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Structure of a Pyrazolopyrimidine Nucleoside 5′-Phosphate

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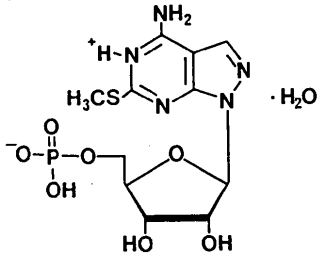
Abstract. 4-Amino-6-methylthio-1-β-D-ribofuranosylpyrazolo[3,4-*d*]pyrimidine 5′-monophosphate monohydrate, $C_{11}H_{16}N_5O_7PS.H_2O$, $M_r = 411{\cdot}33$, triclinic, $P\bar{1}$, $a = 4{\cdot}694\ (2)$, $b = 8{\cdot}025\ (4)$, $c = 11{\cdot}730\ (6)$ Å, $\alpha = 90{\cdot}92\ (4)$, $\beta = 99{\cdot}94\ (4)$, $\gamma = 104{\cdot}92\ (10)°$, $V = 419{\cdot}6\ (4)$ Å^3, $Z = 1$, $D_m = 1{\cdot}572\ (1)$, $D_x = 1{\cdot}628$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 3{\cdot}309$ cm^{-1}, $F(000) = 214$, $T = 295$ K, $R = 0{\cdot}0280$ for 2271 reflections ($F \geq 4\sigma_F$). The molecule exists as the zwitterion with one phosphate proton bound to N5 but hydrogen-bonded back to a phosphate O atom. The sugar ring is C3′-*exo* (conformation $_3T^2$) with angle of pseudorotation, P, of 187·1° and $\tau_m = -30{\cdot}84°$. The conformation around C4′–C5′ is tg [torsion angles: O4′, −179·4 (3); C3′, −60·7 (2)°]. The glycosidic torsion angle, χ = O4′–C1′–N1–N2, is 61·0 (3)°. Nine hydrogen bonds with $d(H\cdots A)$ ranging from 1·67 (5) to 2·48 (4) Å exist in the crystal structure. The base ring system is planar within 0·018 (2) Å. The $-SCH_3$ group is rotated out of this plane by 3·63 (13)°. The dihedral angle between the fused rings of the base is 0·92 (12)°.

Experimental. The synthesis of the title compound (1) was reported previously (Anderson, Revankar & Robins, 1987). Pale-yellow crystals were grown from an acetic acid solution (pH ≃ 4). The data collection and refinement are summarized in Table 1.



(1)

The P···S vector was taken from a sharpened Patterson map; four subsequent electron-density maps revealed the remaining non-H atoms including the solvent O atom. 19 H atoms were located in a difference map as peaks of 0·20–0·51 e Å^{-3} at $R = 0{\cdot}040$; three of these pertained to the disordered water molecule of solvation – one at full occupancy and the others at half occupancy. The half-occupied H atoms were fixed at positions taken from a subsequent map with the occupancies set to 0·5 and the isotropic thermal parameters set equal to each other; all other atomic positions were varied (except S which fixed the origin) as well as all anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. Refinement by full-matrix least squares was carried out with *SHELX*76 (Sheldrick, 1976). Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974) except those for H which were taken from Stewart, Davidson & Simpson (1965). Data were reduced with *SDP-Plus* (Frenz, 1985); least-squares

Table 1. *Crystallographic summary for* (1)

(*a*) Data collection[i,ii]	
Mode	ω scan
Scan range (°)	1·00
Background	scan 0·25 times scan range before and after scan
Scan rate (° min^{-1})	1·5–5·5
Exposure time (h)	25·9
Stability correction range on I	1·000–1·003
2θ range (°)	2·0–60·0
Range in *hkl*, min.	0, −11, −16
max.	6, 10, 16
Total reflections, measured, unique	2437, 2437
Crystal dimensions (mm)	0·41 × 0·28 × 0·13
Crystal volume (mm^3)	0·0179
Crystal faces	{010}; {101}; {001}
Transmission-factor range	0·859–0·961
(*b*) Structure refinement[iii]	
Reflections used ($F \geq 4\sigma_F$)	2271
No. of variables	302
Extinction parameter	4·7 (3) × 10^{-7}
Goodness of fit, S	1·242
R, wR	0·0280, 0·0363
R for all data	0·0332
Max. shift/e.s.d.	0·0054
Max., min. density in difference map (e Å^{-3})	0·33, −0·21

Notes: (i) Unit-cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections with 21·56 < 2θ < 29·46°. Crystal density was measured by flotation in aqueous $ZnCl_2$. (ii) Enraf–Nonius CAD-4 diffractometer with a graphite monochromator was used. Crystal and instrument stability were monitored by remeasurement of three check reflections ($1\bar{3}6$, $1\bar{5}4$, $3\bar{2}\bar{4}$) every hour. A linear fit of the intensities of these reflections was used to correct the data. (iii) Function minimized was $\sum w(F_o - F_c)^2$, where $w^{-1} = (\sigma_F^2 + 0{\cdot}0004F^2)$. $\sigma_F = F\sigma_I/2I$; $\sigma_I = (N_{pk} + N_{bg1} + N_{bg2})^{1/2}$.

