

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

rac-Ethyl(phenyl)phosphinic acid

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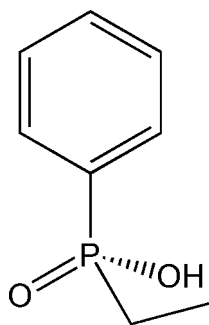
Received 20 November 2012; accepted 22 November 2012

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.045; wR factor = 0.128; data-to-parameter ratio = 25.5.

The crystal structure of the title compound, $\text{C}_8\text{H}_{11}\text{O}_2\text{P}$, features $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, which link molecules related by the b -glide plane into chains along [010].

Related literature

For background to metal-organic frameworks involving phosphonate ligands, see: Gagnon *et al.* (2012). For details of coordination polymers constructed using phosphinic acids as the spacer ligand, see: Siqueira *et al.* (2006); Beckmann *et al.* (2009). For further details of phosphinic acids and the crystal structures of similar compounds, see: Burrow *et al.* (2000); Burrow & Siqueira da Silva (2011*a,b*). For a description of the Cambridge Structural Database, see: Allen (2002). For geometry analysis using *Mogul*, see: Bruno *et al.* (2004).



Experimental

Crystal data

$\text{C}_8\text{H}_{11}\text{O}_2\text{P}$
 $M_r = 170.14$
 Orthorhombic, *Pbcn*
 $a = 13.5314$ (16) Å
 $b = 8.0328$ (9) Å
 $c = 15.922$ (2) Å

$V = 1730.6$ (4) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.27$ mm⁻¹
 $T = 296$ K
 $0.41 \times 0.12 \times 0.11$ mm

Data collection

Bruker X8 Kappa APEXII diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2012)
 $T_{\min} = 0.906$, $T_{\max} = 0.971$

14069 measured reflections
 2650 independent reflections
 1499 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.128$
 $S = 1.09$
 2650 reflections
 104 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.24$ e Å⁻³
 $\Delta\rho_{\min} = -0.34$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{O2}^i$	0.87 (2)	1.64 (2)	2.4931 (19)	168 (2)

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

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2012); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

Financial support from the Conselho Nacional de Desenvolvimento Científico (CNPq, Brazil; grant 479747/2009-1) and the Fundação de Amparo à Pesquisa (FAPERGS, Rio Grande do Sul; grant 10/1645-9) is gratefully acknowledged, as are fellowships from CNPq (RAB; grant 308731/2009-3) and the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil; RMSS). The diffractometer was funded by a CT-INFRA grant from the Financiadora de Estrutos e Projetos (FINEP, Brazil).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2532).

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supplementary materials

Acta Cryst. (2012). E68, o3488 [doi:10.1107/S160053681204812X]

rac-Ethyl(phenyl)phosphinic acid**Robert A. Burrow and Rubia M. Siqueira da Silva****Comment**

Coordination polymers are the basis of metal-organic frameworks usually based on carboxylate ligands or phosphonate ligands (Gagnon *et al.*, 2012). Coordination polymers have also been constructed using phosphinic acids as the spacer ligand (Siqueira *et al.*, 2006; Beckmann *et al.*, 2009). Continuing our research on phosphinic acids (Burrow *et al.*, 2000; Burrow & Siqueira da Silva, 2011*a,b*), we report herein on the synthesis and crystal structure of the title compound.

The title compound, Fig. 1, is found to crystallize as a racemic mixture of enantiomers in the centrosymmetric space group Pbcn. An analysis of the geometry with Mogul [Bruno *et al.*, 2004] using the Cambridge Structural Database [CSD; Allen, 2002] showed a slightly wider C—P—C angle [110.87 (9) °] than average [mean = 106.0(2.2)° of 15 observations] with |z-score| = 2.178. The P—O distance, though not unusual at 1.5529 (14) Å, is slightly longer than average value [mean 1.542 (22) Å of 17 observations] and is similar to that in methyl(phenyl)phosphinic acid [1.5526 (16) Å; Burrow & Siqueira da Silva, 2011*b*].

