C1—P—O2—C6	−104,7 (2)	C3—C4—N—O4	−164,9 (3)
O1—P—O2—C6	23,1 (2)	C4—N—C1—C5	−96,4 (3)
C1—P—O3—C7	176,4 (2)	O4—N—C1—C5	22,9 (2)

Tableau 2. *Valeurs comparatives de paramètres relatifs (Å,°) au cycle pyrrolidine et à l'atome de phosphore dans des composés voisins*

	Paramètres relatifs au cycle pyrrolidine			Paramètres relatifs à l'atome P		
	Angle N	Plan χ^2 *A*	Distance C4/*A*	Angle moyen autour de P	Distance P/(C1,O2,O3)	Distance P═O
(II)[a]	107.0 (3)	99.838	0.669 (4)	109.3 (2)	0.673 (1)	1.467 (3)
(IV)[b]	107.4 (2)	0.279	0.569 (7)	109.2 (2)	0.680 (1)	1.456 (4)
(V)[c]	107.6 (2)	71.965	0.561 (4)	109.3 (2)	0.685 (1)	1.466 (4)
(VI)[c]	109.4 (3)	284.615	0.467 (5)	109.3 (3)	0.675 (1)	1.465 (4)

Notes: (*a*) (*N*-hydroxy-2-méthylpyrrolidin-2-yl)phosphonate de diéthyle (présent travail); (*b*) (2,5-diméthylpyrrolidin-2-yl)phosphonate d'isopropyle (Roubaud, 1996); (*c*) (2,5-diméthylpyrrolidin-2-yl)phosphonate de diéthyle, (V), et (5-isopropyl-2-méthylpyrrolidin-2-yl)phosphonate de diéthyle, (VI) (Le Moigne, 1996).

Collection des données: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Affinement des paramètres de la maille: *CAD*-4 *Operations Manual*. Réduction des données: *SDP* (Frenz, 1978). Programme(s) pour la solution de la structure: *MULTAN*80 (Main *et al.*, 1980). Graphisme moléculaire: *ORTEP* (Johnson, 1965). Logiciel utilisé pour préparer le matériel pour publication: *Word*5,1a sur Macintosh IIvx.

Les listes des coordonnées des atomes, des facteurs d'agitation thermique anisotrope, facteurs de structure et des distances et angles ont été déposées au dépôt d'archives de l'UICr (Référence: PA1234). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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Bis(propane-1,3-diammonium) Diphosphate Tetrahydrate

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Abstract

A new organic diphosphate compound, $2C_3H_{12}N_2^{2+}.P_2O_7^{4-}.4H_2O$, has a non-acidic anion and a mineral-like layered structure similar to the monophosphate, which has an acidic anion. Layers are formed through hydrogen bonding between the water molecules and cohesion between the layers is the result of a hydrogen-bonding network involving NH_3 groups and three aggregated water molecules. The O*W*—H···O-type hydrogen bonds are somewhat stronger than the N—H···O type.

Comment

As the central O atom of the diphosphate $P_2O_7^{4-}$ group is located on the twofold axis of the monoclinic unit cell, this anion has a binary internal symmetry and so is composed of only one independent PO_4 tetrahedron. This uncommon type of internal symmetry has been observed for the diphosphate groups of $Cs_2H_2P_2O_7$ (Larbot, Norbert & Cot, 1979), $Ag_2H_2P_2O_7$ (Averbuch-Pouchot & Durif, 1992) and ethylene diammonium diphosphate, $C_4H_{20}N_2P_2O_7$ (Kamoun, Jouini & Daoud, 1992). The anionic diphosphate $P_2O_7^{4-}$ groups of the title hydrated oligophosphate, (I), are depicted in Fig. 1. They are interconnected by strong hydrogen bonds from the O*W*1 and O*W*2 atoms located on the twofold axis and form linear rows spreading along the **a** direction with a period of two $[P_2O_7(H_2O)_2]^{4-}$ units. Two successive rows are linked by hydrogen bonds from the remaining water molecules (O*W*3), thus, the strong water molecule hydrogen-bonding network connects P_2O_7 groups into layers. These layers, comprising the $[P_2O_7(H_2O)_4]_n^{4n-}$ macroanion, lie parallel to the *ab* plane and are centred at $z = \frac{1}{4}$ and $\frac{3}{4}$ as represented in Fig. 2. They are connected into a three-dimensional network through hydrogen bonds between the NH_3 groups of the organic cation and some external O atoms of the phosphoric layers. Fig. 2, a projection along the **b** direction, clearly shows the side face of the organic layers sandwiched by the $[P_2O_7(H_2O)_4]_n^{4n-}$ macroanion, whereas Fig. 1 represents the two-dimensional macroanion layer, located at $z = \frac{1}{4}$, in projection along the **c** direction.

