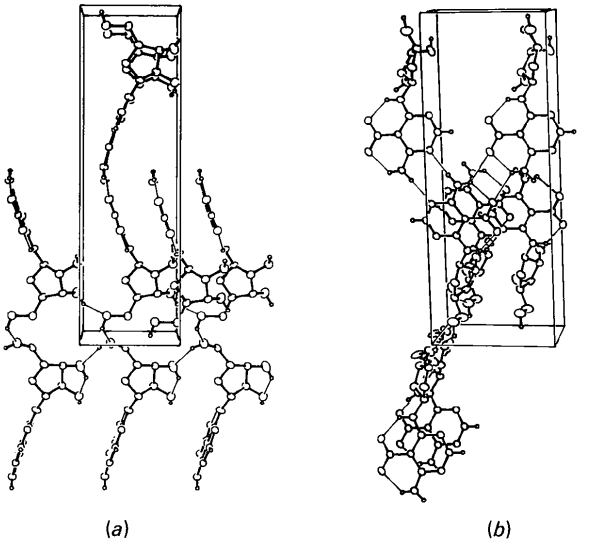

Fig. 2. Crystal packing diagrams illustrating the hydrogen-bonding networks through the crystal structure. (*a*) View of the cell along the *a* axis showing the conformer pairing across the *b* axis (twofold axis) through the sugar moieties. (*b*) View approximately along the *b* axis demonstrating the hydrogen bonding through the aglycon and the lone hydrogen-bonding interaction between sugar and base.

through an O3′···O5′ hydrogen-bonding scheme parallel to the *b* axis. The second anomaly implies that distinct conformers are paired across the twofold axis. The refined occupancy of 50% also confirms this pairing. The paired chains of conformers must be randomly distributed through the lattice, which is plausible since all other hydrogen-bonding interactions are between non-unique atoms of the two conformers. The nitro groups of one chain are intercalated between the pyrimidine rings (specifically, atoms N1, C2, N3) of the adjacent chain related by *C*-centering. This arrangement supports the planarity of the aglycon moiety. The nitro group is 2·973 (6) and 3·130 (6) Å from the sandwiching pyrimidine rings.

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Reaction of 3-Azidopropanol with Tris(dimethylamido)phosphorus and Structure of the Phosphazide Reaction Product

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Abstract. 3-{3-[Tris(dimethylamino)phosphoranylidene]-1-triazenyl}-1-propanol, $C_9H_{25}N_6OP$, M_r = 264·31, monoclinic, $P2_1/c$, a = 8·112 (1), b = 17·497 (1), c = 10·554 (1) Å, β = 104·87 (1)°, V = 1447·8 (2) Å^3, Z = 4, D_x = 1·21 g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 1·6 cm^{-1}, $F(000)$ = 576, T = 123 K, R = 0·046 for 2511 unique reflections. One of the dimethylamino N atoms deviates more from planarity than the other two and this P—N bond is significantly longer than the other P—N bonds. The azide bonds are not delocalized. This is apparently the first crystal structure of a phosphazide. The dimethylamino substituents on the P atom enhanced the stability of this phosphazide intermediate in a Staudinger reaction with 3-azidopropanol. In analogous reactions with phenyl or *n*-butyl substituents on the P atom only later phosphazo intermediates could be isolated.

Introduction. We have been interested in the Staudinger reaction (Gololobov, Zhmurova & Kasukhin, 1981) of 3-azidopropanol (1) with phosphines, and were successful in applying this reaction to the syntheses of azetidine (3) when triphenyl or tri-*n*-butylphosphine was used (Szmuszkovicz, Kane, Laurian, Chidester & Scahill, 1981). In the course of the above, we isolated the phosphazo intermediates (2*a*) and (2*b*) and reported

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