

Two polymorphs of (2-carboxyethyl)-
(phenyl)phosphinic acidQiao-Sheng Hu, Xiu-Zhi Zhang, Shu-Fen Luo, Yu-Hui Sun
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Received 29 January 2011

Accepted 8 April 2011

Online 5 May 2011

Two polymorphs of (2-carboxyethyl)(phenyl)phosphinic acid, $C_9H_{11}O_4P$, crystallize in the chiral $P2_12_12_1$ space group with similar unit-cell parameters. They feature an essentially similar hydrogen-bonding motif but differ slightly in their detailed geometric parameters. For both polymorphs, the unequivocal location of the hydroxy H atoms together with the expected differences in the P—O bond lengths establish unequivocally that both forms contain the *S* isomer; the protonated phosphinic acid and carboxy O atoms serve as hydrogen-bond donors, while the second phosphinic acid O atom acts as a double hydrogen-bond acceptor and the remaining carboxy O atom is not involved in hydrogen bonding. Thus, an undulating two-dimensional supramolecular layer aggregate is formed based on an $R_4^3(20)$ ring unit. Such polymorphism derives from the rotation of the C—C single bonds between the two hydrogen-bond-involved carboxy and phosphinic acid moieties.

Comment

(2-Carboxyethyl)(phenyl)phosphinic acid (H_2L) is a flame-retardant additive for polymers such as polyesters (Levchik & Weil, 2005). Its related homologue, (carboxymethyl)(phenyl)phosphinic acid, has also been investigated for the

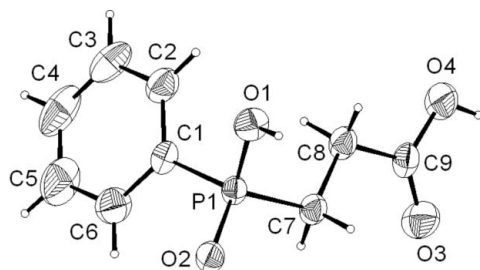
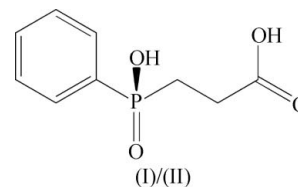


Figure 1

The structure of *S*-configuration polymorph (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The structure of polymorph (II) is very similar to that of polymorph (I).

construction of metal–organic frameworks (Midollini *et al.*, 2005). Such organic molecules feature two polar phosphinic acid and carboxy moieties at both ends of a flexible $-(CH_2)_n-$ spacer ($n = 1$ or 2). Recently, on searching for an efficient asymmetric ligand to induce the formation of noncentrosymmetric structures for metal complexes, we have undertaken research work on the coordination and supramolecular chemistry of (2-carboxyethyl)(phenyl)phosphinic acid. During our initial studies on its crystallization behaviour, we obtained two polymorphs, (I) and (II).



Single-crystal structural determination reveals that both polymorphs crystallize in the chiral space group $P2_12_12_1$. Although a racemic mixture of both *R* and *S* forms might have been expected, the unequivocal location of the hydroxy H atoms together with the expected differences in the P—O bond lengths establish unequivocally that both forms contain the *S* isomer. The Flack values from the refinements [−0.09 (10) for (I) and 0.11 (11) for (II)] are consistent with this. The displacement-ellipsoid drawing of *S*-configuration polymorph (I) is given in Fig. 1.

In the H_2L molecules of (I) and (II), the clear location of the hydroxy H atoms at O1 and O4 in difference maps are entirely consistent with the long P1—O1 bond and the long C9—O4 bond (Tables 1 and 3). The protonated phosphinic acid and carboxy O atoms (O1 and O4) both serve as hydrogen-bond donors, while the second phosphinic acid O atom (O2) acts as a double hydrogen-bond acceptor and the remaining carboxy O atom (O3) is not involved in hydrogen-bond interaction (Table 2). The hydrogen-bond interactions among these H_2L molecules lead to the formation of an

