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Structure of Bis(guaninium) Hydrogenphosphate 2·5-Hydrate

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Abstract. $2C_5H_6N_5O^+.HPO_4^{2-}.2{\cdot}5H_2O$, $M_r = 445{\cdot}3$, triclinic, $P\bar{1}$, $a = 9{\cdot}607\,(4)$, $b = 10{\cdot}221\,(4)$, $c = 10{\cdot}603\,(9)$ Å, $\alpha = 84{\cdot}5\,(1)$, $\beta = 108{\cdot}2\,(1)$, $\gamma = 119{\cdot}7\,(1)°$, $U = 856{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}73$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 1{\cdot}978$ mm^{-1}, $F(000) = 462$, $T = 293$ K, $R = 0{\cdot}07$ for 1085 unique reflections. The title compound consists of two protonated guanine bases which form a network of hydrogen-bonded ribbons which run parallel to each other. Between these ribbons lie channels containing the hydrogenphosphate anion and the water molecules. P—O bond lengths are 1·44 (1)–1·47 (1) Å.

Introduction. The crystals of the title compound were obtained during an attempt to crystallize 2′-deoxyguanosine monophosphate. This compound apparently dissociated giving the title compound. A similar dissociation occurred during an attempt to crystallize ApT, adenine–thymine dinucleoside monophosphate, when an adeninium compound similar to the present compound was formed (Walker, Tollin & Low, 1982).

Experimental. Crystals grown from aqueous solution. Crystal dimensions approx. 0·5 × 0·5 × 0·5 mm. Cell dimensions and intensity data from Weissenberg photographs processed by the SERC Microdensitometer Service. Data collected in range $h = 0$–5 from crystal mounted about **a**, $k = 0$–6 from b-axis crystal and $l = 0$ from c-axis crystal. Range of indices: $-10 < h < 9$, $-11 < k < 12$, $0 < l < 12$. No absorption corrections applied. 2649 reflections measured of which 1088 unique, $R_{\text{int}} = 0{\cdot}085$. 1085 reflections used in refinement: three very strong reflections, 210, $\bar{2}\bar{1}1$ and 003, omitted on grounds of extinction. This number of reflections constitutes about one quarter of those possible in the unique hemisphere of reciprocal space. Atoms of the bases located using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); other atoms obtained after Fourier recycling. Refinement (on F) by blocked-matrix least squares with *SHELX*76 (Sheldrick, 1976). Non-H atoms except water O atoms refined anisotropically; H atoms included at calculated positions with isotropic temperature factors fixed at 0·05 Å^2. Difference map did not reveal any peaks which could be assigned unambiguously to the H atoms; H atom attached to N(7) of each base on the basis of an N(7)···O(6) intermolecular short contact. This short contact, by implying the presence of H on N(7), also implies that the bases exist in a protonated form, H atom of HPO_4^{2-} anion not included; 257 parameters refined, $R = 0{\cdot}070$, unit weights; $(\Delta/\sigma)_{\max} = 0{\cdot}012$; max. difference-map peak 0·47 e Å^{-3}, min. −0·54 e Å^{-3}. Site occupancies of atoms O(2*W*) and O(3*W*) refined initially and, on the basis of this refinement, then fixed at 1·0 and 0·5, respectively. An examination of the Fourier peaks for these two atoms indicated that they were somewhat elongated, indicating a certain amount of positional disorder. This is reflected in their higher temperature parameters. Other programs used, *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978). Scattering factors from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction.