In the crystal, hydrogen bonding interactions (Table 1 and Fig. 2) of the type OH···O=P—OH···O=P join molecules related by the *b* glide plane into continuous chains along [010]. The short P—O···O=P distance of 2.4931 (19) Å indicates a strong hydrogen bond. This is slightly shorter than the average O···O interaction distance in the CSD [2.51 (5) Å of 60 observations] for other phosphinic acids, but is equal that for methyl(phenyl)phosphinic acid, 2.4838 (18) Å [Burrow & Siqueira da Silva, 2011*b*].

The crystal packing diagram, Fig. 2, shows that the hydrogen bonded chains of the title compound form columns in the crystallographic *b* direction, with the chains alternating direction in the other two dimensions. There are no phenyl-phenyl interactions.

Experimental

To a solution of phenylphosphinic acid (2.0 g, 14.1 mmol) in dichloromethane, diisopropylethylamine (5.16 ml, 29.6 mmol) and trimethylsilyl chloride (3.74 ml, 29.6 mmol) were separately added at 273 K under argon. The reaction mixture was stirred at room temperature for 2–3 h, cooled to 273 K and ethyl iodide (1.25 ml, 19.6 mmol) was added. After further stirring at room temperature for 48 h, the solvent was removed under vacuum. The residue was suspended in hydrochloric acid (2 M, 20 ml) and filtered on a glass frit. The white solid was washed with acetone and dried giving a yield of 0.84 g (35%) of pure product. Crystals suitable for single-crystal X-ray analysis were grown from an acetone solution in a desiccator with silica gel. Spectroscopic and TGA data for the title compound are available in the archived CIF.

Refinement

The H atom on O1 was located in a difference Fourier map and its position was allowed to refine freely with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$. The C-bound H atoms were positioned geometrically and allowed to ride on their parent atoms: C—H = 0.93,

0.97 and 0.97 Å for CH, CH₂ and CH₃ H atoms, respectively, with $U_{eq}(C) = k \times U_{eq}(C)$, where $k = 1.5$ for CH₃ H atoms and $k = 1.2$ for other H atoms.

Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2012); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