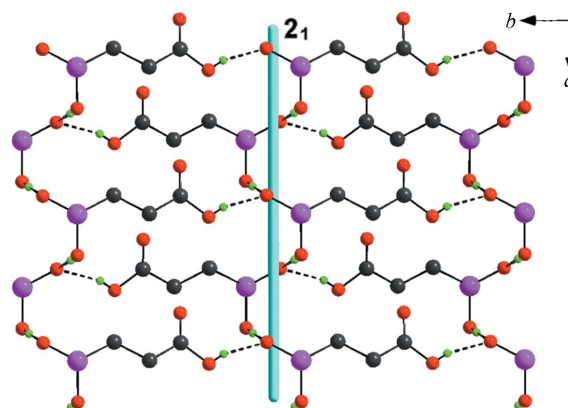
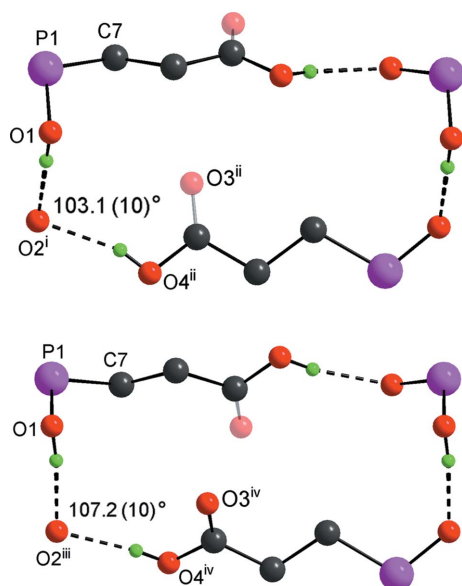
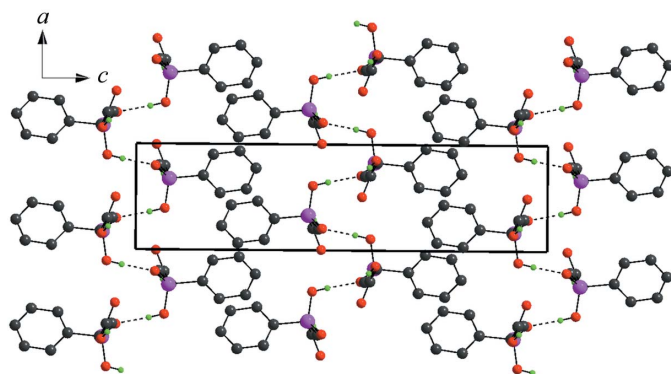


Figure 2

Hydrogen-bond interactions among the (2-carboxyethyl)(phenyl)phosphinic acid molecules in *S*-configuration polymorph (I). Hydrogen bonds are represented by dashed lines. For clarity, the phenyl rings and H atoms attached to C atoms have been omitted. (P, C, O and H atoms are drawn as purple, black, red and green spheres, respectively, in the electronic version of the paper.)


Figure 3

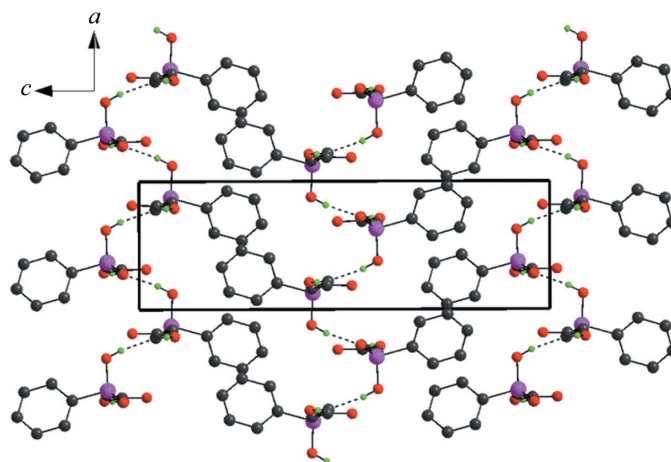
Views of the hydrogen-bond rings of *S*-configuration polymorphs (I) (top) and (II) (bottom). For clarity, the O atoms as well as the C—O bonds attached behind the rings are displayed as translucent. (In the electronic version of the paper, atom labels are coloured as in Fig. 2.) [Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iv) $x + \frac{1}{2}, -y + \frac{3}{2}, -z$.]


Figure 4

View of the structure of *S*-configuration polymorph (I) down the *b* axis.

undulating two-dimensional supramolecular layer aggregate (Fig. 2). The supramolecular layer features a 20-membered ring composed of two H_2L molecules and two phosphinic acid fragments from another two H_2L molecules (Fig. 3), which can be specified as having an $R_4^3(20)$ pattern according to graph-set analysis nomenclature (Bernstein *et al.*, 1995). Adjacent molecules hydrogen bonded *via* $O4-H4B \cdots O2(x, y-1, z)$ are associated by translational symmetry; thus, their phenyl rings are parallel to each other. In contrast, adjacent molecules hydrogen bonded *via* $O1-H1A \cdots O2(x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1)$ are related by 2_1 symmetry, and their phenyl rings are nonparallel with a dihedral angle of $66.31(7)^\circ$. Overall, the undulating supramolecular layers stack along the *c* axis to form a three-dimensional supramolecular architecture (Fig. 4).