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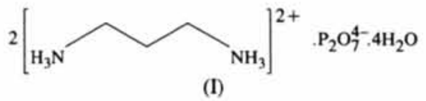

(I)

As expected, there are two types of P—O bond distances in the independent PO_4 tetrahedron, a long one corresponding to the P—O—P bridge [1.613 (1) Å] and three short ones [1.504 (2), 1.507 (2) and 1.519 (3) Å] corresponding to the normal P—O bonds. The average values for the P—O distances and the O—P—O angles, 1.535 (2) Å and 109.3 (1)°, respectively, are normal for this type of tetrahedron.

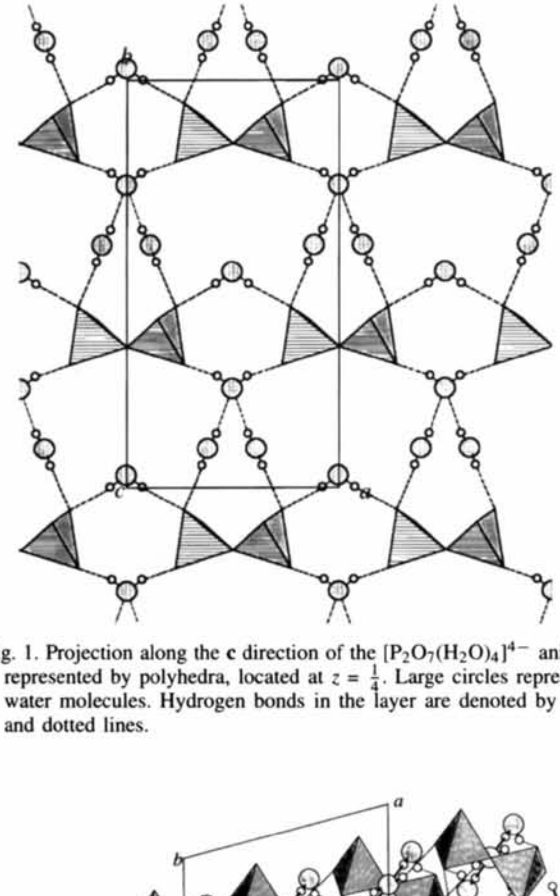

Fig. 1. Projection along the **c** direction of the $[P_2O_7(H_2O)_4]^{4-}$ anions represented by polyhedra, located at $z = \frac{1}{4}$. Large circles represent water molecules. Hydrogen bonds in the layer are denoted by full and dotted lines.

Fig. 2. Projection along the **b** direction of the atomic arrangement in layer profile with P_2O_7 groups represented by polyhedra. In order of decreasing size, circles represent water molecules, N, C and H atoms. Hydrogen bonds are denoted by full and dotted lines.

Each phosphoric P_2O_7 group is connected to its two neighbours by strong hydrogen bonds since the corresponding $OW\cdots O$ distances range from 2.690 (3) to 2.695 (3) Å. In addition, the $H\cdots O$ distances observed in the rows, 1.88 (5) and 1.97 (5) Å, are the shortest of the hydrogen-bonding network of the layer arrangement. Nevertheless, the H atoms of the NH_3 groups form weaker hydrogen bonds than those of the water molecules since the corresponding $N\cdots O$ distances lie in the range 2.780 (4)–2.932 (5) Å.

Infinite networks, sometimes called macroanions, are generally observed in the field of mono- and diphosphates, where the phosphoric groups include acidic anions. These anions have a tendency to assemble *via* strong hydrogen bonds and form infinite chains, ribbons, layers or three-dimensional networks. Having no acidic anion, the title compound exhibits this phenomenon *via* strong hydrogen bonds involving water molecules.

Experimental

Crystals of (I) were obtained by slow evaporation at room temperature of an aqueous solution prepared with $H_4P_2O_7$ and 1,3-diaminopropane. The solution of $H_4P_2O_7$ was prepared using $Na_4P_2O_7$ as starting material and ion-exchange resin Amberlite IR 120.

Crystal data

$2C_3H_{12}N_2^{2+}.P_2O_7^{4-}.4H_2O$
$M_r = 398.30$
Monoclinic
$C2/c$
$a = 8.610\ (3)$ Å
$b = 16.010\ (5)$ Å
$c = 12.878\ (3)$ Å
$\beta = 104.450\ (10)°$
$V = 1719.0\ (9)$ Å^3
$Z = 4$
$D_x = 1.539$ Mg m^{-3}
$D_m = 1.43$ Mg m^{-3}
D_m measured by pycnometry (toluene as pycnometric liquid)

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 10–14°$
$\mu = 2.875$ mm^{-1}
$T = 293\ (2)$ K
Truncated prism
$0.30 \times 0.25 \times 0.20$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: spherical
$T_{min} = 0.556$, $T_{max} = 0.581$
1498 measured reflections
1459 independent reflections
1459 reflections with $I > 2\sigma(I)$

$R_{int} = 0.0066$
$\theta_{max} = 64.91°$
$h = -9 \rightarrow 10$
$k = -18 \rightarrow 0$
$l = -15 \rightarrow 0$
1 standard reflection
frequency: 120 min
intensity decay: 0.21%

