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Zwitterionic (4-benzylpiperidinium-1-yl-methyl)phosphonate

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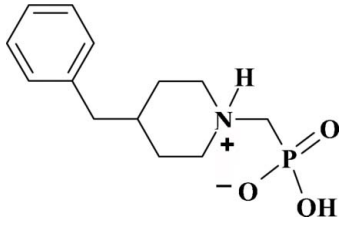
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.002 Å; R factor = 0.033; wR factor = 0.087; data-to-parameter ratio = 19.8.

The title compound, $C_{13}H_{20}NO_3P$, exists as a zwitterion: the phosphonic acid group has transferred its H atom to the amino group. The piperidine ring adopts a chair conformation. Molecules are linked *via* hydrogen bonding to form a linear chain.

Related literature

For similar structures, see: Kotek *et al.* (2000); Mao *et al.* (2002); Ying *et al.* (2007); Vivani *et al.* (2004).



Experimental

Crystal data

$C_{13}H_{20}NO_3P$
M_r = 269.27
Orthorhombic, *Pbca*
a = 9.2791 (6) Å
b = 11.4916 (9) Å
c = 24.915 (2) Å
V = 2656.7 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.21 mm^{-1}
T = 120 (2) K
0.50 × 0.50 × 0.30 mm

Data collection

Stoe IPDS II diffractometer
Absorption correction: numerical [shape of crystal determined optically (*X-RED*; Stoe & Cie, 2005)]
T_{min} = 0.900, T_{max} = 0.938
9369 measured reflections
3536 independent reflections
3336 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.087
S = 1.10
3536 reflections
179 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1C···O2^{i}	0.961 (16)	1.707 (16)	2.651 (1)	166 (2)
O1—H1D···O3^{i}	0.877 (19)	1.682 (19)	2.549 (1)	169 (2)

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

Data collection: *X-AREA* (Stoe & Cie, 2005); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2383).

References

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kotek, J., Vojtisek, P., Cisarova, I., Hermann, P., Jurecka, P., Rohovec, J. & Lukes, I. (2000). *Collect. Czech. Chem. Commun.* **65**, 1289–1316.
Mao, J. G., Wang, Z. & Clearfield, A. (2002). *J. Chem. Soc. Dalton Trans.* pp. 4541–4546.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Stoe & Cie (2005). *X-RED* (Version 1.28b) and *X-AREA* (Version 1.31). Stoe & Cie GmbH, Darmstadt, Germany.
Vivani, R., Costantino, R., Nocchetti, M. & Gatta, G. D. (2004). *J. Solid State Chem.* **177**, 4013–4022.
Ying, S.-M., Lin, J.-Y., Zhou, G.-P., Luo, Q.-Y. & Wu, J.-H. (2007). *Acta Cryst.* E**63**, o1153–o1154.

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supplementary materials

Acta Cryst. (2008). E**64**, o19 [**doi:10.1107/S1600536807061429**]

Zwitterionic (4-benzylpiperidinium-1-ylmethyl)phosphonate

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Comment

Recently, an increasing attention has been focused on the synthesis and designing of aminodiphosphonic acids and new metal phosphonate inorganic–organic hybrid materials with one-, two- or three-dimensional structures due to their potential applications in porous materials, ion exchange reagents, catalysis, sensors, nonlinear optics materials, anti-tumour drugs, photovoltaic devices and biotechnologies (Kotek *et al.*, 2000; Ying *et al.*, 2007; Mao *et al.*, 2002; Vivani *et al.*, 2004). The title compounds, (I), Fig. 1, was prepared by the reaction of benzylpiperidine and formaldehyde with posphorus acid (Scheme I).

The coordination environment around the phosphorus atoms of compound (I) are approximately tetrahedral, since average of six angles involving P are 109.35°. However the coordination is clearly distorted, arising from the presence of different substituents at phosphorus center. The angles O2—P1—O3 and C1—P1—O2 have values of 104.59 (5) and 118.29 (4)°, respectively. The piperidine ring in the titled compound adopt a chair conformation similar to that of cyclohexane. Bond lengths involving phosphorus atom are in good agreement with values found in other similar compounds (Ying *et al.*, 2007; Vivani *et al.*, 2004). The molecules are linked *via* intermolecular hydrogen bonding to form a one-dimensional chain of fused rings (Fig. 2).

