

Cyclohexylphosphonic acid

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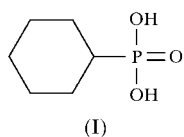
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The title compound, $C_6H_{13}O_3P$, displays a crystallographic mirror plane. Bond lengths in the phosphonic acid moiety are $P-O = 1.5557(13)$ Å and $P=O = 1.5089(18)$ Å. The molecules are linked *via* intermolecular hydrogen bonding to form a one-dimensional chain of fused rings. There are no significant contacts between planes.

Comment

Cyclohexylphosphonic acid, (I), is one of the simplest phosphonic acids. These acids find increasing use in the syntheses of organophosphorus compounds, and in organometallic chemistry as stable bulky ligands. Phosphonates exhibit a rich oxo-cluster chemistry with many different structures, *e.g.* a *tert*-butylphosphonate–zinc cluster (Roesky & Walawalkar, 1999) or a methylphosphonate–gallium cluster (Mason *et al.*, 1998). The present structure determination of (I) was undertaken first because there are few published structures of aliphatic phosphonic acids, and secondly to investigate the nature of the $O-H \cdots O$ hydrogen-bond interactions in the solid state.



The molecule of (I), which displays crystallographic mirror symmetry (the mirror plane passes through atoms P1, O1 and C4), is shown in Fig. 1, with the associated dimensions are given in Table 1. The $P1=O1$ bond length is $1.5089(18)$ Å. Within experimental error, this is similar to the values in phenylphosphonic acid [$1.496(4)$ Å; Weakley, 1976], phosphonoacetic acid [$1.494(2)$ Å; Lis, 1997] and 4-methyl-2,6-bis(phosphonomethyl)phenol dihydrate [$1.4981(13)$ and $1.5015(14)$ Å; Ferguson *et al.*, 1993].

The other two $P-O$ distances, which are symmetry-equivalent, are $1.5557(13)$ Å. A search of the October 2001 release of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) for structures containing the $C-P=O(-OH)_2$ fragment revealed only a few aliphatic phosphonic acids. The $P-O$ distances are in agreement with the reported

standard bond lengths of $1.503(6)$ Å for $P=O$ and $1.57(1)$ Å for $P-O$ (Allen *et al.*, 1987), *e.g.* 1-hydroxycyclohexane-phosphonic acid (Ohms *et al.*, 1996) shows two $P-O$ distances of $1.548(2)$ and $1.542(2)$ Å, and a $P=O$ bond length of $1.495(2)$ Å.

The results of theoretical studies for free cyclohexylphosphonic acid (6-31G** using BL3YP in TITAN; Wavefunction, 1999) are not exactly identical to the present experimental determination of the molecular structure of (I) in the solid state. Whilst the predicted $O-P-O$ angle (113 and 105°), and $P=O$ (1.49 Å) and $P-O$ (1.57 Å) distances are very similar, within experimental error, to the values in (I), the calculations predict a value for the $H8-O2-P1-O2A$ torsion angle of 103.5° , which is significantly different from the observed $H8-O2-P1-O2$ torsion angle of $151.6(19)^\circ$. This is clearly a consequence of the molecular packing in (I).

There is one short $O-H \cdots O$ hydrogen bond, with $O2 \cdots O1 = 2.5915(17)$ Å, consistent with the values of $2.458(2)$ – $2.753(2)$ Å in 4-methyl-2,6-bis(phosphonomethyl)phenol dihydrate (Ferguson *et al.*, 1993). A search of the CSD revealed that more than 80% of phosphonic acids have $P-O-H \cdots O=P$ systems, with $O \cdots O$ distances in the range 2.5 – 2.6 Å. Each $P=O$ O atom is an acceptor of two intermolecular hydrogen bonds (Table 2).

