

O2—S1—O1	116.58 (14)	C7—N1—S1	115.1 (2)
O2—S1—N1	110.51 (14)	O120—C12—O121	122.6 (3)
O1—S1—N1	109.88 (13)	O120—C12—C11	123.5 (3)
N1—S1—C1	93.07 (12)	O121—C12—C11	113.9 (3)
C7—N1—C8—C9	-101.8 (3)	C10—C11—C12—O120	64.7 (4)
S1—N1—C8—C9	89.2 (3)	C10—C11—C12—O121	-114.4 (3)

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $x-1, 1+y, 1+z$; (iii) $x, y, 1+z$; (iv) $1-x, 1-y, 1-z$.

In both structures, the phenyl and alkyl H atoms were placed geometrically at the expected positions, riding on the attached C atoms, and refined with isotropic displacement parameters. The other H atoms could not be located.

Data collection: Rigaku AFC-7R software for (I); CAD-4 Software (Enraf-Nonius, 1989) for (II). Cell refinement: Rigaku AFC-7R software for (I); SETANG (Enraf-Nonius, 1989) for (II). For both compounds, data reduction: TEXSAN (Molecular Structure Corporation, 1995); program(s) used to solve structures: SHELXS86 (Sheldrick, 1990); program(s) used to refine structures: SHELXL93 (Sheldrick, 1993); molecular graphics: TEXSAN; software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: HA1157). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ammonium Salts of Phosphoglycolic Acid (H₃PG): NH₄.H₂PG, 3NH₄.H₂PG.HPG, 2NH₄.HPG and 3NH₄.PG.H₂O at 150 K

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Abstract

The structures have been determined of four ammonium phosphoglycolate (PG) salts: ammonium phosphoglycolate(1⁻), NH₄.H₂PG (I), triammonium phosphoglycolate(1⁻) phosphoglycolate(2⁻), 3NH₄.H₂PG.HPG (II), diammonium phosphoglycolate(2⁻), 2NH₄.HPG (III) and triammonium phosphoglycolate(3⁻) monohydrate, 3NH₄.PG.H₂O (IV) (PG = C₂H₂O₆P³⁻). The P—O(ester) bond in the doubly ionized phosphate group of (IV) [1.625 (2) Å] is longer than those in mono-ionized phosphate groups of (I)–(III) [1.580 (2)–1.600 (1) Å]. There are extensive networks of hydrogen bonds in all four crystals in which every O- and N-bonded H atom is involved.

Comment

This work is part of a systematic study of the structures of phosphoglycolate residues in different ionization states and different chemical environments (Lis, 1993, 1995). The triammonium and other phosphoglycolate and phosphoenolpyruvate salts are now the subject of investigations aimed at finding the experimental electron density in organic phosphate esters (Lis & Starynowicz, 1995). The structures of (I), (II), (III) and (IV) are reported here. The same atom-numbering scheme has been used for each phosphoglycolate (PG) residue.

Crystals of (I) are composed of phosphoglycolate H₂PG⁻ monoanions (Fig. 1) and ammonium cations. As in most PG moieties, the carboxylic hydroxyl group is *trans* to the O2 ester atom (Lis, 1993), although in potassium phosphoglycolate these groups are *cis* to one another. All O- and N-bonded H atoms are utilized in intermolecular hydrogen bonding (Table 2, Fig. 2). The O4 atoms (as donors) form infinite chains with O1ⁱ atoms along *a*. The O6 atoms (as donors) form infinite chains with O1ⁱⁱ along the (101) direction. The NH₄⁺ cations hydrogen-bond through carboxylic O5 and phosphate O3 atoms to four symmetry-related PG moieties.

The asymmetric unit of (II) contains three ammonium cations, a phosphoglycolate monoanion [denoted *A*; Fig. 3(a)] and a phosphoglycolate dianion [denoted *B*;

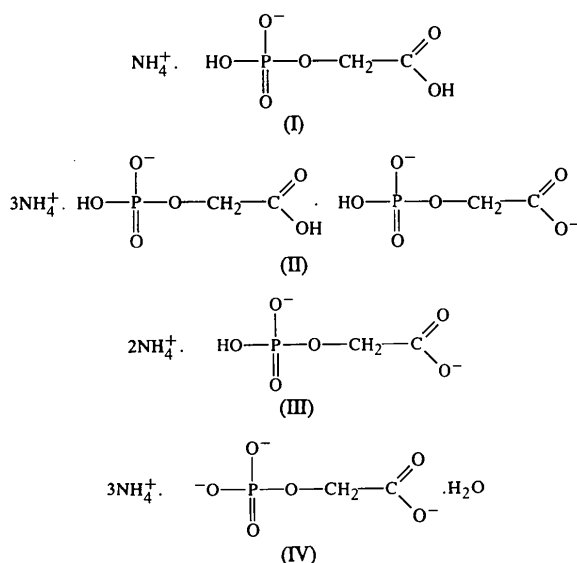


Fig. 3(b)]. The O6A carboxylic atom forms a medium-strong hydrogen bond with the O6B carboxyl atom. This contrasts with the structure of tripotassium bis(phosphoglycolate) (Lis, 1993) in which two phosphoglycolate residues each have a formal negative charge of -1.5 and form strongly hydrogen-bonded dimeric bis(phosphoglycolate) units. Furthermore, the phosphate groups of anions A and B are linked by the phosphate hydroxyl groups to form a polymeric structure (Fig. 4). Three independent NH_4^+ cations form hydrogen bonds with phosphate and carboxyl O atoms (Table 4).