Experimental

A quantity of 0.33 mole of benzylpiperidne was dissolved in 75 ml of concentrated HCl and a concentrated aqueous solution of 2 moles of phosphorous acid. The resulting solution was heated to reflux temperature and 160 ml of 37% aqueous formaldehyde solution (2 moles) was added dropwise in the course of 1 hr and the reaction mixture was kept at reflux temperature for 3 additional hr. Upon cooling to room temperature the acids crystallized. Calc for $C_{13}H_{20}NO_3P$: C 57.99, H 7.49, N 5.20%; found C 57.96, H 7.50, N 5.21%.

Refinement

H1A, H1B (for CH_2) and H1C, H1D (for NH and OH) were located in difference syntheses and refined isotropically [C—H = 0.955 (16) and 0.971 (15) Å, U_{iso}(H) = 0.024 (4) and 0.018 (4) Å^2; N—H = 0.961 (16), U_{iso}(H) = 0.026 (4) Å^2 and O—H = 0.87 (2), U_{iso}(H) = 0.025 (6) Å^2]. The remaining H atoms were positioned geometrically, C—H = 0.93 and 0.97 Å, for aromatic and methylene H atoms and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

Figures

Fig. 1. Molecular structure of (I) showing the atom-labelling scheme with thermal ellipsoids drawn at the 50% probability level.

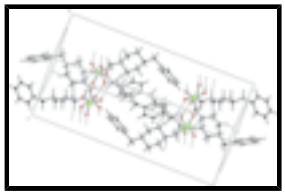

Fig. 2. Packing of molecules, **I** in the unit cell, showing the hydrogen bonding.

(4-benzylpiperidinium-1-ylmethyl)phosphonate

Crystal data

$C_{13}H_{20}N_1O_3P_1$	F_{000} = 1152
M_r = 269.27	D_x = 1.345 Mg m^{-3}
Orthorhombic, *Pbca*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 2500 reflections
a = 9.2791 (6) Å	θ = 2.7–29.2º
b = 11.4916 (9) Å	μ = 0.21 mm^{-1}
c = 24.915 (2) Å	*T* = 120 (2) K
V = 2656.7 (3) Å^3	Block, colourless
Z = 8	0.50 × 0.50 × 0.30 mm

Data collection

Stoe IPDS II diffractometer	3536 independent reflections
Radiation source: fine-focus sealed tube	3336 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.029
Detector resolution: 0.15 pixels mm^{-1}	θ_{max} = 29.2º
T = 120(2) K	θ_{min} = 2.7º
rotation method scans	*h* = −12→9
Absorption correction: numerical shape of crystal determined optically	*k* = −15→15
T_{min} = 0.900, T_{max} = 0.938	*l* = −34→22
9369 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.033$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.087$	$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 1.177P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.013$
3536 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
179 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.13013 (11)	0.26512 (9)	0.27800 (4)	0.01598 (19)
H1A	0.0464 (18)	0.3020 (14)	0.2923 (6)	0.024 (4)*
H1B	0.1752 (16)	0.3137 (13)	0.2509 (6)	0.018 (4)*
C2	0.17889 (11)	0.19257 (9)	0.37040 (4)	0.01476 (19)
H2A	0.1523	0.1145	0.3595	0.018*
H2B	0.0929	0.2313	0.3834	0.018*
C3	0.28979 (12)	0.18585 (9)	0.41550 (4)	0.0168 (2)
H3A	0.3722	0.1411	0.4034	0.020*
H3B	0.2478	0.1456	0.4460	0.020*
C4	0.34034 (11)	0.30678 (9)	0.43324 (4)	0.0164 (2)
H4	0.2572	0.3492	0.4476	0.020*
C5	0.39579 (12)	0.37187 (9)	0.38385 (4)	0.0187 (2)
H5A	0.4230	0.4503	0.3941	0.022*
H5B	0.4812	0.3330	0.3703	0.022*
C6	0.28336 (12)	0.37782 (9)	0.33957 (4)	0.0186 (2)
H6A	0.2003	0.4212	0.3522	0.022*
H6B	0.3231	0.4184	0.3088	0.022*
C7	0.45790 (12)	0.30258 (11)	0.47679 (4)	0.0205 (2)
H7A	0.5386	0.2574	0.4634	0.025*
H7B	0.4920	0.3811	0.4834	0.025*
C8	0.40779 (11)	0.25042 (10)	0.52920 (4)	0.0171 (2)
C9	0.43625 (13)	0.13470 (10)	0.54190 (5)	0.0232 (2)
H9	0.4878	0.0888	0.5179	0.028*

