Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Pentane-1,5-bisphosphonic acid

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.096
Data-to-parameter ratio = 18.7

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

Received 31 March 2005
Accepted 11 April 2005
Online 16 April 2005

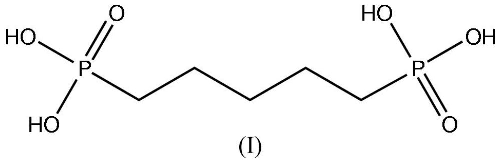
The title compound, $C_5H_{14}O_6P_2$ or $(CH_2)_5[PO(OH)_2]_2$, commonly known as 1,5-pentylenebisphosphonic acid, was prepared by hydrolysis of the corresponding tetraethyl pentylenebisphosphonate with 6 *M* HCl. Crystals suitable for X-ray crystallography were obtained upon cooling a hot saturated 1:1 (*v*/*v*) acetone–ethanol solution of the acid to room temperature. The compound exists in the solid state as a hydrogen-bonded extended structure.

Comment

Alkylenebisphosphonic acids have been recognized for many years for their ability to form stable complexes with a wide variety of metal ions in aqueous solution (Rizkalla, 1983). The metal-complexing ability of a bisphosphonic acid for actinides and lanthanides is especially remarkable under acidic conditions, where it exceeds that of the analogous carboxylic acid by several orders of magnitude (Chiarizia *et al.*, 1996; Nash, 1991; Nash & Horwitz, 1990). This feature of bisphosphonate complexation chemistry makes these ligands promising candidates for remediation of aqueous acidic mixed waste (Nash & Horwitz, 1990).

Alkylenebisphosphonic acids have also been employed as linkers in extended structures as phosphonates. For example, 1,5-pentylenebisphosphonate has recently been reported in extended structures containing copper, nickel/molybdenum, or copper/oxovanadium systems (Arnold *et al.*, 2002; Burkholder *et al.*, 2004; Oullette *et al.*, 2004).

Moedritzer & Irani (1961) reported chemical and physical properties for the bisphosphonic acids $(CH_2)_n(PO_3H_2)_2$ with n = 1–6 and 10, without X-ray structural characterization. Since that time, structural parameters deduced by X-ray diffraction have been shown to correlate well with the reported chemical and physical properties for these compounds with n = 1–4 (Peterson *et al.*, 1977; Gebert *et al.*, 1977; Mahmoudkhani & Langer, 2002).



(I)

The present single-crystal X-ray structure determination of the title compound, (I) (H_4[PBP]), was undertaken in order to continue the investigation of the impact that structure has on the chemical and physical properties of bisphosphonic acids, and to provide a better understanding of the ligand conformational changes required for effective metal-ion complexation.