The asymmetric unit of (III) contains two crystallographically independent phosphoglycolate dianions (denoted A and B; Fig. 5) and four ammonium cations. The phosphate hydroxyl O1A atoms (as donors) form infinite chains with O6Aⁱ along *b*. Similarly, the O1B atoms form infinite chains with O6Bⁱⁱ. These chains are interlinked by hydrogen bonds formed by four independent NH_4^+ cations (Fig. 6, Table 6).

The crystals of (IV) are built up of phosphoglycolate trianions (Fig. 7), three crystallographically independent

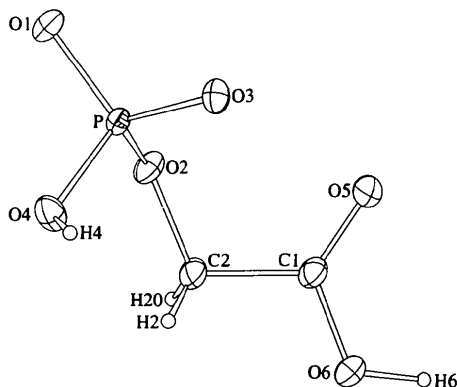


Fig. 1. The structure and numbering scheme of the phosphoglycolate monoanion in (I). Displacement ellipsoids are shown at the 50% probability level.

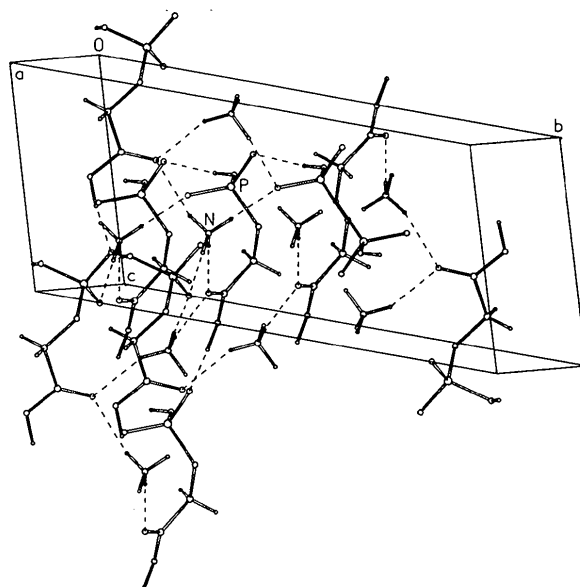


Fig. 2. The packing in the ammonium phosphoglycolate crystal (I). Dashed lines show hydrogen bonds.

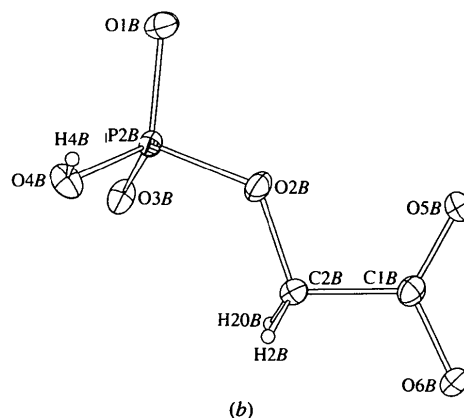
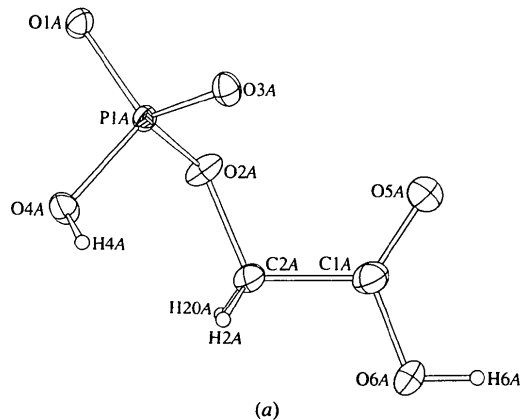


Fig. 3. The molecular structure of phosphoglycolate monoanion A and phosphoglycolate dianion B in (II). (For the disordered atom O5A, only the major component is shown.) Displacement ellipsoids are shown at the 50% probability level.

NH_4^+ cations and water molecules. Details of the hydrogen bonds shown in Fig. 8 are given in Table 8. The carboxylate O5 atom accepts three hydrogen bonds, one from a water molecule and two from ammonium cations. The carboxylate O6 atom accepts two hydrogen bonds.

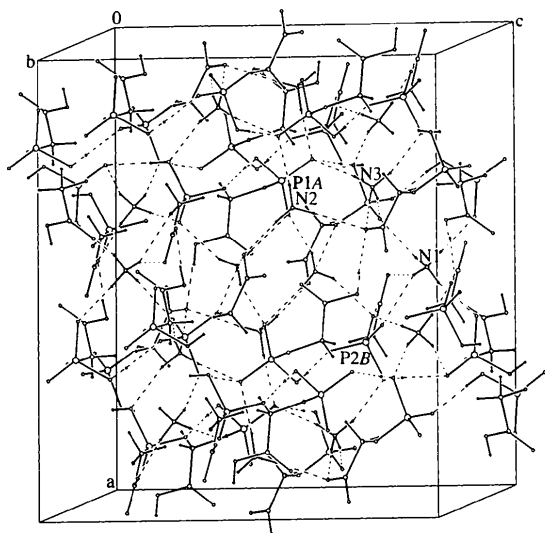


Fig. 4. The packing in (II).