C10	0.38867 (15)	0.08657 (11)	0.59010 (6)	0.0293 (3)
H10	0.4094	0.0093	0.5981	0.035*
C11	0.31058 (14)	0.15354 (14)	0.62611 (5)	0.0308 (3)
H11	0.2775	0.1212	0.6580	0.037*
C12	0.28203 (13)	0.26958 (13)	0.61413 (5)	0.0274 (3)
H12	0.2304	0.3152	0.6382	0.033*
C13	0.33060 (12)	0.31742 (11)	0.56609 (4)	0.0206 (2)
H13	0.3114	0.3951	0.5585	0.025*
N1	0.23706 (9)	0.25759 (7)	0.32299 (3)	0.01285 (16)
H1C	0.3240 (17)	0.2205 (14)	0.3109 (7)	0.026 (4)*
O1	−0.02029 (8)	0.06162 (7)	0.28658 (3)	0.01733 (16)
H1D	−0.112 (2)	0.0696 (19)	0.2790 (9)	0.025 (6)*
O2	−0.00660 (8)	0.16513 (8)	0.19677 (3)	0.01869 (17)
O3	0.21224 (8)	0.05809 (7)	0.23662 (3)	0.01744 (16)
P1	0.07816 (3)	0.12808 (2)	0.245156 (10)	0.01325 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0144 (4)	0.0193 (5)	0.0142 (4)	0.0022 (4)	−0.0014 (4)	0.0033 (4)
C2	0.0152 (4)	0.0181 (4)	0.0110 (4)	−0.0024 (4)	0.0017 (3)	0.0016 (3)
C3	0.0185 (5)	0.0196 (5)	0.0123 (4)	−0.0013 (4)	−0.0011 (3)	0.0014 (4)
C4	0.0143 (4)	0.0206 (5)	0.0144 (4)	0.0008 (4)	0.0003 (3)	−0.0030 (4)
C5	0.0190 (5)	0.0178 (5)	0.0194 (5)	−0.0033 (4)	−0.0016 (4)	0.0003 (4)
C6	0.0208 (5)	0.0148 (5)	0.0202 (5)	−0.0024 (4)	−0.0025 (4)	0.0020 (4)
C7	0.0150 (5)	0.0308 (6)	0.0158 (5)	−0.0019 (4)	−0.0005 (4)	−0.0032 (4)
C8	0.0124 (4)	0.0241 (5)	0.0147 (4)	−0.0007 (4)	−0.0027 (3)	−0.0044 (4)
C9	0.0218 (5)	0.0224 (5)	0.0252 (5)	−0.0018 (4)	−0.0047 (4)	−0.0074 (4)
C10	0.0274 (6)	0.0255 (6)	0.0349 (6)	−0.0099 (5)	−0.0105 (5)	0.0052 (5)
C11	0.0208 (6)	0.0496 (8)	0.0220 (5)	−0.0131 (6)	−0.0042 (4)	0.0084 (5)
C12	0.0158 (5)	0.0493 (8)	0.0170 (5)	0.0011 (5)	0.0009 (4)	−0.0057 (5)
C13	0.0158 (5)	0.0286 (6)	0.0175 (5)	0.0049 (4)	−0.0022 (4)	−0.0054 (4)
N1	0.0119 (4)	0.0149 (4)	0.0117 (3)	0.0007 (3)	0.0013 (3)	0.0012 (3)
O1	0.0094 (3)	0.0269 (4)	0.0157 (3)	−0.0011 (3)	−0.0008 (3)	0.0056 (3)
O2	0.0117 (3)	0.0317 (4)	0.0127 (3)	0.0020 (3)	−0.0013 (3)	0.0044 (3)
O3	0.0094 (3)	0.0236 (4)	0.0194 (4)	0.0015 (3)	0.0004 (3)	−0.0001 (3)
P1	0.00793 (13)	0.02066 (14)	0.01116 (12)	0.00100 (9)	−0.00030 (8)	0.00220 (9)