The structure of polymorph (II) is similar to that of polymorph (I). As shown in Fig. 3, both polymorphs feature an essentially similar hydrogen-bond motif based on the $R_4^3(20)$


Figure 5

View of the structure of *S*-configuration polymorph (II) down the *b* axis.

pattern, but differ slightly in the detailed geometric parameters (Tables 2 and 4). The attachment of two non-hydrogen-bonding O3 atoms on the $R_4^3(20)$ ring is also different for the two polymorphs: in (II) they are on the same side whereas in (I) they are on opposite sides of the ring. On the whole, the three-dimensional supramolecular architecture of (II) is also similar to that of (I) (Fig. 5). The two polymorphs can be attributed to the two different conformations of the molecule, resulting from the rotation of the C—C single bonds between the two hydrogen-bond-involved carboxy and phosphinic acid groups; the rotation around the C—C single bonds is also regulated by the hydrogen-bonding interaction.

Experimental

(2-Carboxyethyl)(phenyl)phosphinic acid was synthesized according to a published procedure (Birum & Jansen, 1978). A portion (0.08 g) was dissolved in distilled water (12 ml) by heating and stirring, with the addition of two drops of 10% HCl solution. The resulting solution was then left to stand at room temperature. About a week later, plate-shaped crystals formed. The structure of (I) indicated formation of a racemic mixture, so an attempt was made to select a crystal of the opposite enantiomer. The surprising result was the discovery of the second dimorph, (II). Since crystals of the two polymorphs have very similar shapes, it is hard to distinguish them by appearance.

Polymorph (I)

Crystal data

$C_9H_{11}O_4P$	$V = 1019.71(3) \text{ \AA}^3$
$M_r = 214.15$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 5.4948(1) \text{ \AA}$	$\mu = 0.26 \text{ mm}^{-1}$
$b = 8.6830(1) \text{ \AA}$	$T = 296 \text{ K}$
$c = 21.3724(4) \text{ \AA}$	$0.30 \times 0.20 \times 0.10 \text{ mm}$

Table 1

Selected bond lengths (\AA) for polymorph (I).

P1—O2	1.5010 (14)	C9—O3	1.200 (3)
P1—O1	1.5605 (16)	C9—O4	1.321 (3)

Table 2

Hydrogen-bond geometry (Å, °) for polymorph (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1A\cdots O2^i$	0.81 (1)	1.76 (1)	2.5699 (18)	177 (3)
$O4-H4B\cdots O2^{ii}$	0.82 (1)	1.90 (1)	2.6925 (19)	162 (3)

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

Selected bond lengths (Å) for polymorph (II).

P1–O2	1.5087 (15)	C9–O3	1.203 (2)
P1–O1	1.5527 (17)	C9–O4	1.331 (3)

Table 4

Hydrogen-bond geometry (Å, °) for polymorph (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1A\cdots O2^i$	0.81 (1)	1.77 (1)	2.566 (2)	169 (3)
$O4-H4B\cdots O2^{ii}$	0.82 (1)	1.85 (1)	2.658 (2)	169 (3)

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (ii) $x, y + 1, z$.**Data collection**

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.673, T_{\max} = 0.746$

5497 measured reflections
2326 independent reflections
2089 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.087$
 $S = 1.05$
2326 reflections
133 parameters
2 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.24 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{Å}^{-3}$
Absolute structure: Flack (1983), 893 Friedel pairs
Flack parameter: -0.09 (10)

Polymorph (II)**Crystal data**

$C_9H_{11}O_4P$
 $M_r = 214.15$
Orthorhombic, $P2_12_12_1$
 $a = 6.1741$ (15) Å
 $b = 8.7308$ (19) Å
 $c = 19.844$ (4) Å

$V = 1069.7$ (4) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.24 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 $0.34 \times 0.16 \times 0.14 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.679, T_{\max} = 0.746$

5593 measured reflections
2422 independent reflections
1977 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.090$
 $S = 1.03$
2422 reflections
133 parameters
2 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.18 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{Å}^{-3}$
Absolute structure: Flack (1983), 989 Friedel pairs
Flack parameter: 0.11 (11)

C-bound H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C–H distances of 0.93 or 0.97 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. O-bound H atoms were located in a difference map and refined with $U_{\text{iso}}(\text{H})$ values set at $1.2U_{\text{eq}}(\text{O})$. The O–H distances were restrained to be 0.82 (1) Å.

For both compounds, data collection: SMART (Bruker, 2008); cell refinement: SMART; data reduction: SAINT (Bruker, 2008); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXTL (Bruker, 2008).

This work was supported by the NNSF of China (grant No. 21061001), the NSF of Jiangxi Province (grant No. 2008GQH0013) and the NSF of Jiangxi Provincial Education Department (grant No. GJJ10714).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3148). Services for accessing these data are described at the back of the journal.

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