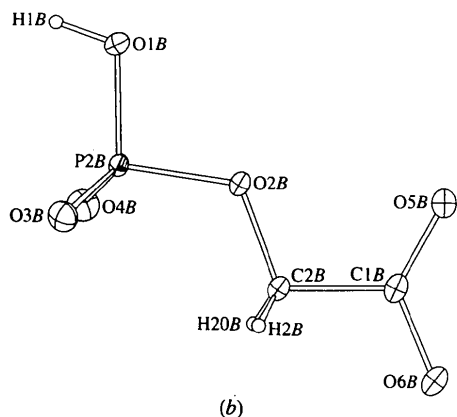
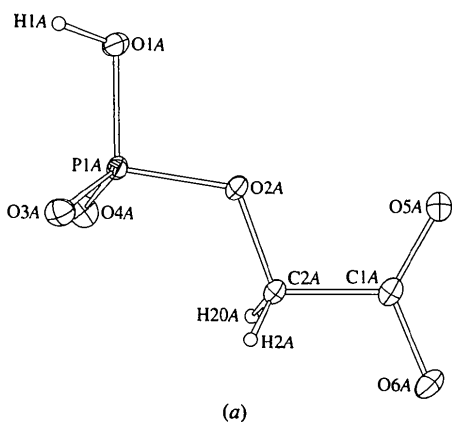


Fig. 5. The molecular structure of the two crystallographically independent phosphoglycolate dianions A and B in (III). Displacement ellipsoids are shown at the 50% probability level.

The phosphate O1, O4 and O3 atoms accept three, three and two hydrogen bonds, respectively. The water molecule (O7) forms two hydrogen bonds as a donor and one as acceptor.

In this paper the molecular structures of ammonium phosphoglycolates at all levels of protonation have been described. The geometry of the phosphate groups (Table 9) does not depart from that commonly found in other monophosphate organic esters and is similar to that found in phosphoglycolic acid and its salts (Lis, 1993, 1994, 1995). The C—COO atoms of each PG residue are quite close to planar. There is also an evident tendency for the ester O2 atom to lie in this plane, as indicated by the O2—C2—C1—O5 and O2—C2—C1—O6 torsion angles (Table 9). The orientation of the phosphate group relative to the acetate moiety may be described by the conformational angles P—O2—C2—C1 and O—P—O2—C2. The values of these angles in ammonium (Table 9) and other salts (Lis, 1993, 1994, 1995) suggest considerable conformational flexibility

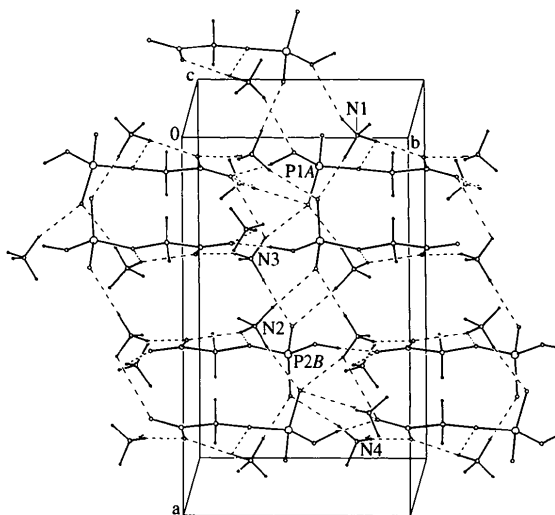


Fig. 6. The packing in (III).

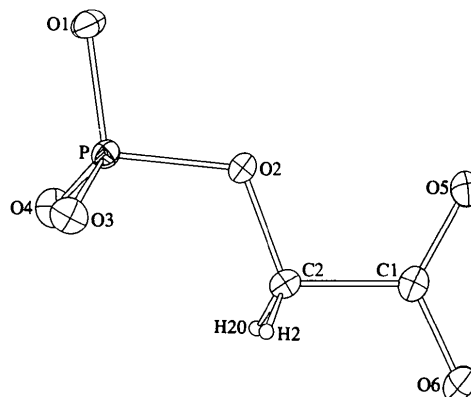


Fig. 7. The structure of the phosphoglycolate trianion in triammonium phosphoglycolate monohydrate (IV). Displacement ellipsoids are shown at the 50% probability level.

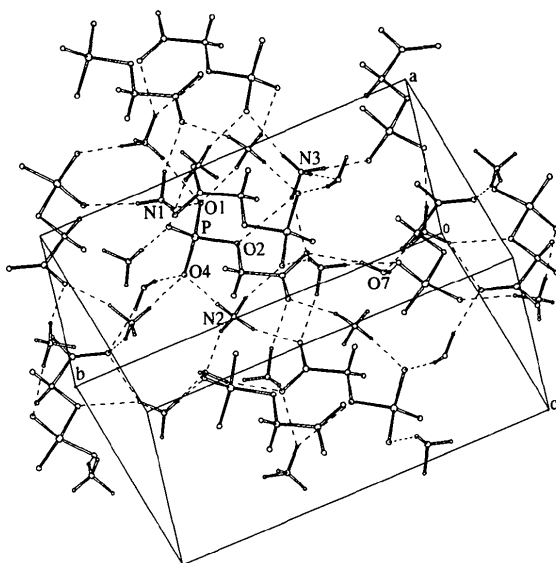


Fig. 8. The packing in (IV).

around the P—O2 and O2—C2 bonds and show that the phosphate group favours the position away from carboxyl group.