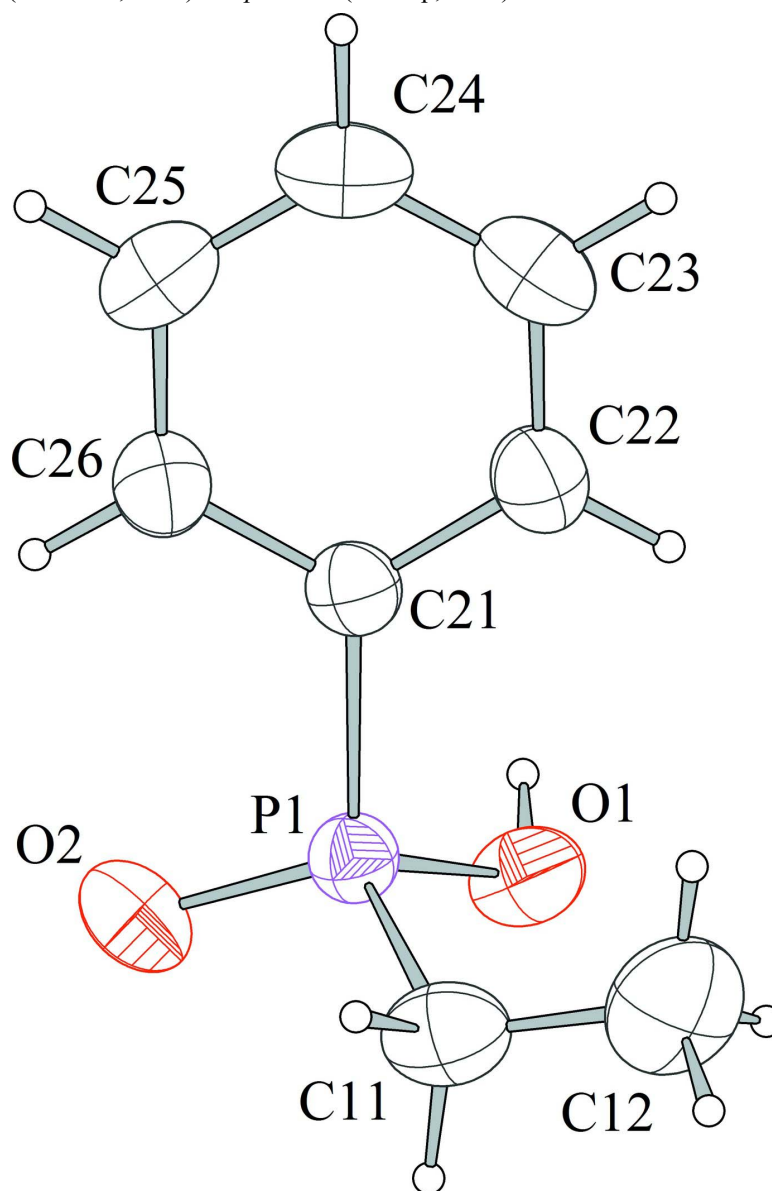
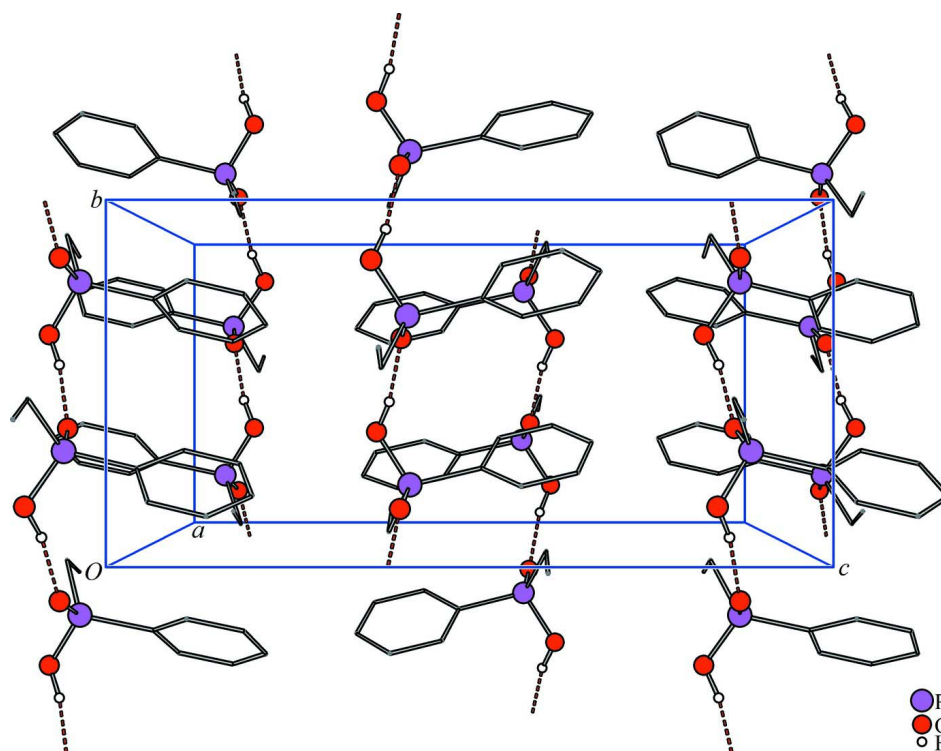


Figure 1

The molecular structure of the title molecule, with the atom numbering. The displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

A perspective view along the *a* axis of the crystal packing of the title compound. The O-H \cdots O hydrogen bonds are shown as dashed lines.

