

## Symmetric hydrogen bonding in dimethylammonium hydrogen diphenyldiphosphonate

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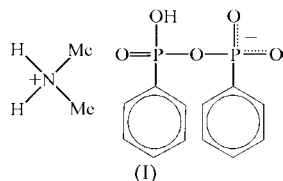
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In the title compound,  $C_2H_8N^+ \cdot C_{12}H_{11}O_5P_2^-$ , pairs of hydrogen diphenyldiphosphonate anions form dimers across a twofold axis, with two symmetric  $O \cdots H \cdots O$  hydrogen bonds [ $O \cdots O = 2.406(3)$  and  $2.418(3)$  Å]. The 12-membered ring thus formed has crystallographic 2 and quasi-222 symmetry. Cations on either side of the ring form  $N-H \cdots O$  hydrogen bonds to the four extraannular O atoms, with  $N \cdots O$  distances of  $2.765(2)$  and  $2.748(3)$  Å.

### Comment

As part of our interest in preparing and characterizing bridging methylene-phosphine complexes, the title compound, (I), was isolated during the synthesis of  $Ph(H)PCH_2P(H)Ph$  by Stelzer's reaction (Langhans & Stelzer, 1987), during which the order of addition of dimethylformamide and water was reversed.

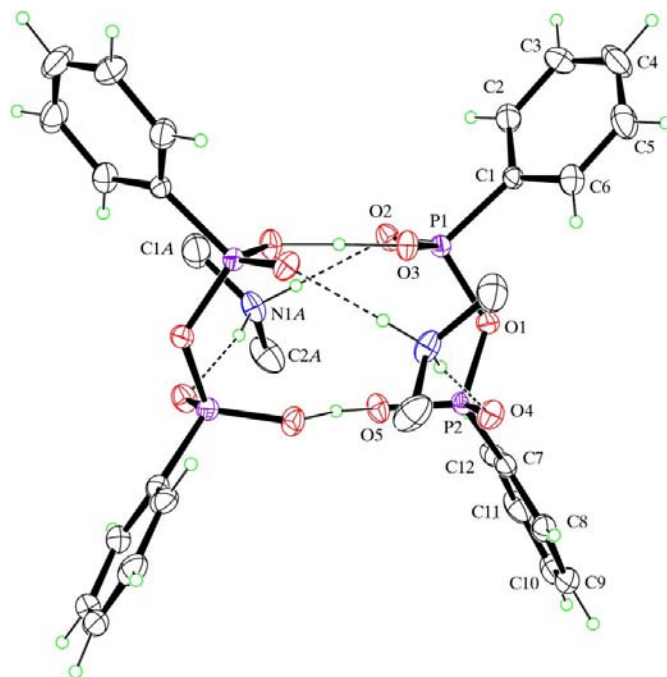


The chemically significant species,  $[(CH_3)_2NH_2]_2[(C_6H_5)_2P_2O_5H]_2$ , consists of two hydrogen diphenyldiphosphonate anions fused into a  $P_4O_6H_2$  ring by two short hydrogen bonds (Fig. 1 and Table 2), both apparently symmetric, with their H atoms centrally located on a twofold axis. While we cannot rule out the possibility that these hydrogen bonds involve disordered H atoms, with half-occupied sites slightly off the twofold axis, difference maps (see Fig. 2) show no elongation of the density along the  $O \cdots O$  lines. The  $O-H$  distances are quite long, approximately  $1.2$  Å. Steiner & Saenger (1994), by examining  $O-H \cdots O$  hydrogen-bonded structures determined from low-temperature neutron-diffraction data ( $T <$

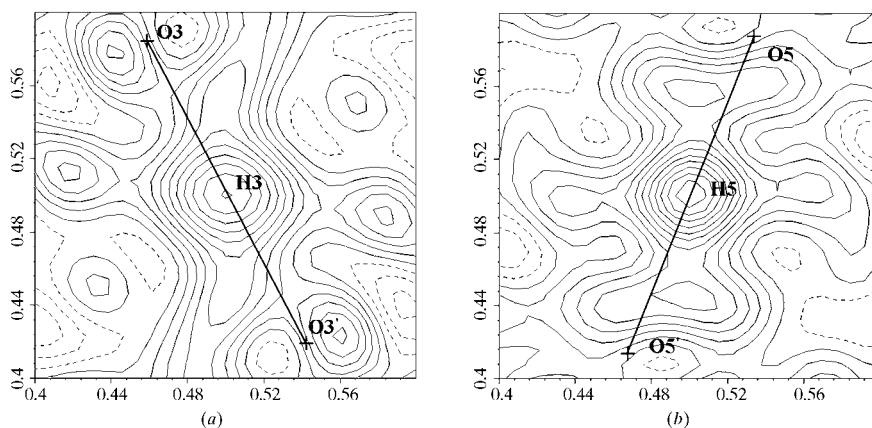
$130$  K,  $R > 0.06$ ), noted a smooth lengthening of the  $O-H$  distances of the donors with a shortening of the  $O \cdots O$  distance. Although their data set contained no instances of hydrogen bonds across symmetry elements, they found a minimum  $O \cdots O$  distance of *ca*  $2.39$  Å, with equal  $O-H$  and  $H \cdots O$  distances at that distance. Thus, the symmetric hydrogen bonds observed in (I) are in accordance with their findings. In (I), the  $P1-O3$  and  $P2-O5$  distances (Table 1) to O atoms involved in the symmetric hydrogen bonds are intermediate in length between the  $P=O$  distance [ $1.506(2)$  Å] and the  $P-OH$  distances [ $1.536(2)$  and  $1.554(2)$  Å] in benzenephosphonic acid (Mahmoudkhani & Langer, 2002).