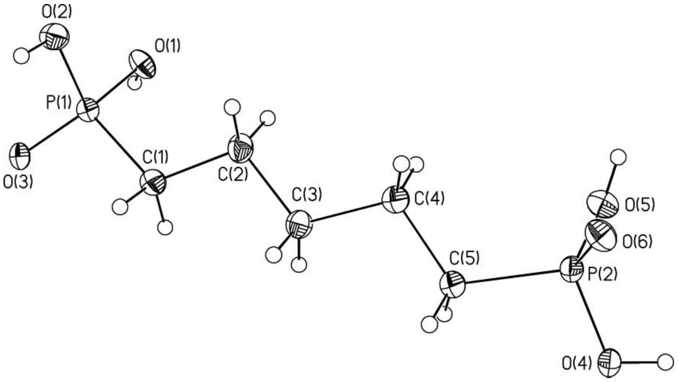
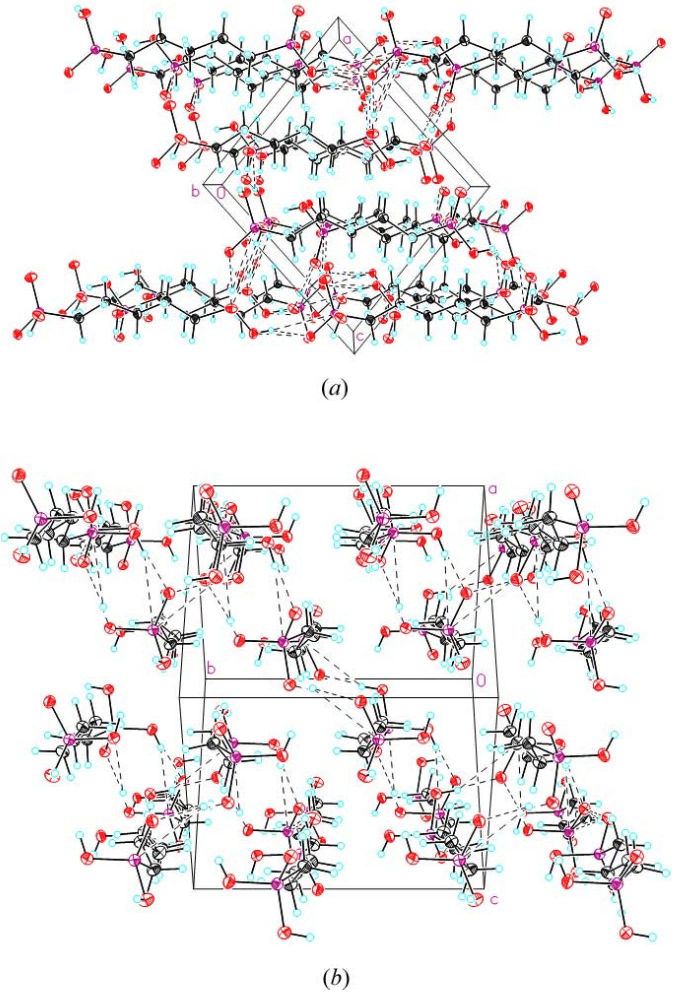


Figure 1
A view of the asymmetric unit of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



(*a*)

(*b*)

Figure 2
The extended structure of (I), viewed along (*a*) the *b* axis, and (*b*) the [101] direction. C atoms are black, H atoms blue, O atoms red and P atoms purple. Dashed lines indicate hydrogen bonds.

The molecular structure of (I) is shown in Fig. 1, and selected geometric parameters are listed in Table 1. Compound (I) exists in the solid state as a hydrogen-bonded extended structure, with individual molecules forming hydrogen bonds to produce chains extending along the [101] direction and sheets when viewed along the *b* axis (Fig. 2). Each molecule makes a total of eight hydrogen bonds with its symmetry-generated neighbors; one hydrogen bond is formed from each P—OH and two are formed from each P═O. Selected hydrogen-bond parameters are listed in Table 2. The intermolecular forces are fairly weak for complexes of this type, as evidenced by the low melting point (Moedritzer & Irani, 1961).

The torsion angles of the molecule (Table 1) illlustrate that the pentylene backbone is slightly bowed, as also seen in $(CH_2)_3(PO_3H_2)_2$ (Gebert *et al.*, 1977), unlike the planar P_2-alkylene portions of the molecule observed in H_4[EtBP], $(CH_2)_2(PO_3H_2)_2$, and the two polymorphs of H_4[BuBP], $(CH_2)_4(PO_3H_2)_2$ (Peterson *et al.*, 1977; Mahmoudkhani & Langer, 2002).

Experimental

The title compound was synthesized using the method of Griffith *et al.* (1998), by hydrolysis of tetraethyl pentylenebisphosphonate using 6 *M* HCl. The tetraethyl ester precursor was prepared *via* the Arbuzov–Michaelis reaction, using a 4:1 molar ratio of triethyl phosphite with 1,5-dibromopentane (Ford-Moore & Williams, 1947). The solid acid product was washed with hexane, recrystallized from a 1:1:1 (*v*/*v*/*v*) methanol–hexane–acetone solution and dried by rotary evaporation at 333 K. Crystals of (I) were collected by washing the acid product with acetone to remove residual solvent. A gram sample of purified (I) was dissolved at reflux in a 1:1 (*v*/*v*) mixed acetone–ethanol solvent (20 ml). The solution was placed in an ice bath for 20 min with scratching to induce crystallization, and it was left standing at room temperature overnight. Crystals of (I) suitable for X-ray analysis [m.p. 426 (1) K] were collected by filtration. The melting point and IR and ^{31}P NMR spectra are consistent with those previously reported (Moedritzer & Irani, 1961).