Discussion. Atomic coordinates are given in Table 1,* with bond lengths and angles in Table 2. The atomic numbering is given in Fig. 1. The two independent bases have almost identical bond lengths and angles. The bases form hydrogen-bonded ribbons as shown in Fig. 2: N(2*A*)···N(3*A*)($-x$, $1-y$, $2-z$) 3·03 (2), N(2*B*)···N(3*B*)($1-x$, $1-y$, $2-z$) 3·01 (2), N(7*A*)···O(6*B*)($1-x$, $-y$, $2-z$) 2·69 (2), N(7*B*)···O(6*A*)($1-x$, $-y$, $2-z$) 2·71 (2) Å. There are several other short contacts involving the bases, the phosphate O atoms and O(1*W*). N(1*A*)···O(1*P*)(x, y, z) 2·75 (2), N(9*A*)···O(2*P*)(x, y, $1+z$) 2·66 (2), N(9*B*)···O(4*P*)($1-x$,

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* Lists of structure amplitudes, anisotropic thermal parameters and calculated H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42863 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1−*y*, 2−*z*) 2·65 (2) and N(1*B*)···O(1*W*)(*x*, *y*, *z*) 2·74 (2) Å. These contacts can, on the basis of the lengths and angles involving the H atoms in their calculated positions, be safely assumed to be H bonds. There are several other short contacts of less than 3 Å between the phosphate anion and the water molecules which lie in a channel between the base ribbons. The guanine bases exist in a protonated form. Taylor & Kennard (1982) suggest that guanine bases can be classified according to the rule: protonated if C(5)–N(7)–C(8) > 106·1°, neutral if C(5)–N(7)–C(8) < 106·1°. The present structure confirms this conclusion, C(5)–N(7)–C(8) is 109 (1)° for both bases.

Table 1. *Coordinates* ($\times 10^4$) *for non*-H *atoms with e.s.d.'s in parentheses and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$); *for water* O *atoms, temperature factors are refined isotropic values*

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

	x	y	z	U_{eq}
Molecule *A*				
N(1)	840 (11)	2643 (10)	8453 (8)	22 (3)
C(2)	458 (14)	3509 (13)	9056 (10)	19 (3)
N(2)	−155 (12)	4323 (10)	8258 (9)	30 (3)
N(3)	652 (12)	3566 (10)	10335 (9)	23 (3)
C(4)	1301 (14)	2701 (12)	11003 (10)	21 (3)
C(5)	1690 (14)	1820 (13)	10473 (11)	23 (4)
C(6)	1470 (14)	1715 (12)	9129 (10)	21 (3)
O(6)	1764 (10)	977 (8)	8491 (7)	30 (2)
N(7)	2311 (11)	1133 (10)	11540 (9)	24 (3)
C(8)	2269 (15)	1574 (13)	12648 (11)	28 (4)
N(9)	1633 (12)	2530 (10)	12331 (8)	24 (3)
Molecule *B*				
N(1)	5848 (11)	2604 (10)	8565 (9)	21 (3)
C(2)	5560 (14)	3530 (13)	9169 (11)	23 (3)
N(2)	4981 (12)	4355 (11)	8345 (9)	33 (3)
N(3)	5853 (12)	3670 (11)	10458 (9)	25 (3)
C(4)	6461 (15)	2767 (13)	11134 (11)	24 (4)
C(5)	6751 (15)	1810 (13)	10609 (11)	23 (4)
C(6)	6440 (14)	1653 (13)	9261 (12)	26 (4)
O(6)	6675 (10)	861 (8)	8604 (7)	32 (2)
N(7)	7379 (11)	1143 (10)	11680 (9)	25 (3)
C(8)	7453 (16)	1684 (13)	12791 (12)	34 (4)
N(9)	6870 (12)	2686 (11)	12475 (9)	30 (3)
Phosphate and oxygen (water)				
P(1)	1739 (4)	3999 (3)	5286 (3)	21 (1)
O(1P)	397 (11)	3518 (10)	5888 (8)	41 (3)
O(2P)	1104 (10)	4038 (9)	3864 (7)	33 (3)
O(3P)	2397 (11)	2947 (10)	5551 (9)	47 (3)
O(4P)	3107 (11)	5522 (9)	5858 (8)	45 (3)
O(1*W*)	5149 (12)	2682 (11)	5860 (9)	55 (3)
O(2*W*)	6894 (20)	815 (17)	5733 (16)	138 (6)
O(3*W*)*	870 (30)	9868 (28)	5216 (24)	96 (8)

* Site occupancy 0·5.