The ester P—O2 bond length of 1.625 (2) Å in the doubly ionized phosphate group of (IV) is a little longer than the values of 1.580 (2)–1.600 (1) Å in the mono-ionized phosphate groups of (I)–(III).

Experimental

Colourless crystals of ammonium salts of phosphoglycolic acid were grown by slow concentration of an aqueous solution containing an equimolar ratio of phosphoglycolic acid (Lis, 1993) and NH_4HCO_3 .

Compound (I)

Crystal data

$\text{NH}_4\text{C}_2\text{H}_4\text{O}_6\text{P}^-$

$M_r = 173.06$

Monoclinic

$P2_1/n$

$a = 4.495 (4) \text{ \AA}$

$b = 19.982 (12) \text{ \AA}$

$c = 7.822 (4) \text{ \AA}$

$\beta = 105.47 (6)^\circ$

$V = 677.1 (8) \text{ \AA}^3$

$Z = 4$

$D_x = 1.698 (2) \text{ Mg m}^{-3}$

$D_m = 1.665 \text{ Mg m}^{-3}$

D_m measured by flotation in $\text{CCl}_4/1,2$ -dibromethane at room temperature

Data collection

Kuma KM4 computer-controlled four-circle diffractometer

$\omega/2\theta$ scans

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 81 reflections

$\theta = 10\text{--}15^\circ$

$\mu = 0.386 \text{ mm}^{-1}$

$T = 150 (1) \text{ K}$

Needle-like

$0.8 \times 0.2 \times 0.15 \text{ mm}$

Colourless

$R_{\text{int}} = 0.0258$

$\theta_{\text{max}} = 30^\circ$

$h = -6 \rightarrow 6$

$k = 0 \rightarrow 28$

Absorption correction: none
2728 measured reflections
1971 independent reflections
1619 observed reflections
 $[I > 2\sigma(I)]$

$l = -11 \rightarrow 10$
3 standard reflections monitored every 100 reflections
intensity decay: 2%

Refinement

Refinement on F^2

$R(F) = 0.0274$

$wR(F^2) = 0.0776$

$S = 1.150$

1971 reflections

123 parameters

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 0.27P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.196$

$\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (I)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
P	0.57575 (7)	0.37558 (2)	0.42106 (4)	0.01086 (10)
O1	0.2609 (2)	0.36937 (5)	0.29221 (12)	0.0160 (2)
O2	0.5101 (3)	0.41285 (5)	0.58775 (12)	0.0157 (2)
O3	0.7429 (3)	0.31112 (5)	0.47619 (12)	0.0155 (2)
O4	0.7763 (3)	0.42557 (5)	0.34553 (14)	0.0187 (2)
O5	0.7880 (3)	0.34151 (5)	0.89264 (14)	0.0233 (3)
O6	1.1341 (3)	0.42318 (6)	0.98173 (14)	0.0229 (3)
C1	0.8922 (3)	0.39599 (7)	0.8723 (2)	0.0153 (3)
C2	0.7579 (4)	0.44243 (7)	0.7188 (2)	0.0197 (3)
N	0.3036 (3)	0.25950 (6)	0.6780 (2)	0.0170 (3)

Table 2. Hydrogen-bonding geometry ($\text{\AA}, ^\circ$) for (I)

D—H...A	D—H	H...A	D...A	D—H...A
O4—H4...O1 ⁱ	0.73 (4)	1.86 (4)	2.582 (2)	170 (4)
O6—H6...O1 ⁱⁱ	0.98 (4)	1.60 (4)	2.577 (2)	174 (4)
N—H11...O3 ⁱⁱⁱ	0.95 (3)	1.85 (3)	2.801 (2)	173 (3)
N—H12...O5	0.91 (3)	2.02 (3)	2.880 (2)	156 (3)
N—H13...O3 ^{iv}	0.90 (3)	1.89 (3)	2.790 (2)	177 (3)
N—H14...O5 ^v	0.84 (3)	2.20 (3)	2.997 (2)	158 (3)

Symmetry codes: (i) $1+x, y, z$; (ii) $1+x, y, 1+z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $x - 1, y, z$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

Compound (II)

Crystal data

$3\text{NH}_4\text{C}_2\text{H}_3\text{O}_6\text{P}^{2-} \cdot$

$\text{C}_2\text{H}_4\text{O}_6\text{P}^-$

$M_r = 363.16$

Monoclinic

$C2/c$

$a = 17.732 (6) \text{ \AA}$

$b = 9.626 (4) \text{ \AA}$

$c = 16.628 (6) \text{ \AA}$

$\beta = 93.18 (3)^\circ$

$V = 2834 (2) \text{ \AA}^3$

$Z = 8$

$D_x = 1.702 (2) \text{ Mg m}^{-3}$

$D_m = 1.665 \text{ Mg m}^{-3}$

D_m measured by flotation in $\text{CCl}_4/1,2$ -dibromethane at room temperature

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 40 reflections

$\theta = 10\text{--}15^\circ$

$\mu = 0.375 \text{ mm}^{-1}$

$T = 150 (2) \text{ K}$

Irregular

$0.3 \times 0.3 \times 0.3 \text{ mm}$

Colourless

Data collection

Kuma KM4 computer-controlled four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 3369 measured reflections
 3262 independent reflections
 2336 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0293$
 $\theta_{\text{max}} = 30^\circ$
 $h = 0 \rightarrow 15$
 $k = 0 \rightarrow 13$
 $l = -23 \rightarrow 23$
 3 standard reflections monitored every 100 reflections
 intensity decay: 2%