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

	x	y	z	U_{eq}*(Å²)
S	0·35	1·2	0·78	0·0400 (2)
P	0·4850 (2)	0·15432 (11)	0·16705 (7)	0·0204 (2)
N1	0·7193 (5)	0·7401 (3)	0·5907 (2)	0·0245 (6)
N2	0·8729 (6)	0·6221 (3)	0·6305 (2)	0·0293 (6)
C3	0·9177 (7)	0·6406 (4)	0·7449 (2)	0·0319 (8)
C4	0·7683 (6)	0·8502 (3)	0·8866 (2)	0·0299 (7)
N5	0·6206 (6)	0·9757 (3)	0·8745 (2)	0·0322 (7)
C6	0·5124 (6)	1·0285 (3)	0·7687 (2)	0·0281 (7)
N7	0·5249 (5)	0·9604 (3)	0·6680 (2)	0·0268 (6)
C8	0·6666 (5)	0·8315 (3)	0·6788 (2)	0·0231 (6)
C9	0·7920 (6)	0·7710 (3)	0·7812 (2)	0·0269 (7)
N10	0·8807 (8)	0·8112 (4)	0·9898 (2)	0·0429 (9)
C11	0·2504 (11)	1·2426 (5)	0·6303 (3)	0·0479 (12)
C1′	0·6162 (5)	0·7472 (3)	0·4670 (2)	0·0201 (6)
C2′	0·8708 (5)	0·7787 (3)	0·3981 (2)	0·0235 (6)
C3′	0·7295 (6)	0·6671 (3)	0·2847 (2)	0·0241 (6)
C4′	0·5009 (5)	0·5185 (3)	0·3240 (2)	0·0229 (6)
C5′	0·6223 (6)	0·3642 (3)	0·3567 (2)	0·0270 (7)
O4′	0·4140 (4)	0·5857 (2)	0·4242 (2)	0·0274 (5)
O2′	0·9733 (6)	0·9567 (3)	0·3877 (2)	0·0389 (7)
O3′	0·5994 (6)	0·7561 (3)	0·1960 (2)	0·0384 (7)
O5′	0·7109 (4)	0·2996 (2)	0·2567 (2)	0·0262 (5)
O6′	0·3306 (5)	0·0041 (2)	0·2268 (2)	0·0303 (6)
O7′	0·2479 (5)	0·2434 (3)	0·1011 (2)	0·0318 (6)
O8′	0·6783 (4)	0·1192 (2)	0·0845 (2)	0·0284 (5)
OW	0·2231 (9)	0·5658 (4)	0·0021 (3)	0·0699 (13)

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

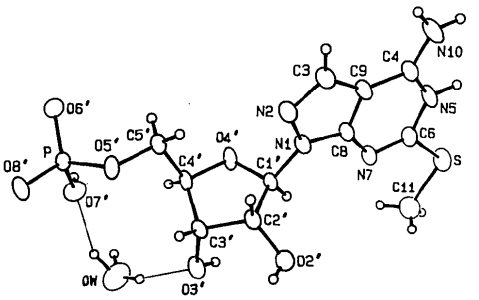

Fig. 1. Perspective drawing of (1) indicating atom labeling. Thermal ellipsoids are drawn at the 50% probability level.

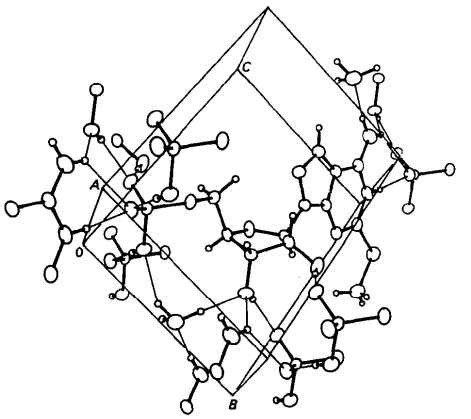

Fig. 2. Perspective drawing of the unit cell and hydrogen-bonding environment of the asymmetric unit with hydrogen bonds indicated by thin lines.

planes calculated with program *PLANES* from Cordes (1983); thermal-ellipsoid plots produced with *ORTEP*II (Johnson, 1976). Parameter, geometry and structure-factor amplitude tables were prepared with programs *FUER* and *LISTFC* (Larson, 1980).