The four remaining O atoms, *viz.* O2, O4 and their symmetry equivalents, accept hydrogen bonds from two cations on either side of the plane. The  $P=O$  distances are typical of double bonds (Corbridge, 1974).

The structure of the same dimerized anion has been reported at  $213$  K, with a complex palladium cation (Kingsley *et al.*, 2001), but with asymmetric ordered hydrogen bonds [ $O \cdots O = 2.424(3)$  Å]. That dimer lies on an inversion center rather than a twofold axis, so that symmetry does not require either disorder of the H-atom positions or a symmetric hydrogen bond. In the presence of palladium, uncertainties in H-atom positions are rather large; the reported  $O-H$  distance is  $1.02(6)$  Å and the  $H \cdots O$  distance is  $1.43(6)$  Å. Thus, the deviation of the H-atom position from the  $O \cdots O$  mid-point is of marginal statistical significance, and that hydrogen bond may approach the apparently symmetric one observed in the title compound.



**Figure 1**  
The structure of (I), showing the atomic numbering scheme and displacement ellipsoids at the 50% probability level. Dashed lines indicate hydrogen bonds.



**Figure 2**

Fourier difference maps showing the two symmetric hydrogen bonds *viz.* (a)  $\text{O3}-\text{H3O}\cdots\text{O3}^i$  and (b)  $\text{O5}-\text{H5O}\cdots\text{O5}^i$  (see Table 2). The peak heights at the H-atom positions are approximately  $1 \text{ e } \text{Å}^{-3}$ .

## Experimental

Phenylphosphine (19.75 g, 0.180 mol) was added to  $\text{CH}_2\text{Cl}_2$  (7.63 g, 0.090 mol) with stirring in an ice-cooled Schlenk flask. To this mixture was added degassed water (150 ml). Dimethylformamide (56 ml) was added *via* syringe to the mixture and the solution turned cloudy. Degassed 56% KOH solution (27 ml) was added slowly by canula over a period of 20 min, and stirring was continued for 10 h. The reaction mixture separated into two layers, and the organic layer was extracted three times with pentane (50 ml). The pentane was removed by distillation, and the remaining residue was separated by fractional distillation, yielding the starting material, phenylphosphine. The second fraction, collected at 307 K, was the title compound, and shiny colorless crystals formed by sublimation.

### Crystal data

$\text{C}_2\text{H}_8\text{N}^+\cdot\text{C}_{12}\text{H}_{11}\text{O}_5\text{P}_2^-$	Mo $K\alpha$ radiation
$M_r = 343.24$	Cell parameters from 5490 reflections
Tetragonal, $I4_1cd$	$\theta = 2.5\text{--}32.5^\circ$
$a = 13.110$ (3) Å	$\mu = 0.28 \text{ mm}^{-1}$
$c = 38.751$ (8) Å	$T = 102 \text{ K}$
$V = 6660$ (3) Å <sup>3</sup>	Fragment, colorless
$Z = 16$	$0.33 \times 0.30 \times 0.18 \text{ mm}$
$D_x = 1.369 \text{ Mg m}^{-3}$	

### Data collection

Nonius KappaCCD diffractometer (with an Oxford Cryosystems Cryostream cooler)	33359 measured reflections
$\omega$ scans with $\kappa$ offsets	5654 independent reflections
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	4268 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.887$ , $T_{\max} = 0.951$	$R_{\text{int}} = 0.052$
	$\theta_{\text{max}} = 32.6^\circ$
	$h = -19 \rightarrow 19$
	$k = -14 \rightarrow 14$
	$l = -57 \rightarrow 56$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 1.9071P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.095$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.33 \text{ e } \text{Å}^{-3}$
5654 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{Å}^{-3}$
212 parameters	Absolute structure: Flack (1983),
H atoms treated by a mixture of independent and constrained refinement	2590 Friedel pairs
	Flack parameter: 0.21 (8)

The two  $\text{O}-\text{H}\cdots\text{O}$  hydrogens occupy twofold positions; positional parameter  $z$  and the  $U_{\text{iso}}$  value were refined for each atom. The positions of the NH hydrogens were refined, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  of the attached N atom. All aromatic H atoms were placed in calculated

**Table 1**

Selected geometric parameters (Å, °).

P1—O2	1.4811 (15)	P2—O5	1.5260 (15)
P1—O3	1.5269 (16)	P2—O1	1.6193 (17)
P1—O1	1.6190 (16)	P2—C7	1.782 (2)
P1—C1	1.782 (2)	N1A—C2A	1.475 (3)
P2—O4	1.4791 (16)	N1A—C1A	1.481 (3)
P1—O1—P2	124.96 (8)		
O2—P1—O1—P2	−89.86 (13)	O4—P2—O1—P1	−88.63 (13)
O3—P1—O1—P2	38.52 (13)	O5—P2—O1—P1	39.93 (13)

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H3O}\cdots\text{O3}^i$	1.2028 (15)	1.2028 (15)	2.406 (3)	179 (5)
$\text{O5}-\text{H5O}\cdots\text{O5}^i$	1.211 (3)	1.211 (3)	2.418 (3)	174 (5)
$\text{N1A}-\text{H1N}\cdots\text{O2}$	0.89 (3)	1.89 (3)	2.765 (2)	170 (3)
$\text{N1A}-\text{H2N}\cdots\text{O4}^i$	0.88 (3)	1.89 (3)	2.748 (3)	165 (3)

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

positions, with C—H distances of 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  of the attached C atom, and thereafter treated as riding. All methyl H atoms were placed in calculated positions, with C—H distances of 0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$  of the attached C atom and thereafter treated as riding. A torsional parameter was refined for each methyl group.

Data collection: COLLECT (Nonius, 2000); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1093). Services for accessing these data are described at the back of the journal.

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