For molecules of the type $RPO(OH)_2$, three-dimensional networks, planes or chains of hydrogen bonds have been observed. Examples are a chain structure for 1-(benzyloxy-

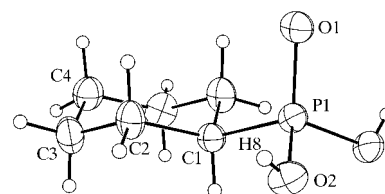


Figure 1

A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

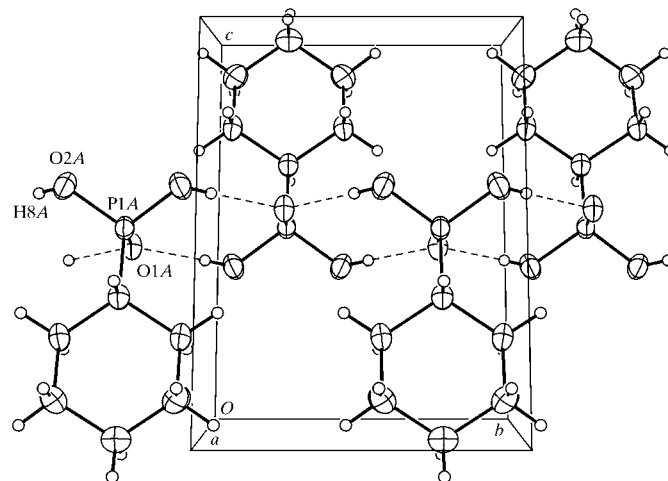


Figure 2

The packing in the crystal of (I). Dashed lines show hydrogen bonds.

carbonylamino)ethylphosphonic acid (Chadha & Oesapay, 1995), a double-layer structure for benzenephosphonic acid (Weakley, 1976) and a network for 2-fluorobenzylphosphonic acid (Langley *et al.*, 1996). In the case of (I), the hydrogen bonding leads to eight-membered rings, which form one-dimensional chains with oppositely oriented cyclohexyl groups. No intermolecular C—H...O hydrogen bonds are observed in (I), nor are there any other significant contacts between the layers.

Experimental

Cyclohexylphosphonic acid was heated in tetrahydrofuran until most of the solid had dissolved. Crystals suitable for X-ray analysis were obtained by slowly cooling a solution containing a few drops of hexane.

Crystal data

C₆H₁₃O₃P
M_r = 164.13
 Monoclinic, *P*2₁/*m*
a = 6.8193 (14) Å
b = 6.7291 (13) Å
c = 9.0902 (18) Å
 β = 104.72 (3)°
V = 403.43 (14) Å³
Z = 2

D_x = 1.351 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 75 reflections
 θ = 3.4–19.5°
 μ = 0.29 mm⁻¹
T = 203 (2) K
 Needle, colourless
 0.4 × 0.1 × 0.1 mm

Data collection

Bruker SMART CCD 1000 area-detector diffractometer
 ω scans
 Absorption correction: empirical (Blessing, 1995)
T_{min} = 0.890, *T_{max}* = 0.971
 1901 measured reflections

762 independent reflections
 697 reflections with *I* > 2σ(*I*)
R_{int} = 0.024
 θ_{\max} = 25°
h = -6 → 8
k = -7 → 7
l = -10 → 8

Refinement

Refinement on *F*²
R(*F*) = 0.037
wR(*F*²) = 0.103
S = 1.16
 762 reflections
 56 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 0.1287P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.58 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e } \text{Å}^{-3}$

All H atoms were visible in difference maps. The hydroxyl H atom was refined isotropically, while those attached to C atoms were positioned geometrically, with C—H = 0.98–0.99 Å, and refined as riding atoms, with *U*_{iso}(H) = 1.2*U*_{eq}(C).

Table 1

Selected geometric parameters (Å, °).

P1—O1	1.5089 (18)	P1—C1	1.795 (3)
P1—O2	1.5557 (13)		
O1—P1—O2	112.76 (7)	C2—C1—P1	111.14 (12)
O1—P1—C1	111.13 (11)	P1—O2—H8	113.8 (19)
O2—P1—C1	108.23 (7)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H8...O1 ⁱ	0.79 (3)	1.80 (3)	2.5915 (17)	178 (3)

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1491). Services for accessing these data are described at the back of the journal.

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