Atomic coordinates are listed in Table 2;* bond lengths and bond angles are in Table 3. Fig. 1 is a perspective drawing of the molecule illustrating atom labeling; Fig. 2 illustrates the intermolecular hydrogen bonding which is detailed in Table 4.

Related literature. Sugar conformations in nucleosides and nucleotides were discussed by Altona & Sundaralingam (1972). A summary of nucleoside and nucleotide structures has been given by Jeffrey & Sundaralingam (1985).

* 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 44340 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond lengths* (Å) *and bond angles* (°) *in* (1)

1	2	3	1–2	1–2–3
C11	S	C6	1·800 (4)	101·8 (2)
O5′	P	O6′	1·590 (2)	111·78 (13)
O5′	P	O7′		105·64 (12)
O6′	P	O7′	1·491 (2)	109·79 (14)
O6′	P	O8′		116·85 (14)
O7′	P	O8′	1·575 (3)	108·88 (13)
O8′	P	O5′	1·506 (3)	103·18 (12)
N2	N1	C8	1·372 (4)	111·7 (2)
C8	N1	C1′	1·351 (4)	127·7 (2)
C1′	N1	N2	1·455 (3)	120·4 (2)
C3	N2	N1	1·322 (4)	105·9 (2)
C9	C3	N2	1·419 (5)	110·8 (3)
N5	C4	C9	1·358 (4)	114·9 (2)
C9	C4	N10	1·416 (4)	124·4 (3)
N10	C4	N5	1·311 (4)	120·7 (3)
C6	N5	C4	1·375 (3)	123·2 (2)
N7	C6	S	1·309 (4)	121·9 (2)
N7	C6	N5		125·0 (3)
S	C6	N5	1·750 (3)	113·1 (2)
C8	N7	C6	1·363 (4)	112·4 (2)
C9	C8	N1	1·395 (3)	106·5 (2)
C9	C8	N7		127·4 (2)
N1	C8	N7		126·0 (2)
C3	C9	C4		138·0 (2)
C3	C9	C8		105·1 (2)
C4	C9	C8		117·0 (3)
C2′	C1′	O4′	1·526 (4)	107·2 (2)
C2′	C1′	N1		112·8 (2)
O4′	C1′	N1	1·419 (3)	108·5 (2)
C3′	C2′	O2′	1·537 (3)	116·3 (2)
C3′	C2′	C1′		103·6 (2)
O2′	C2′	C1′	1·400 (3)	108·4 (2)
C4′	C3′	O3′	1·522 (4)	112·9 (2)
C4′	C3′	C2′		102·4 (2)
O3′	C3′	C2′	1·412 (4)	113·7 (2)
C5′	C4′	O4′	1·519 (4)	109·3 (2)
C5′	C4′	C3′		113·4 (2)
O4′	C4′	C3′	1·449 (3)	106·6 (2)
O5′	C5′	C4′	1·441 (4)	108·8 (2)
C1′	O4′	C4′		110·5 (2)
P	O5′	C5′		121·9 (2)

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*) (°)
N5 H5	O8′	*x*, 1+*y*, 1+*z*	2·643 (3)	1·78 (4)	164· (4)
N10 H10*A*	O*W*	1+*x*, *y*, 1+*z*	2·836 (5)	1·99 (4)	168· (4)
N10 H10*B*	O3′	*x*, *y*, 1+*z*	2·937 (3)	2·23 (4)	137· (4)
N10 H10*B*	O8′	*x*, 1+*y*, 1+*z*	3·120 (4)	2·48 (4)	130· (3)
O2′ HO2′	O6′	1+*x*, 1+*y*, *z*	2·703 (3)	2·09 (4)	168· (5)
O3′ HO3′	O6′	*x*, 1+*y*, *z*	2·667 (3)	1·97 (4)	145· (4)
O7′ HO7′	O8′	*x*−1, *y*, *z*	2·573 (3)	1·67 (5)	175· (5)
O*W* HO*WB*	O7′	*x*, *y*, *z*	2·874 (4)	2·040 (2)	150·1 (2)
O*W* HO*WC*	O3′	*x*, *y*, *z*	2·782 (4)	1·816 (2)	155·1 (2)