Refinement

Refinement on F^2
 $R(F) = 0.0297$
 $wR(F^2) = 0.0807$
 $S = 1.071$
 3262 reflections
 271 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 1.5P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = -0.185$
 $\Delta\rho_{\text{max}} = 0.53 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.45 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

N2—H23...O3A	0.82 (4)	2.03 (4)	2.851 (2)	177 (3)
N2—H24...O1A ⁱⁱⁱ	0.91 (4)	1.99 (3)	2.900 (3)	175 (3)
N3—H31...O1A	0.82 (4)	2.27 (3)	3.005 (3)	148 (3)
N3—H32...O4B ⁱⁱⁱ	0.89 (3)	2.05 (3)	2.924 (2)	166 (3)
N3—H33...O1B ⁱⁱⁱ	0.88 (4)	1.86 (4)	2.737 (2)	170 (4)
N3—H34...O6B ^v	0.94 (3)	1.87 (3)	2.804 (2)	174 (3)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, 2 - y, z - \frac{1}{2}$; (iii) $1 - x, y, \frac{1}{2} - z$; (iv) $x, 1 - y, \frac{1}{2} + z$; (v) $1 - x, y - 1, \frac{1}{2} - z$; (vi) $x, 1 - y, z - \frac{1}{2}$; (vii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (viii) $x - \frac{1}{2}, y - \frac{1}{2}, z$.

Compound (III)

Crystal data

2NH₄⁺.C₂H₃O₆P²⁻
 $M_r = 190.10$
 Monoclinic
 $P2_1/c$
 $a = 13.202 (5) \text{ \AA}$
 $b = 8.072 (3) \text{ \AA}$
 $c = 13.792 (5) \text{ \AA}$
 $\beta = 91.12 (3)^\circ$
 $V = 1469.5 (9) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.719 (2) \text{ Mg m}^{-3}$
 $D_m = 1.675 \text{ Mg m}^{-3}$
 D_m measured by flotation in CCl₄/1,2-dibromethane at room temperature

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 60 reflections
 $\theta = 10\text{--}14^\circ$
 $\mu = 0.367 \text{ mm}^{-1}$
 $T = 150 (1) \text{ K}$
 Prism
 $0.6 \times 0.6 \times 0.3 \text{ mm}$
 Colourless

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (II)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
P1A	0.30724 (3)	0.47464 (4)	0.50926 (2)	0.01021 (12)
P2B	0.65226 (3)	0.62067 (4)	0.74688 (2)	0.01026 (13)
O1A	0.26178 (8)	0.45342 (13)	0.58210 (7)	0.0135 (3)
O2A	0.31022 (9)	0.63896 (13)	0.49775 (7)	0.0166 (3)
O3A	0.38590 (8)	0.41646 (14)	0.51448 (7)	0.0151 (3)
O4A	0.26113 (9)	0.41659 (14)	0.43415 (8)	0.0157 (3)
O5A†	0.4464 (4)	0.7715 (11)	0.4900 (3)	0.060 (3)
O51A†	0.4580 (8)	0.7250 (12)	0.4679 (12)	0.012 (5)
O6A	0.42020 (11)	0.8288 (2)	0.36168 (8)	0.0265 (4)
O1B	0.60642 (9)	0.49061 (12)	0.74115 (8)	0.0167 (3)
O2B	0.61020 (9)	0.71744 (13)	0.80673 (8)	0.0176 (3)
O3B	0.66522 (8)	0.69726 (13)	0.67016 (7)	0.0150 (3)
O4B	0.73337 (9)	0.59269 (14)	0.78742 (8)	0.0163 (3)
O5B	0.49254 (9)	0.85572 (14)	0.84931 (8)	0.0193 (3)
O6B	0.55373 (9)	1.05722 (13)	0.86077 (8)	0.0186 (3)
C1A	0.40623 (13)	0.7659 (2)	0.42908 (11)	0.0191 (5)
C2A	0.33024 (12)	0.6986 (2)	0.42379 (10)	0.0163 (4)
C1B	0.54921 (12)	0.9273 (2)	0.84344 (9)	0.0139 (4)
C2B	0.62053 (13)	0.8636 (2)	0.81327 (11)	0.0160 (4)
N1	0.49669 (11)	0.5606 (2)	0.89036 (9)	0.0149 (5)
N2	0.39028 (12)	0.1309 (2)	0.46957 (10)	0.0157 (4)
N3	0.34012 (11)	0.2466 (2)	0.69334 (9)	0.0147 (4)

† Site occupancies: O5A 0.86(3), O51A 0.14(3).

