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4,4′-Methylenedianilinium hemi(cyclotetraphosphate)

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The title compound, $C_{13}H_{16}N_2^{2+}\cdot 0.5P_4O_{12}^{4-}$, has been prepared at room temperature and studied by single-crystal X-ray diffraction. The asymmetric unit consists of one 4,4′-diphenylmethylendiammonium organic cation and two PO_4 tetrahedra that form one half of a cyclic $P_4O_{12}^{4-}$ anion that lies about an inversion centre. The P_4O_{12} rings are linked through N—H···O hydrogen bonds to build layers parallel to the *ab* plane. The two NH_3^+ groups at the 4- and 4′-positions of the cations link these layers into a three-dimensional network.

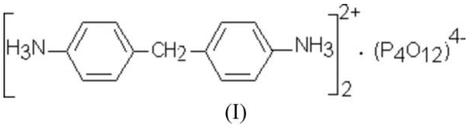
Key indicators

Single-crystal X-ray study
T = 300 K
Mean σ(C–C) = 0.004 Å
R factor = 0.038
wR factor = 0.118
Data-to-parameter ratio = 12.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The structure of the title compound, (I), has been determined as part of an investigation of materials resulting from the reaction between cyclotetraphosphoric acid and organic molecules such as amines, amino acids and aminoalcohols, with the aim of preparing new protonic conductors which are of interest as solid electrolytes.



(I)

The structure of (I) can be described as layered, consisting of alternating organic and inorganic sheets parallel to the *ab* plane (Fig. 2). This atomic arrangement is characteristic of this family of phosphate salts (Thabet *et al.*, 1997; Soumhi *et al.*, 1998, 1999*a*). The cyclic $P_4O_{12}^{4-}$ anions are located around inversion centres at (0, 0, $\frac{1}{2}$) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). The cyclotetraphosphate anion is, as usual, made up of a ring of four PO_4 tetrahedra sharing corners. However, the phosphate ring is distorted from the square arrangement normally adopted by the four P atoms [P—P—P angles are 82.40 (2) and 97.60 (2)°; note that the sum of these angles is 180°, in good agreement with earlier results concerning $P_4O_{12}^{4-}$ systems with C_i local symmetry]. Within each PO_4 tetrahedron, two types of P—O distances are observed. The P—O*L* bonds that link the P atoms to form the P_4O_4 ring are substantially longer than the P—O bonds on the periphery. The P—O distances vary from 1.474 (2) to 1.613 (2) Å, while the O—P—O angles vary from 100.59 (8) to 120.5 (1)°. Such values agree with those previously reported for other cyclotetraphosphates (Durif, 1995). The salt contains only one independent organic cation which is located between two adjacent inorganic layers. C—C/C—N distances and C—C—C/C—C—N angles are in good agreement with those observed in similar phosphate salts of organic amines. (Soumhi & Jouini, 1995*a*,*b*, 1996*a*,*b*,*c*; Soumhi *et al.*, 1998, 1999*b*, 2001). The existence of the ammonium

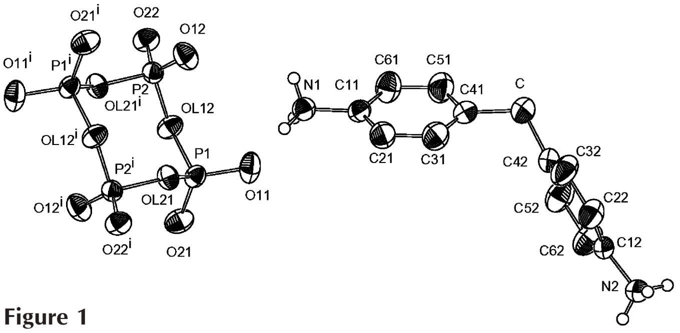


Figure 1

The asymmetric unit and equivalent second half of the anion, showing 50% probability ellipsoids and the atom-numbering scheme [symmetry code: (i) $-x, 2-y, 1-z$]. H atoms bound to C atoms have been omitted.

substituents at the 4- and 4′-positions on the organic cation leads to a three dimensional network by means of N—H$\cdots$O hydrogen bonds. The structure contains six hydrogen bonds involving atoms N1 and N2 of the organic cation and the exocyclic O atoms of the $P_4O_{12}^{4-}$ anion. The corresponding N—O distances range from 2.700 (3) to 2.880 (3) Å. Following the well known criteria of Blessing and Brown, one could assume that among the six hydrogen bonds, two are weak and four are relatively strong (Blessing, 1986; Brown, 1976). Thus, this study confirms that the network stability of most organic cation phosphates is largely due to the hydrogen-bonding network.

Experimental

The title compound was prepared by neutralizing $H_4P_4O_{12}$ with 4,4′-diphenylmethylendiamine in a 2:1 molar ratio. The $H_4P_4O_{12}$ solution was prepared using an aqueous solution of $Na_4P_4O_{12}\cdot 4H_2O$ and an ion-exchange resin (Amberlite IR-120). Colourless single crystals appeared after evaporation of the solution at room temperature for a few days.