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Structure of 1,5,6-Trimethyl-1*H*-pyrazolo[3,4-*d*]pyridazine-4,7(5*H*,6*H*)-dione

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Abstract. $C_8H_{10}N_4O_2$, $M_r = 194{\cdot}2$, monoclinic, $P2_1$, $a = 3{\cdot}997$ (1), $b = 8{\cdot}474$ (2), $c = 13{\cdot}092$ (3) Å, $\beta = 96{\cdot}96$ (2)°, $V = 440{\cdot}2$ (3) Å^3, $Z = 2$, $D_m = 1{\cdot}45$ (5), $D_x = 1{\cdot}465$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}19$ cm^{-1}, $F(000) = 204$, $T = 293$ (1) K, final $R = 0{\cdot}069$ for 776 observed reflexions. The two fused rings are coplanar with a dihedral angle between the ring planes of 0·8 (6)°; the bond lengths and angles agree with expected values.

Table 1. *Fractional coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3) (*Hamilton*, 1959)

	x	*y*	*z*	U_{eq}
O(4)	8756 (13)	2667 (9)	4642 (3)	53 (2)
O(7)	1291 (13)	2670 (9)	941 (3)	57 (2)
N(1)	5159 (13)	5527 (9)	1776 (4)	38 (2)
N(2)	7102 (13)	6493 (10)	2410 (4)	45 (2)
N(5)	5388 (13)	1426 (9)	3386 (4)	43 (2)
N(6)	3396 (12)	1449 (9)	2422 (4)	43 (2)
C(1)	3620 (20)	6107 (11)	776 (6)	57 (3)
C(3)	8163 (16)	5633 (10)	3238 (5)	42 (3)
C(3a)	6821 (14)	4099 (9)	3127 (4)	34 (3)
C(4)	7145 (15)	2716 (10)	3794 (4)	39 (3)
C(5)	4894 (21)	93 (11)	4059 (6)	61 (4)
C(6)	2008 (20)	−60 (11)	2021 (6)	61 (3)
C(7)	3034 (15)	2719 (10)	1775 (4)	40 (3)
C(7a)	4966 (15)	4077	2203 (4)	37 (3)

Experimental. It has been reported that cycloaddition of diazomethane to 6-hydroxy-3(2*H*)-pyridazinone yields not only 6-methoxy-2-methyl-3(2*H*)-pyridazinone and 6-methoxy-3(2*H*)-pyridazinone, but also a third product which has been suggested to be 1,5,6-

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O(4)–C(4)	1·215 (7)	N(5)–C(5)	1·461 (11)
O(7)–C(7)	1·223 (7)	N(6)–C(6)	1·466 (11)
N(1)–N(2)	1·344 (9)	N(6)–C(7)	1·366 (10)
N(1)–C(1)	1·463 (9)	C(3)–C(3a)	1·407 (11)
N(1)–C(7a)	1·356 (8)	C(3a)–C(4)	1·458 (10)
N(2)–C(3)	1·332 (9)	C(3a)–C(7a)	1·340 (7)
N(5)–N(6)	1·408 (7)	C(7)–C(7a)	1·459 (8)
N(5)–C(4)	1·372 (10)		

N(2)–N(1)–C(1)	119·8 (7)	C(3)–C(3a)–C(7a)	105·6 (5)
N(2)–N(1)–C(7a)	110·8 (5)	C(4)–C(3a)–C(7a)	121·9 (6)
C(1)–N(1)–C(7a)	129·4 (6)	O(4)–C(4)–N(5)	121·2 (7)
N(1)–N(2)–C(3)	105·8 (7)	O(4)–C(4)–C(3a)	125·0 (7)
N(6)–N(5)–C(4)	123·0 (6)	N(5)–C(4)–C(3a)	113·8 (5)
N(6)–N(5)–C(5)	116·6 (6)	O(7)–C(7)–N(6)	122·2 (7)
C(4)–N(5)–C(5)	118·8 (5)	O(7)–C(7)–C(7a)	126·0 (7)
N(5)–N(6)–C(6)	117·2 (6)	N(6)–C(7)–C(7a)	111·8 (5)
N(5)–N(6)–C(7)	124·9 (6)	N(1)–C(7a)–C(3a)	107·9 (5)
C(6)–N(6)–C(7)	117·3 (5)	N(1)–C(7a)–C(7)	127·6 (5)
N(2)–C(3)–C(3a)	110·0 (6)	C(3a)–C(7a)–C(7)	124·5 (5)
C(3)–C(3a)–C(4)	132·5 (5)		

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