Table 4. Hydrogen-bonding geometry ($\text{\AA}, ^\circ$) for (II)

D—H...A	D—H	H...A	D...A	D—H...A
O4A—H4A...O3B ⁱ	0.77 (4)	1.72 (3)	2.483 (2)	176 (5)
O6A—H6A...O6B ⁱⁱ	0.83 (4)	1.78 (4)	2.611 (2)	175 (4)
O4B—H4B...O1A ⁱⁱⁱ	0.73 (4)	1.82 (4)	2.548 (2)	178 (4)
N1—H11...O3A ^{iv}	0.86 (3)	2.08 (3)	2.936 (3)	173 (3)
N1—H12...O1B ⁱⁱⁱ	0.80 (3)	2.12 (3)	2.852 (2)	151 (3)
N1—H13...O2B	0.91 (3)	2.28 (3)	2.929 (2)	127 (3)
N1—H13...O5B	0.91 (3)	2.05 (3)	2.922 (2)	159 (3)
N1—H14...O3A ⁱⁱⁱ	0.86 (3)	2.07 (3)	2.898 (2)	162 (3)
N2—H21...O6B ^v	0.89 (3)	2.18 (3)	3.023 (2)	157 (3)
N2—H22...O5B ^{vi}	0.92 (4)	1.86 (4)	2.776 (3)	174 (4)

Data collection

Kuma KM4 computer-controlled four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 4238 measured reflections
 4076 independent reflections
 3331 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0299$
 $\theta_{\text{max}} = 30^\circ$
 $h = -18 \rightarrow 1$
 $k = -11 \rightarrow 0$
 $l = -19 \rightarrow 19$
 3 standard reflections monitored every 100 reflections
 intensity decay: 3%

Refinement

Refinement on F^2
 $R(F) = 0.0309$
 $wR(F^2) = 0.0814$
 $S = 1.103$
 4076 reflections
 288 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.094P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.221$

$\Delta\rho_{\text{max}} = 0.67 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.52 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL93 (Sheldrick, 1993)
 Extinction coefficient: 0.0066 (9)
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (III)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
P1A	0.12892 (2)	0.58217 (3)	0.35422 (2)	0.00899 (8)
P2B	0.63299 (2)	0.43478 (3)	0.39237 (2)	0.00882 (8)
O1A	0.10714 (7)	0.46273 (10)	0.444043 (6)	0.0143 (2)

O2A	0.14557 (7)	0.75135 (9)	0.41279 (6)	0.0153 (2)
O3A	0.22454 (6)	0.53498 (10)	0.30328 (6)	0.0137 (2)
O4A	0.03815 (6)	0.60074 (10)	0.28752 (6)	0.0148 (2)
O5A	0.12970 (8)	1.03038 (10)	0.51455 (6)	0.0193 (2)
O6A	0.16167 (7)	1.18634 (10)	0.38457 (6)	0.0176 (2)
C1A	0.14634 (8)	1.04966 (13)	0.42694 (8)	0.0121 (2)
C2A	0.14595 (9)	0.90263 (13)	0.35890 (7)	0.0138 (2)
O1B	0.62072 (7)	0.54885 (10)	0.48199 (6)	0.0148 (2)
O2B	0.61893 (7)	0.25947 (10)	0.44431 (6)	0.0157 (2)
O3B	0.54855 (6)	0.45870 (10)	0.31777 (6)	0.0147 (2)
O4B	0.73569 (6)	0.44717 (10)	0.34856 (6)	0.0161 (2)
O5B	0.62033 (7)	-0.02348 (10)	0.54154 (6)	0.0157 (2)
O6B	0.62797 (7)	-0.17326 (11)	0.40489 (6)	0.0202 (2)
C1B	0.62481 (8)	-0.03873 (13)	0.45199 (8)	0.0124 (2)
C2B	0.62640 (9)	0.11303 (13)	0.38767 (7)	0.0129 (2)
N1	0.08757 (8)	0.73238 (13)	0.61250 (7)	0.0149 (2)
N2	0.59917 (8)	0.26875 (13)	0.65321 (7)	0.0149 (2)
N3	0.36951 (8)	0.27734 (13)	0.32002 (7)	0.0147 (2)
N4	0.85384 (8)	0.74046 (14)	0.33596 (7)	0.0153 (2)

Table 6. Hydrogen-bonding geometry (\AA , $^\circ$) for (III)

D—H...A	D—H	H...A	D...A	D—H...A
O1A—H1A...O6A ⁱ	0.90 (3)	1.59 (3)	2.472 (2)	165 (3)
O1B—H1B...O6B ⁱⁱⁱ	0.85 (3)	1.66 (3)	2.485 (2)	164 (3)
N1—H11...O1A ⁱⁱⁱ	0.85 (3)	2.26 (3)	3.090 (2)	163 (2)
N1—H12...O2A	0.86 (3)	2.41 (3)	2.877 (2)	115 (2)
N1—H12...O5A	0.86 (3)	1.97 (3)	2.820 (2)	169 (2)
N1—H13...O4A ^{iv}	0.92 (3)	1.93 (3)	2.851 (2)	174 (2)
N1—H14...O4B ^v	0.91 (3)	1.88 (3)	2.790 (2)	176 (2)
N2—H21...O3B ^v	0.95 (3)	2.06 (3)	2.972 (2)	161 (2)
N2—H22...O3B ^{vi}	0.87 (3)	2.13 (3)	3.005 (2)	175 (2)
N2—H23...O2B	0.92 (3)	2.13 (3)	2.899 (2)	140 (2)
N2—H23...O5B	0.92 (3)	2.05 (3)	2.834 (2)	142 (2)
N2—H24...O3A ^v	0.86 (3)	2.01 (3)	2.869 (2)	172 (2)
N3—H31...O3A	0.89 (3)	1.98 (3)	2.833 (2)	159 (2)
N3—H31...O6A ⁱ	0.89 (3)	2.54 (3)	2.993 (2)	112 (2)
N3—H32...O6B ⁱⁱⁱ	0.78 (3)	2.53 (3)	3.128 (2)	135 (2)
N3—H33...O5B ⁱⁱⁱ	0.84 (3)	1.98 (3)	2.802 (2)	167 (2)
N3—H34...O3B	0.87 (3)	1.92 (3)	2.781 (2)	171 (2)
N4—H41...O4B	0.83 (3)	2.01 (3)	2.842 (2)	171 (2)
N4—H42...O3A ⁱⁱⁱ	0.83 (3)	2.41 (3)	3.215 (2)	162 (2)
N4—H42...O6A ^{ix}	0.83 (3)	2.58 (3)	3.076 (2)	120 (2)
N4—H43...O5A ^x	0.84 (3)	1.95 (3)	2.775 (2)	168 (2)
N4—H44...O4A ^{ix}	0.89 (3)	1.89 (3)	2.775 (2)	178 (2)