Geometric parameters (Å, °)

C1—N1	1.4993 (13)	C7—C8	1.5101 (15)
C1—P1	1.8391 (11)	C7—H7A	0.9700
C1—H1A	0.955 (16)	C7—H7B	0.9700
C1—H1B	0.971 (15)	C8—C9	1.3922 (16)
C2—N1	1.4984 (12)	C8—C13	1.3966 (15)
C2—C3	1.5256 (14)	C9—C10	1.3939 (18)
C2—H2A	0.9700	C9—H9	0.9300
C2—H2B	0.9700	C10—C11	1.386 (2)
C3—C4	1.5319 (15)	C10—H10	0.9300

C3—H3A	0.9700	C11—C12	1.392 (2)
C3—H3B	0.9700	C11—H11	0.9300
C4—C5	1.5293 (15)	C12—C13	1.3921 (17)
C4—C7	1.5394 (15)	C12—H12	0.9300
C4—H4	0.9800	C13—H13	0.9300
C5—C6	1.5199 (15)	N1—H1C	0.961 (16)
C5—H5A	0.9700	O1—P1	1.5758 (8)
C5—H5B	0.9700	O1—H1D	0.87 (2)
C6—N1	1.5047 (13)	O2—P1	1.5010 (8)
C6—H6A	0.9700	O3—P1	1.4967 (8)
C6—H6B	0.9700		
N1—C1—P1	117.17 (7)	C8—C7—H7A	108.8
N1—C1—H1A	106.5 (9)	C4—C7—H7A	108.8
P1—C1—H1A	109.5 (10)	C8—C7—H7B	108.8
N1—C1—H1B	105.6 (9)	C4—C7—H7B	108.8
P1—C1—H1B	107.1 (9)	H7A—C7—H7B	107.7
H1A—C1—H1B	110.8 (13)	C9—C8—C13	118.31 (11)
N1—C2—C3	111.28 (8)	C9—C8—C7	121.14 (10)
N1—C2—H2A	109.4	C13—C8—C7	120.54 (11)
C3—C2—H2A	109.4	C8—C9—C10	120.98 (11)
N1—C2—H2B	109.4	C8—C9—H9	119.5
C3—C2—H2B	109.4	C10—C9—H9	119.5
H2A—C2—H2B	108.0	C11—C10—C9	120.19 (12)
C2—C3—C4	111.91 (8)	C11—C10—H10	119.9
C2—C3—H3A	109.2	C9—C10—H10	119.9
C4—C3—H3A	109.2	C10—C11—C12	119.50 (12)
C2—C3—H3B	109.2	C10—C11—H11	120.2
C4—C3—H3B	109.2	C12—C11—H11	120.2
H3A—C3—H3B	107.9	C11—C12—C13	120.07 (12)
C5—C4—C3	108.33 (8)	C11—C12—H12	120.0
C5—C4—C7	110.13 (9)	C13—C12—H12	120.0
C3—C4—C7	113.07 (9)	C12—C13—C8	120.94 (12)
C5—C4—H4	108.4	C12—C13—H13	119.5
C3—C4—H4	108.4	C8—C13—H13	119.5
C7—C4—H4	108.4	C2—N1—C1	112.32 (8)
C6—C5—C4	112.03 (9)	C2—N1—C6	110.13 (8)
C6—C5—H5A	109.2	C1—N1—C6	109.95 (8)
C4—C5—H5A	109.2	C2—N1—H1C	109.2 (10)
C6—C5—H5B	109.2	C1—N1—H1C	110.3 (10)
C4—C5—H5B	109.2	C6—N1—H1C	104.7 (9)
H5A—C5—H5B	107.9	P1—O1—H1D	111.8 (14)
N1—C6—C5	110.74 (8)	O3—P1—O2	118.29 (4)
N1—C6—H6A	109.5	O3—P1—O1	108.33 (5)
C5—C6—H6A	109.5	O2—P1—O1	111.09 (4)
N1—C6—H6B	109.5	O3—P1—C1	107.78 (5)
C5—C6—H6B	109.5	O2—P1—C1	104.59 (5)
H6A—C6—H6B	108.1	O1—P1—C1	106.00 (5)
C8—C7—C4	113.81 (9)		