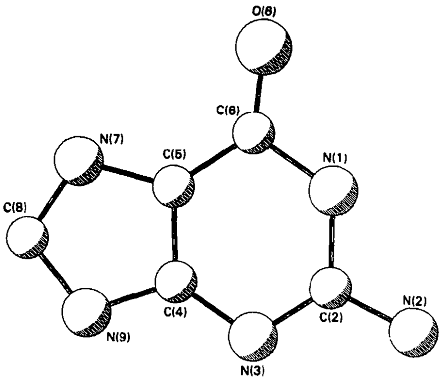

Fig. 1. Atomic numbering of the guaninium base.

Table 2. *Interatomic distances* (Å) *and angles* (°)

	A	*B*
C(2)–N(1)	1·38 (2)	1·37 (2)
C(6)–N(1)	1·40 (2)	1·40 (2)
N(2)–C(2)	1·34 (2)	1·34 (2)
N(3)–C(2)	1·31 (1)	1·31 (2)
C(4)–N(3)	1·35 (2)	1·36 (2)
C(5)–C(4)	1·35 (2)	1·35 (2)
N(9)–C(4)	1·36 (1)	1·36 (1)
C(6)–C(5)	1·38 (2)	1·37 (2)
N(7)–C(5)	1·40 (2)	1·40 (2)
O(6)–C(6)	1·24 (2)	1·26 (2)
C(8)–N(7)	1·32 (2)	1·32 (2)
N(9)–C(8)	1·36 (2)	1·36 (2)
O(1P)–P(1)	1·46 (1)	
O(2P)–P(1)	1·44 (1)	
O(3P)–P(1)	1·46 (1)	
O(4P)–P(1)	1·47 (1)	
C(6)–N(1)–C(2)	124 (1)	123 (1)
N(2)–C(2)–N(1)	116 (1)	115 (1)
N(3)–C(2)–N(1)	124 (1)	124 (1)
N(3)–C(2)–N(2)	120 (1)	120 (1)
C(4)–N(3)–C(2)	112 (1)	112 (1)
C(5)–C(4)–N(3)	126 (1)	127 (1)
N(9)–C(4)–N(3)	126 (1)	125 (1)
N(9)–C(4)–C(5)	108 (1)	109 (1)
C(6)–C(5)–C(4)	122 (1)	121 (1)
N(7)–C(5)–C(4)	106 (1)	106 (1)
N(7)–C(5)–C(6)	131 (1)	132 (1)
C(5)–C(6)–N(1)	111 (1)	112 (1)
O(6)–C(6)–N(1)	119 (1)	118 (1)
O(6)–C(6)–C(5)	131 (1)	130 (1)
C(8)–N(7)–C(5)	109 (1)	109 (1)
N(9)–C(8)–N(7)	108 (1)	108 (1)
C(8)–N(9)–C(4)	109 (1)	108 (1)
O(2P)–P(1)–O(1P)	110 (1)	
O(3P)–P(1)–O(1P)	110 (1)	
O(3P)–P(1)–O(2P)	109 (1)	
O(4P)–P(1)–O(1P)	109 (1)	
O(4P)–P(1)–O(2P)	109 (1)	
O(4P)–P(1)–O(3P)	109 (1)	

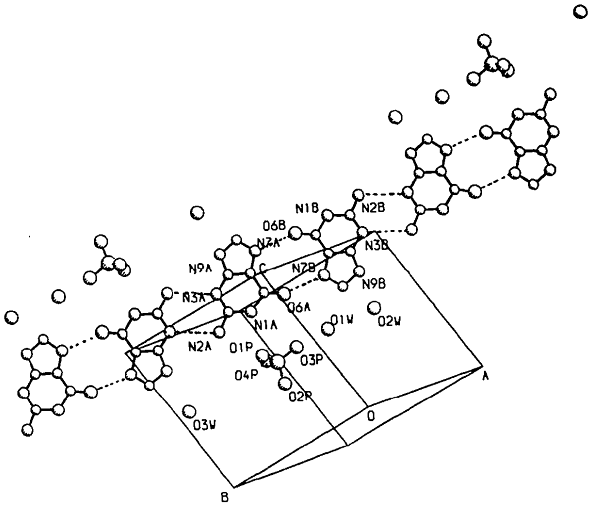

Fig. 2. View perpendicular to base *A* showing the hydrogen-bonded ribbon formed by bases.