Crystal data

$C_5H_{14}O_6P_2$
$M_r = 232.10$
Monoclinic, $P2_1/c$
$a = 9.4776$ (9) Å
$b = 10.7072$ (12) Å
$c = 10.0023$ (11) Å
$\beta = 99.463$ (8)°
$V = 1001.21$ (18) Å^3
$Z = 4$

$D_x = 1.540$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2233 reflections
$\theta = 4.3$–30.0°
$\mu = 0.43$ mm^{-1}
$T = 100$ (2) K
Prism, colorless
0.21 × 0.13 × 0.06 mm

Data collection

Oxford Xcalibur3 CCD area-detector diffractometer
φ and ω scans
Absorption correction: numerical (Clark & Reid, 1995)
$T_{min} = 0.858$, $T_{max} = 0.950$
5150 measured reflections

2285 independent reflections
1789 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 27.5°$
$h = -7 \rightarrow 12$
$k = -13 \rightarrow 12$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.096$
$S = 1.12$
2285 reflections
122 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.1207P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

o1360 McLauchlan *et al.* • $C_5H_{14}O_6P_2$ *Acta Cryst.* (2005). E**61**, o1359–o1361

Table 1
Selected geometric parameters (Å, °).

P1—O1	1.5536 (14)	P2—O4	1.5483 (14)
P1—O2	1.5506 (14)	P2—O5	1.5552 (14)
P1—O3	1.5105 (14)	P2—O6	1.5088 (14)
P1—C1	1.777 (2)	P2—C5	1.784 (2)
O1—P1—C1	108.56 (9)	O6—P2—O4	114.40 (8)
O2—P1—O1	102.49 (8)	O6—P2—O5	110.96 (8)
O2—P1—C1	109.92 (9)	O6—P2—C5	111.89 (9)
O3—P1—O1	112.90 (7)	C2—C1—P1	117.01 (14)
O3—P1—O2	113.64 (8)	C3—C2—C1	109.95 (16)
O3—P1—C1	109.10 (9)	C2—C3—C4	114.84 (16)
O4—P2—C5	102.41 (9)	C3—C4—C5	109.55 (16)
O4—P2—O5	107.10 (8)	C4—C5—P2	115.94 (13)
O5—P2—C5	109.65 (9)		
O3—P1—C1—C2	170.05 (14)	C1—C2—C3—C4	173.63 (16)
O4—P2—C5—C4	−167.70 (15)	C3—C4—C5—P2	−178.53 (14)
P1—C1—C2—C3	−170.42 (14)	C5—C4—C3—C2	−171.36 (17)

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O6$^{\rm i}$	0.82	1.79	2.6016 (18)	173
O2—H2⋯O6$^{\rm ii}$	0.82	1.75	2.5629 (19)	174
O4—H4⋯O3$^{\rm iii}$	0.82	1.78	2.5688 (19)	162
O5—H5⋯O3$^{\rm iv}$	0.82	1.78	2.5935 (19)	172

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

H atoms were refined using a riding model with fixed individual displacement parameters [C—H = 0.97 Å and O—H = 0.82 Å, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C$_{\rm methylene}$) and 1.5$U_{\rm eq}$(O)]. In addition, the torsion angles about the P—OH bonds were refined.

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2005); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This research was supported by Illinois State University (CCM) and, in part, by grant No. N66001–03-1–8941 from the Department of Defense, Space and Naval Warfare Systems Center (AWH). CCM thanks Dr A. A. Narducci Sarjeant of Johns Hopkins University for experimental assistance and helpful discussion.

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Acta Cryst. (2005). E**61**, o1359–o1361 McLauchlan *et al.* • $C_5H_{14}O_6P_2$ **o1361**