Symmetry codes: (i) $x, y - 1, z$; (ii) $x, 1 + y, z$; (iii) $-x, 1 - y, 1 - z$; (iv) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (vii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (viii) $1 - x, -y, 1 - z$; (ix) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (x) $1 - x, 2 - y, 1 - z$; (xi) $1 + x, y, z$.

Compound (IV)*Crystal data*3NH₄.C₂H₂O₆P³⁻.H₂O $M_r = 225.15$

Monoclinic

 $P2_1/c$ $a = 7.318 (4) \text{ \AA}$ $b = 14.086 (5) \text{ \AA}$ $c = 9.657 (4) \text{ \AA}$ $\beta = 93.37 (4)^\circ$ $V = 993.7 (8) \text{ \AA}^3$ $Z = 4$ $D_x = 1.505 (2) \text{ Mg m}^{-3}$ $D_m = 1.490 \text{ Mg m}^{-3}$ D_m measured by flotation in CCl₄/CHCl₃ at room temperatureMo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 48 reflections

 $\theta = 10\text{--}12^\circ$ $\mu = 0.294 \text{ mm}^{-1}$ $T = 150 (2) \text{ K}$

Columnar

 $0.4 \times 0.2 \times 0.1 \text{ mm}$

Colourless

Data collection

Kuma KM4 computer-controlled four-circle diffractometer

 $\omega/2\theta$ scans

Absorption correction:

none

2502 measured reflections

2317 independent reflections

1517 observed reflections

 $[I > 2\sigma(I)]$ $R_{\text{int}} = 0.0238$ $\theta_{\text{max}} = 30^\circ$ $h = 0 \rightarrow 7$ $k = 0 \rightarrow 19$ $l = -13 \rightarrow 13$

3 standard reflections

monitored every 100

reflections

intensity decay: 2%

*Refinement*Refinement on F^2 $R(F) = 0.0335$ $wR(F^2) = 0.0843$ $S = 1.100$

2317 reflections

182 parameters

All H-atom parameters

refined

 $w = 1/[\sigma^2(F_o^2) + (0.064P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.122$ $\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)Table 7. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (IV)

	x	y	z	U_{eq}
P	0.74878 (7)	0.63400 (3)	0.11147 (4)	0.01067 (12)
O1	0.7576 (2)	0.57952 (9)	-0.02356 (12)	0.0160 (3)
O2	0.7584 (2)	0.55095 (9)	0.22841 (11)	0.0175 (3)
O3	0.9117 (3)	0.69792 (9)	0.14061 (13)	0.0164 (3)
O4	0.5677 (2)	0.68544 (9)	0.12402 (13)	0.0166 (3)
O5	0.7755 (3)	0.41485 (9)	0.41832 (12)	0.0172 (3)
O6	0.7715 (3)	0.51713 (10)	0.59413 (12)	0.0233 (4)
O7	0.6765 (3)	0.26112 (10)	0.57400 (14)	0.0203 (3)
C1	0.7706 (3)	0.49708 (12)	0.4671 (2)	0.0131 (4)
C2	0.7633 (4)	0.58147 (12)	0.3694 (2)	0.0192 (4)
N1	0.5532 (3)	0.63640 (13)	-0.2616 (2)	0.0176 (4)
N2	0.2358 (3)	0.59328 (11)	0.1667 (2)	0.0147 (4)
N3	0.9715 (3)	0.34509 (12)	0.1937 (2)	0.0173 (4)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i.a_j.$$

Table 8. Hydrogen-bonding geometry (\AA , $^\circ$) for (IV)

D—H...A	D—H	H...A	D...A	D—H...A
O7—H7...O5	0.82 (4)	1.96 (4)	2.757 (2)	163 (4)
O7—H70...O4 ⁱ	0.77 (4)	1.99 (4)	2.754 (2)	170 (4)
N1—H11...O1	0.75 (3)	2.09 (3)	2.786 (2)	153 (3)
N1—H12...O4 ⁱⁱ	0.83 (3)	1.92 (3)	2.746 (2)	171 (3)
N1—H13...O6 ⁱⁱⁱ	0.98 (3)	1.79 (3)	2.752 (2)	168 (3)
N1—H14...O5 ^{iv}	0.70 (4)	2.27 (4)	2.859 (2)	142 (3)
N2—H21...O6 ^v	0.91 (3)	1.90 (3)	2.788 (2)	165 (3)
N2—H22...O1 ^{iv}	0.88 (3)	1.94 (3)	2.801 (2)	164 (3)
N2—H23...O3 ^{vi}	0.83 (4)	2.00 (4)	2.791 (3)	160 (3)
N2—H24...O4	0.88 (4)	1.93 (4)	2.805 (3)	176 (3)
N3—H31...O5	0.95 (3)	2.02 (3)	2.845 (2)	143 (3)
N3—H31...O2	0.95 (3)	2.50 (3)	3.319 (2)	144 (3)
N3—H32...O3 ^{vii}	0.95 (3)	1.78 (3)	2.725 (2)	175 (3)
N3—H33...O1 ^{viii}	0.84 (4)	2.02 (4)	2.853 (3)	172 (4)
N3—H34...O7 ^{ix}	0.88 (3)	1.94 (3)	2.819 (3)	173 (3)