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Structure of 9,10-Dihydro-9,10-ethenoanthracene-11,12-dicarbonitrile

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Abstract. $C_{18}H_{10}N_2$, $M_r = 254\cdot2$, monoclinic, $P2_1/c$, $a = 9\cdot885\,(5)$, $b = 14\cdot210\,(7)$, $c = 9\cdot6066\,(5)$ Å, $\beta = 103\cdot08\,(10)^\circ$, $U = 1314$ Å^3, $Z = 4$, $D_m = 1\cdot28\,(1)$, $D_x = 1\cdot28$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 5\cdot21$ cm^{-1}, $F(000) = 528$, room temperature, $R = 0\cdot046$ for 1052 observed reflections. The X-ray crystallographic structure is similar to that of 1-bromotriptycene [Palmer & Templeton (1968). *Acta Cryst.* B**24**, 1048–1052]. The short cyanide–ethane bond lengths [1·439 (5), 1·429 (5) Å] may furnish some evidence of electron delocalization, though the cyanide bond lengths [1·141 (4), 1·139 (4) Å] are of the expected magnitude. The other bond lengths and angles do not reveal any peculiarities.

Introduction. The Diels–Alder addition reaction of dicyanoacetylene with anthracene has been used for the preparation of the title compound (Weis, 1963). No doubt prompted by the similarity of the dicyano grouping in this compound to that of phthalonitrile, a commonly used precursor in the synthesis of phthalocyanines, the use of the former compound has been described (Kopranenkov & Rumyantseva, 1975). In order to gain some idea of the volume available in the axial positions of the metallobarrelenoporphoryrazine as well as pave the way to the interpretation of their X-ray crystallographic data the molecular structure of the title compound has been determined. In addition, such a study provides the opportunity of studying the structural effect of a single ethene group, which is not part of a peripheral benzene group, on the central ring system.

Experimental. A more convenient method for the preparation of the dicyano compound starts with the Diels–Alder addition of the dimethyl ester of dicarboxyacetylene to anthracene (Diels & Thiele, 1931; Holmes, 1949), followed by conversion of the diester product to the diamide by treatment with ammonia and final conversion to the dicyano form by reaction of the diamide with thionyl chloride in dimethylformamide. The final product after recrystallization from acetonitrile was characterized as follows: m.p. 540–541 K; composition: calculated: C 85·02, H 3·96, N 11·02%, found: C 85·38, H 4·20, N 10·72%; MS m/e (rel. int. %) 254 (M^+, 100%), 227 (38), 203 (12), 178 (38). ^{1}H NMR 7·54 (4H), 7·13 (4H), 6·03 (2H) p.p.m.

Crystal dimensions 0·2 × 0·1 × 0·1 mm. D_m by flotation. Cell dimensions determined from 24 reflections. 1948 reflections measured, $\theta = 3$–60°, Philips PW 1100 diffractometer, 1052 [$I \geq 3\sigma(I)$] used, index range h −11/10, k 0/15, l 0/10; Lorentz-polarization and absorption corrections (transmission coefficients max. 0·955, min. 0·924) applied; standard reflections measured every 4 h showed no reduction in intensity over the data-collection period; structure solved by direct methods; refined by full-matrix least squares using *SHELX76* (Sheldrick, 1976), F values, anisotropic temperature factors for non-hydrogen atoms and H atoms in geometrically calculated positions (riding model, C—H 1·08 Å) with a common isotropic temperature factor [U 0·071 (4) Å^2], $R = 0\cdot046$, $wR = 0\cdot047$, where $w = \sigma^{-2}(F)$; $\Delta/\sigma_{\max}$ 0·001 in final cycle; no correction for extinction; scattering factors taken from *International Tables for X-ray Crystallography*

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