***rac*-Ethyl(phenyl)phosphinic acid**

Crystal data

$C_8H_{11}O_2P$

$M_r = 170.14$

Orthorhombic, *Pbcn*

$a = 13.5314 (16) \text{ \AA}$

$b = 8.0328 (9) \text{ \AA}$

$c = 15.922 (2) \text{ \AA}$

$V = 1730.6 (4) \text{ \AA}^3$

$Z = 8$

$F(000) = 720$

$D_x = 1.306 \text{ Mg m}^{-3}$

Melting point = 336–341 K

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2263 reflections

$\theta = 2.6\text{--}26.5^\circ$

$\mu = 0.27 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Block, colourless

$0.41 \times 0.12 \times 0.11 \text{ mm}$

Data collection

Bruker X8 Kappa APEXII
diffractometer

Radiation source: sealed ceramic X ray tube,
Siemens KFF

Graphite crystal monochromator

Detector resolution: $8.3333 \text{ pixels mm}^{-1}$

$0.5^\circ \omega$ & φ scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2012)

$T_{\min} = 0.906$, $T_{\max} = 0.971$

14069 measured reflections

2650 independent reflections

1499 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

$\theta_{\max} = 30.5^\circ$, $\theta_{\min} = 3.2^\circ$

$h = -19 \rightarrow 19$

$k = -9 \rightarrow 11$

$l = -18 \rightarrow 22$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.128$
 $S = 1.09$
 2650 reflections
 104 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.0622P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. Spectroscopic and TGA data for the title compound:

IR: 1438 (*m*), 1177 (*versus*), 1137 (*s*), 998 (*versus*), 935 (*versus*), 745 (*m*), 718 (*s*), 692 (*versus*), 565 (*m*), 537 (*m*), 495 (*m*) cm^{-1} . TGA: 483 - 603 K; 88% loss.

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
P1	0.31872 (4)	0.19541 (6)	0.40958 (3)	0.03859 (18)
O1	0.34640 (11)	0.35269 (17)	0.35798 (8)	0.0468 (4)
H1	0.3212 (16)	0.444 (3)	0.3780 (15)	0.07*
O2	0.21554 (10)	0.13429 (17)	0.39751 (8)	0.0496 (4)
C11	0.40682 (16)	0.0441 (3)	0.37446 (13)	0.0539 (5)
H11A	0.4004	-0.0541	0.4095	0.065*
H11B	0.3897	0.012	0.3176	0.065*
C12	0.51433 (18)	0.0978 (3)	0.37521 (16)	0.0740 (7)
H12C	0.5222	0.1953	0.341	0.111*
H12A	0.5547	0.0096	0.3533	0.111*
H12B	0.5341	0.1224	0.4318	0.111*
C21	0.33743 (13)	0.2444 (2)	0.51841 (11)	0.0368 (4)
C22	0.41968 (14)	0.3314 (2)	0.54585 (13)	0.0474 (5)
H22	0.4675	0.3645	0.5073	0.057*
C23	0.43146 (16)	0.3697 (3)	0.62986 (14)	0.0584 (6)
H23	0.4868	0.4286	0.6476	0.07*
C24	0.36130 (17)	0.3207 (3)	0.68740 (14)	0.0579 (6)
H24	0.3694	0.3464	0.7439	0.069*
C25	0.28001 (17)	0.2344 (3)	0.66167 (13)	0.0576 (6)
H25	0.2329	0.2012	0.7008	0.069*
C26	0.26725 (15)	0.1960 (2)	0.57756 (12)	0.0466 (5)
H26	0.2115	0.1374	0.5605	0.056*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0484 (3)	0.0289 (3)	0.0386 (3)	0.0015 (2)	-0.0015 (2)	0.0000 (2)
O1	0.0652 (9)	0.0336 (8)	0.0416 (8)	0.0046 (7)	0.0087 (6)	0.0029 (6)
O2	0.0536 (8)	0.0376 (8)	0.0576 (9)	-0.0038 (7)	-0.0134 (7)	-0.0018 (6)
C11	0.0701 (13)	0.0399 (12)	0.0516 (12)	0.0116 (11)	0.0031 (10)	-0.0035 (9)
C12	0.0666 (15)	0.0666 (17)	0.0887 (19)	0.0219 (13)	0.0124 (13)	-0.0028 (14)
C21	0.0423 (10)	0.0295 (9)	0.0386 (9)	0.0002 (8)	0.0005 (7)	0.0011 (8)
C22	0.0479 (11)	0.0445 (12)	0.0498 (12)	-0.0086 (9)	-0.0002 (9)	-0.0006 (9)
C23	0.0613 (14)	0.0576 (14)	0.0563 (13)	-0.0077 (11)	-0.0151 (11)	-0.0097 (11)
C24	0.0732 (16)	0.0599 (15)	0.0405 (11)	0.0076 (12)	-0.0076 (11)	-0.0081 (10)
C25	0.0620 (14)	0.0667 (15)	0.0442 (12)	0.0032 (11)	0.0132 (10)	0.0001 (11)
C26	0.0444 (11)	0.0458 (12)	0.0496 (12)	-0.0047 (9)	0.0028 (8)	-0.0014 (9)