Crystal data

$C_{13}H_{16}N_2^{2+}\cdot 0.5P_4O_{12}^{4-}$
$M_r = 358.22$
Monoclinic, $P2_1/a$
$a = 8.467$ (2) Å
$b = 13.808$ (3) Å
$c = 14.453$ (2) Å
$\beta = 106.62$ (2)°
$V = 1619.2$ (6) Å^3
$Z = 4$

$D_x = 1.47$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.30$ mm^{-1}
$T = 300$ (2) K
Prism, colourless
0.30 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4086 measured reflections
3528 independent reflections
2874 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$

$\theta_{\rm max} = 27.0°$
$h = 0 \rightarrow 10$
$k = -1 \rightarrow 17$
$l = -18 \rightarrow 17$
2 standard reflections
frequency: 60 min
intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.118$
$S = 1.08$
3528 reflections
273 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.1136P)^2 + 1.5906P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.70$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.007 (2)

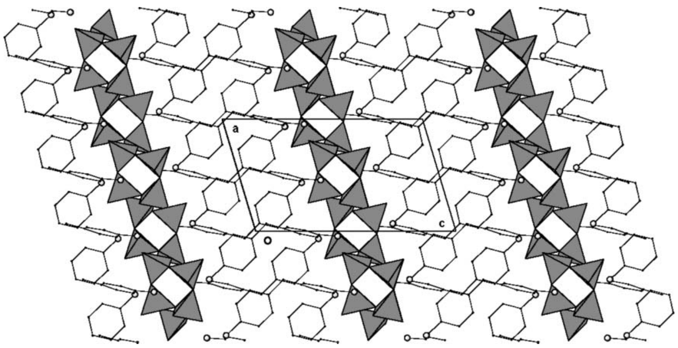


Figure 2

Projection along the *b* axis of the structure of (I). In order of decreasing size, the circles represent N and C atoms. H atoms have been omitted.

Table 1

Selected geometric parameters (Å, °).

P1—O11	1.477 (2)	C31—C41	1.389 (4)
P1—O21	1.490 (2)	C41—C51	1.385 (4)
P1—O*L*21	1.600 (2)	C41—C	1.522 (4)
P1—O*L*12	1.613 (2)	C51—C61	1.382 (4)
P2—O12	1.474 (2)	C—C42	1.522 (4)
P2—O22	1.486 (2)	N2—C12	1.465 (3)
P2—O*L*21^{i}	1.604 (2)	C12—C22	1.371 (3)
P2—O*L*12	1.609 (2)	C12—C62	1.380 (3)
O*L*21—P2^{i}	1.604 (2)	C22—C32	1.385 (4)
N1—C11	1.462 (3)	C32—C42	1.386 (4)
C11—C21	1.373 (3)	C42—C52	1.382 (4)
C11—C61	1.388 (4)	C52—C62	1.394 (4)
C21—C31	1.393 (4)		
O11—P1—O21	119.5 (1)	C41—C31—C21	121.4 (3)
O11—P1—O*L*21	106.64 (9)	C51—C41—C31	118.2 (2)
O21—P1—O*L*21	110.47 (9)	C51—C41—C	120.3 (3)
O11—P1—O*L*12	110.4 (1)	C31—C41—C	121.4 (3)
O21—P1—O*L*12	105.79 (9)	C61—C51—C41	121.2 (3)
O*L*21—P1—O*L*12	102.82 (8)	C51—C61—C11	119.5 (3)
O12—P2—O22	120.5 (1)	C42—C—C41	115.9 (3)
O12—P2—O*L*21^{i}	110.49 (9)	C22—C12—C62	121.3 (2)
O22—P2—O*L*21^{i}	106.92 (9)	C22—C12—N2	119.9 (2)
O12—P2—O*L*12	111.6 (1)	C62—C12—N2	118.7 (2)
O22—P2—O*L*12	104.67 (8)	C12—C22—C32	119.0 (3)
O*L*21^{i}—P2—O*L*12	100.59 (8)	C42—C32—C22	121.4 (3)
P2—O*L*12—P1	132.1 (1)	C52—C42—C32	118.4 (2)
P1—O*L*21—P2^{i}	135.5 (1)	C52—C42—C	120.5 (3)
C21—C11—C61	120.6 (2)	C32—C42—C	121.0 (3)
C21—C11—N1	120.7 (2)	C42—C52—C62	121.0 (3)
C61—C11—N1	118.7 (2)	C12—C62—C52	118.8 (3)
C11—C21—C31	119.1 (3)		

Symmetry code: (i) $-x, -y+2, -z+1$.

Table 2

Hydrogen-bond geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N1—H1*N*1$\cdots$O22^{ii}	0.89 (4)	1.85 (4)	2.728 (3)	172 (3)
N1—H2*N*1$\cdots$O21^{iii}	0.90 (3)	1.83 (3)	2.724 (3)	171 (3)
N1—H3*N*1$\cdots$O11	0.88 (1)	1.86 (2)	2.728 (3)	170 (3)
N2—H1*N*2$\cdots$O21^{iv}	0.90 (4)	2.13 (4)	2.880 (3)	141 (3)
N2—H2*N*2$\cdots$O22^{v}	0.88 (4)	1.96 (4)	2.764 (3)	151 (3)
N2—H3*N*2$\cdots$O12^{vi}	0.99 (4)	1.72 (4)	2.700 (3)	169 (4)

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

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All H atoms were refined without constraints, except for the H1*C*—C and H3*N*1—N1 distances which are fixed to be equal to 0.96 (1) and 0.88 (1) Å, respectively.

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 1995) and *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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