Refinement

Refinement on F^2
$R(F) = 0.0424$
$wR(F^2) = 0.1113$
$S = 1.189$
1459 reflections
169 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0819P)^2 + 0.7356P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.017$
$\Delta\rho_{\max} = 0.645$ e Å^{-3}
$\Delta\rho_{\min} = -0.485$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: $1.28\,(4) \times 10^4$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for dap*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P	0.32933 (9)	0.12033 (5)	0.67981 (6)	0.0192 (5)
O*L*	1/2	0.1539 (2)	3/4	0.0307 (9)
O*E*1	0.2291 (3)	0.1984 (2)	0.6609 (2)	0.0299 (7)
O*E*2	0.3557 (3)	0.0860 (2)	0.5756 (2)	0.0301 (7)
O*E*3	0.2697 (3)	0.0549 (2)	0.7446 (2)	0.0317 (7)
O*W*1	1/2	0.4714 (2)	3/4	0.0341 (9)
O*W*2	1/2	−0.2425 (3)	3/4	0.087 (3)
O*W*3	0.1138 (4)	0.4051 (2)	0.6673 (3)	0.0481 (8)
N1	0.8399 (3)	0.4329 (2)	0.4667 (2)	0.0255 (7)
N2	0.3734 (4)	0.3383 (2)	0.5957 (3)	0.0244 (7)
C1	0.7551 (4)	0.3614 (2)	0.5017 (3)	0.0285 (8)
C2	0.5996 (4)	0.3878 (2)	0.5248 (3)	0.0290 (9)
C3	0.5229 (4)	0.3136 (2)	0.5678 (3)	0.0255 (8)

Table 2. *Selected geometric parameters (Å, °)*

P—O*E*1	1.504 (2)	N2—C3	1.474 (4)
P—O*E*3	1.507 (2)	C1—C2	1.502 (5)
P—O*E*2	1.519 (3)	C2—C3	1.528 (5)
P—O*L*	1.613 (1)	P—P$^{\rm i}$	3.042 (2)
N1—C1	1.487 (4)		
O*E*1—P—O*E*3	114.0 (2)	O*E*2—P—O*L*	107.4 (1)
O*E*1—P—O*E*2	111.4 (2)	P—O*L*—P$^{\rm i}$	141.0 (2)
O*E*3—P—O*E*2	112.6 (1)	N1—C1—C2	111.9 (3)
O*E*1—P—O*L*	102.7 (2)	C1—C2—C3	109.9 (3)
O*E*3—P—O*L*	108.1 (1)	N2—C3—C2	111.2 (3)

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*1—H*W*1···O*E*3$^{\rm i}$	0.83 (5)	1.87 (5)	2.695 (3)	170 (5)
O*W*2—H*W*2···O*E*1$^{\rm ii}$	0.77 (5)	1.97 (5)	2.690 (3)	156 (6)
O*W*3—H1*W*3···O*E*3$^{\rm iii}$	0.89 (6)	1.96 (6)	2.734 (4)	145 (5)
O*W*3—H2*W*3···O*W*2$^{\rm iv}$	0.86 (7)	2.06 (6)	2.863 (5)	156 (6)
N1—H1N1···O*E*3$^{\rm v}$	0.93 (5)	1.86 (5)	2.780 (4)	167 (4)
N1—H2N1···O*E*2$^{\rm vi}$	0.95 (6)	1.92 (6)	2.823 (4)	160 (5)
N1—H3N1···O*E*2$^{\rm i}$	0.99 (5)	1.81 (5)	2.809 (4)	179 (4)
N2—H1N2···O*E*2$^{\rm vii}$	0.76 (6)	2.11 (6)	2.838 (4)	160 (5)
N2—H2N2···O*E*1	0.73 (5)	2.07 (5)	2.791 (5)	178 (4)
N2—H3N2···O*W*1	0.84 (6)	2.11 (6)	2.932 (5)	168 (5)
H*W*1—O*W*1···H*W*1$^{\rm viii}$	–	–	–	111 (7)
H*W*2—O*W*2···H*W*2$^{\rm viii}$	–	–	–	107 (9)
H1*W*3—O*W*3···H2*W*3	–	–	–	101 (5)

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: DU1165). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,4-Phenylenebis(diphenylphosphine oxide)

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Abstract

The structure of the title compound, 1,4-C_6H_4[PO-$(C_6H_5)_2$]$_2$ ($C_{30}H_{24}O_2P_2$), is the first to be reported of a phenylenebis(phosphine oxide). The molecule lies about an inversion centre and the unique P atom has a distorted tetrahedral environment; P═O 1.489 (3), average P—C 1.812 (4) Å, average C—P—C 106.9 (8) and average O—P—C 112.0 (2)°. The structure is stabilized by C—H···O intermolecular hydrogen bonds.

Comment

To our knowledge, no comparable structures of phenylenebis(phosphine oxide) derivatives have been

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