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (iii) $x, y, z - 1$; (iv) $1 - x, 1 - y, -z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $x - 1, y, z$; (vii) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (viii) $2 - x, 1 - y, -z$; (ix) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

Table 9. Selected geometry (\AA , $^\circ$) for phosphoglycolate moieties

	(I)	(IIA)	(IIB)	(IIIA)	(IIIB)	(IV)
P—O1	1.508 (2)	1.506 (2)	1.493 (2)	1.562 (1)	1.552 (1)	1.518 (2)
P—O2	1.596 (2)	1.594 (2)	1.580 (2)	1.600 (1)	1.599 (1)	1.625 (2)
P—O3	1.496 (2)	1.501 (2)	1.502 (2)	1.506 (1)	1.514 (1)	1.507 (2)
P—O4	1.563 (2)	1.558 (2)	1.577 (2)	1.504 (1)	1.498 (1)	1.521 (2)
O2—C2	1.425 (2)	1.420 (2)	1.422 (2)	1.430 (2)	1.421 (2)	1.426 (2)
O5—C1	1.212 (2)	1.207 (3)	1.227 (3)	1.242 (2)	1.244 (2)	1.252 (2)
O6—C1	1.309 (2)	1.309 (2)	1.285 (2)	1.267 (2)	1.267 (2)	1.259 (2)
C1—C2	1.510 (2)	1.493 (3)	1.516 (3)	1.513 (2)	1.513 (2)	1.517 (2)
O1—P—O2	103.9 (1)	104.7 (1)	105.1 (1)	99.7 (1)	98.8 (1)	103.3 (1)
O1—P—O3	115.6 (1)	116.1 (1)	117.8 (1)	111.6 (1)	112.2 (1)	112.9 (1)
O1—P—O4	109.4 (1)	108.4 (1)	111.4 (1)	111.8 (1)	113.0 (1)	113.0 (1)
O2—P—O3	110.7 (1)	109.9 (1)	110.2 (1)	110.1 (1)	109.1 (1)	107.4 (1)
O2—P—O4	105.2 (1)	106.2 (1)	106.4 (1)	108.9 (1)	110.7 (1)	106.9 (1)
O3—P—O4	111.3 (1)	110.9 (1)	105.5 (1)	113.9 (1)	112.2 (1)	112.6 (1)
C2—O2—P	120.1 (2)	121.1 (2)	124.6 (2)	117.9 (1)	118.7 (1)	116.4 (2)
O2—C2—C1	112.8 (2)	113.1 (2)	108.6 (2)	110.3 (1)	110.4 (1)	110.8 (2)
O5—C1—O6	124.7 (2)	124.5 (3)	124.8 (2)	126.2 (1)	126.6 (1)	125.1 (2)
O5—C1—C2	124.7 (2)	123.9 (3)	120.1 (2)	120.4 (1)	120.2 (1)	119.5 (2)
O6—C1—C2	110.5 (2)	111.3 (2)	115.2 (2)	113.3 (1)	113.1 (1)	115.4 (2)
O1—P—O2—C2	-164.4 (1)	-162.8 (2)	-161.6 (2)	-166.5 (1)	-178.9 (1)	176.5 (2)
O3—P—O2—C2	70.9 (2)	71.8 (2)	-33.8 (2)	76.1 (1)	63.8 (1)	57.0 (2)
O4—P—O2—C2	-49.4 (2)	-48.2 (2)	80.2 (2)	-49.4 (1)	-60.1 (1)	-64.1 (2)
P—O2—C2—C1	-93.4 (2)	-109.0 (2)	153.4 (2)	171.3 (1)	172.5 (1)	179.5 (2)
O5—C1—C2—O2	-6.0 (2)	-1.1 (8)	-7.9 (3)	-11.8 (2)	-1.9 (2)	1.6 (3)
O6—C1—C2—O2	174.9 (2)	-175.1 (2)	172.5 (2)	170.2 (1)	177.8 (1)	-178.6 (2)

The collection of data at low temperature was carried out using an Oxford Cryosystem cooler for all compounds. In the case of (II), an additional peak near O5A was found on a difference map. It was interpreted in terms of the disordering of this atom over the sites O5A and O51A.

For all compounds, data collection: *KM4 Software* (Kuma Diffraction, 1989); cell refinement: *KM4 Software*; data reduction: *KM4 Software*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1249). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Amino-1-(2-deoxy- β -D-ribofuranosyl)-6,7-dihydro-1H,5H-cyclopentapyrimidine-2-one

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Abstract

The crystal structure of $\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_4$ has been determined. This modified base is in a *syn* conformation with respect to the deoxyribose sugar, which adopts a distorted $\text{C3}'/\text{O4}'$ -*endo* pucker.

Comment

The crystal structure of this modified nucleoside, (I), was determined as part of a project to assess the effect of the bulky cyclopentene ring on the conformation of cytosine itself, and ultimately on DNA structures when incorporated into an oligonucleotide. Results from these studies will be reported elsewhere. This is the first reported crystal structure of a cytosine derivative with a cyclic aliphatic group attached at the 5 and 6 positions.