Geometric parameters (\AA , $^\circ$)

P1—O2	1.4925 (14)	C21—C22	1.385 (2)
P1—O1	1.5529 (14)	C21—C26	1.393 (3)
P1—C11	1.792 (2)	C22—C23	1.382 (3)
P1—C21	1.7950 (19)	C22—H22	0.93
O1—H1	0.87 (2)	C23—C24	1.377 (3)
C11—C12	1.517 (3)	C23—H23	0.93
C11—H11A	0.97	C24—C25	1.363 (3)
C11—H11B	0.97	C24—H24	0.93
C12—H12C	0.96	C25—C26	1.385 (3)
C12—H12A	0.96	C25—H25	0.93
C12—H12B	0.96	C26—H26	0.93
O2—P1—O1	115.16 (8)	C22—C21—C26	118.40 (18)
O2—P1—C11	111.05 (10)	C22—C21—P1	121.91 (14)
O1—P1—C11	103.08 (9)	C26—C21—P1	119.69 (14)
O2—P1—C21	109.17 (8)	C23—C22—C21	120.68 (19)
O1—P1—C21	107.36 (8)	C23—C22—H22	119.7
C11—P1—C21	110.87 (9)	C21—C22—H22	119.7
P1—O1—H1	113.5 (16)	C24—C23—C22	120.06 (19)
C12—C11—P1	116.28 (16)	C24—C23—H23	120.0
C12—C11—H11A	108.2	C22—C23—H23	120.0
P1—C11—H11A	108.2	C25—C24—C23	120.1 (2)
C12—C11—H11B	108.2	C25—C24—H24	119.9
P1—C11—H11B	108.2	C23—C24—H24	119.9
H11A—C11—H11B	107.4	C24—C25—C26	120.3 (2)
C11—C12—H12C	109.5	C24—C25—H25	119.8
C11—C12—H12A	109.5	C26—C25—H25	119.8
H12C—C12—H12A	109.5	C25—C26—C21	120.43 (19)
C11—C12—H12B	109.5	C25—C26—H26	119.8
H12C—C12—H12B	109.5	C21—C26—H26	119.8
H12A—C12—H12B	109.5		
O2—P1—C11—C12	174.11 (16)	C26—C21—C22—C23	-0.3 (3)

O1—P1—C11—C12	50.26 (18)	P1—C21—C22—C23	179.01 (16)
C21—P1—C11—C12	-64.34 (19)	C21—C22—C23—C24	0.3 (3)
O2—P1—C21—C22	-168.19 (15)	C22—C23—C24—C25	-0.1 (3)
O1—P1—C21—C22	-42.73 (17)	C23—C24—C25—C26	-0.2 (3)
C11—P1—C21—C22	69.16 (18)	C24—C25—C26—C21	0.2 (3)
O2—P1—C21—C26	11.07 (18)	C22—C21—C26—C25	0.0 (3)
O1—P1—C21—C26	136.53 (16)	P1—C21—C26—C25	-179.28 (15)
C11—P1—C21—C26	-111.58 (17)		

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H1...O2 ⁱ	0.87 (2)	1.64 (2)	2.4931 (19)	168 (2)

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