N1—C2—C3—C4	57.02 (11)	C10—C11—C12—C13	0.56 (18)
C2—C3—C4—C5	−54.79 (11)	C11—C12—C13—C8	0.24 (17)
C2—C3—C4—C7	−177.15 (9)	C9—C8—C13—C12	−0.62 (16)
C3—C4—C5—C6	55.62 (11)	C7—C8—C13—C12	178.99 (10)
C7—C4—C5—C6	179.76 (9)	C3—C2—N1—C1	179.84 (8)
C4—C5—C6—N1	−58.18 (12)	C3—C2—N1—C6	−57.25 (11)
C5—C4—C7—C8	174.20 (9)	P1—C1—N1—C2	−65.29 (10)
C3—C4—C7—C8	−64.45 (12)	P1—C1—N1—C6	171.70 (7)
C4—C7—C8—C9	98.50 (12)	C5—C6—N1—C2	57.69 (11)
C4—C7—C8—C13	−81.09 (13)	C5—C6—N1—C1	−178.02 (9)
C13—C8—C9—C10	0.20 (16)	N1—C1—P1—O3	−43.51 (9)
C7—C8—C9—C10	−179.40 (10)	N1—C1—P1—O2	−170.22 (7)
C8—C9—C10—C11	0.60 (18)	N1—C1—P1—O1	72.31 (8)
C9—C10—C11—C12	−0.98 (18)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1C···O2^{i}	0.961 (16)	1.707 (16)	2.651 (1)	166 (2)
O1—H1D···O3^{i}	0.877 (19)	1.682 (19)	2.549 (1)	169 (2)

Symmetry codes: (i) , , .

Fig. 1

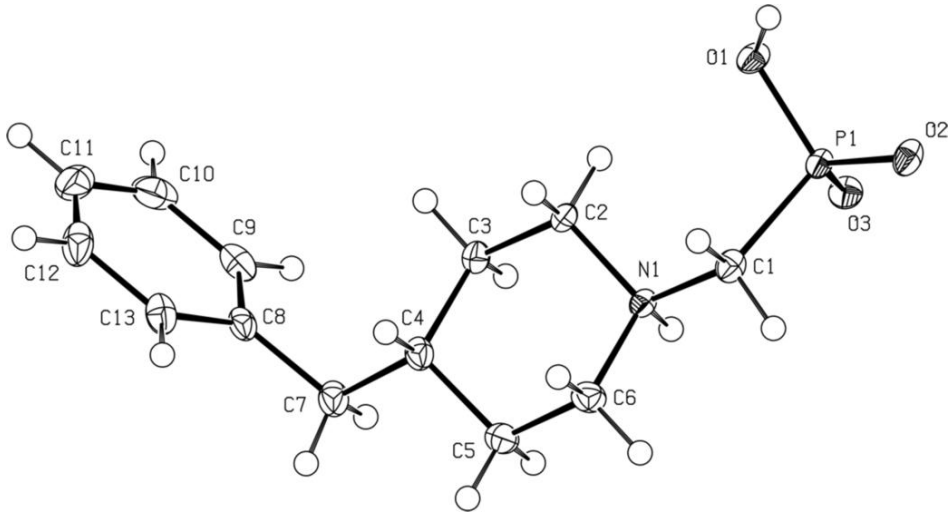

Fig. 2