

## A second polymorph of bis(dimethylphosphino)dimethylphosphonium trifluoromethanesulfonate

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Received 24 January 2007

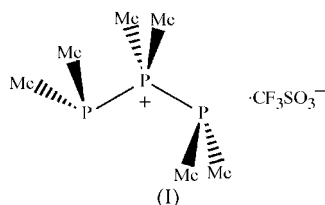
Accepted 8 February 2007

Online 28 February 2007

The title compound,  $C_6H_{18}P_3^+ \cdot CF_3SO_3^-$ , crystallizes in two polymorphic forms in the space groups  $P2_1/c$  and  $Pnma$ . In the orthorhombic form, the two crystallographically independent molecular units lie across a crystallographic mirror plane. The compound lacks traditional hydrogen-bond donors and, hence, is held together by weak  $C-H \cdots O$  and  $C-H \cdots F$  interactions, forming layers. The second polymorph was obtained as a by-product from the reaction of 1,3-bis(2,6-dimethylphenyl)-2,4-ditriflate-1,3,2,4-diazadiphosphetidine with tetramethyldiphosphine.

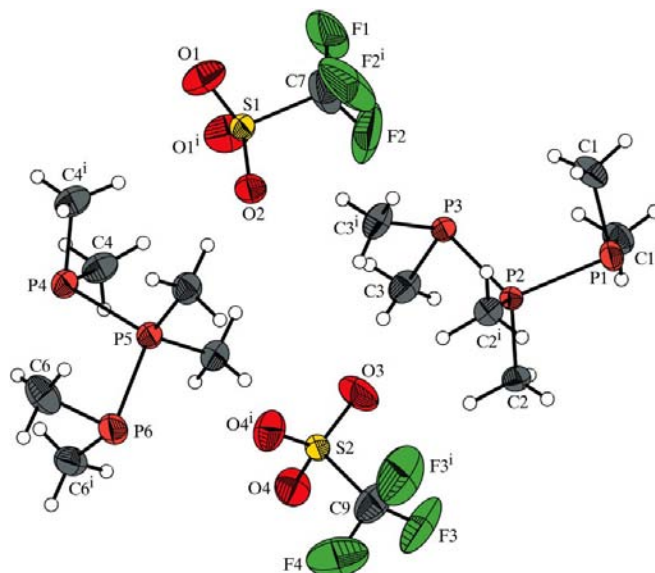
### Comment

P-Donor ligands on  $P^{III}$  systems have recently become pivotal in the development of molecular main-group coordination chemistry. These donor–acceptor interactions are recognized as ‘homoatomic’ coordination complexes in inter- and intramolecular phosphine–phosphonium complexes and are essentially unique to phosphorus (Burford *et al.*, 2003). Facile synthetic methods for the diversification of *catena*-polyphosphorus cations yielded a series of new organo-substituted diphosphinophosphonium and cyclotetraphosphinodiphosphonium cations (Weigand *et al.*, 2006). Recently, we reported the crystal structure of *catena*-hexamethyldiphosphinophosphonium trifluoromethanesulfonate, which crystallizes in

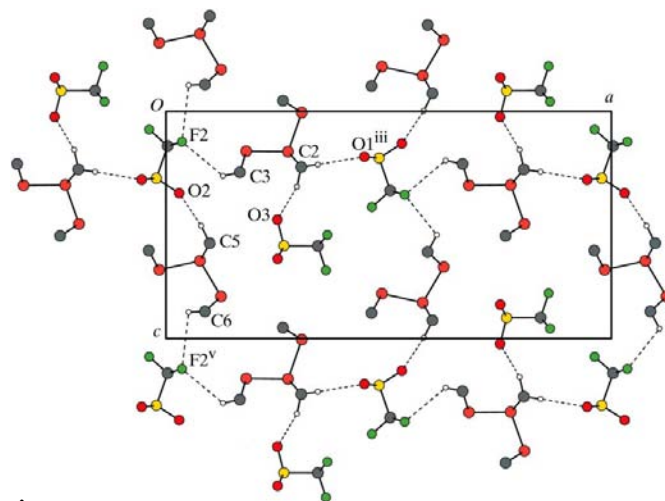


the monoclinic crystal system  $P2_1/c$  (Burford *et al.*, 2005). During our further investigation, we obtained a second polymorph of the title compound, (I), by chance, as a by-product from the reaction of 1,3-bis(2,6-dimethylphenyl)-2,4-ditriflate-1,3,2,4-diazadiphosphetidine with tetramethyldiphosphine.

The orthorhombic polymorph crystallizes with two half-formula units in the asymmetric unit. A view of the molecular structure along with the numbering scheme is depicted in Fig. 1. X-ray investigation has shown that the bond lengths in (I) do not significantly differ from those found in the monoclinic polymorph. The same unusual eclipsed/staggered conformation (local molecular symmetry  $C_s$ ) of the cation is observed. The geometry of the trifluoromethanesulfonate anions in (I) are in accordance with that previously determined (You & Zhu, 2004). The interatomic distances and bond angles in the two independent ion pairs are almost identical, and selected molecular parameters of the cations are



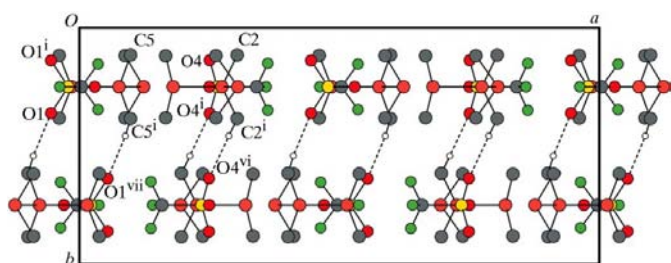
**Figure 1**  
A view of the molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of an arbitrary radius. [Symmetry code: (i)  $x, -y + \frac{1}{2}, z$ .]



**Figure 2**  
The arrangement of the ions of (I), viewed along the [010] axis. The weak  $C-H \cdots O$  and  $C-H \cdots F$  interactions are represented by dashed lines. H atoms not involved in these interactions have been omitted for clarity. [Symmetry codes: (iii)  $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$ ; (v)  $x, -y + \frac{1}{2}, z + 1$ .]

presented in Table 1. The cations and anions lie across a crystallographic mirror plane passing through atoms P1–P6, S1, S2, C7 and C9.

Compound (I) lacks traditional hydrogen-bond donor groups; hence, the structure is stabilized by weak C–H···O and C–H···F interactions (Table 2). These C–H···O hydrogen bonds (C2–H4···O3, C2–H6···O1<sup>iii</sup> and C5–H14···O2; symmetry codes and geometric parameters are given in Table 2) account for the observation of subunits consisting of two cations and two anions, and, together with the weak C–H···F interactions (C3–H8···F2 and C6–H16···F2<sup>v</sup>; Table 2), form two-dimensional sheets (Fig. 2). The two hydrogen bonds found between these sheets (C2–H5···O4<sup>ii</sup> and C5–H13···O1<sup>iv</sup>; Table 2) are the main contributors that lead to a lateral packing of the layers. The resulting layers are arranged in an antiparallel manner (*ABA* layer sequence), which is compatible with the space group *Pnma* (Fig. 3). In the case of the monoclinic polymorph, a lateral packing of layers is found, similar to that of the orthorhombic polymorph. However, the layers are composed of alternating strands of cations and anions running along the *c* axis, stabilized by weak C–H···O and C–H···F interactions.



**Figure 3**  
The arrangement of the ions of (I), viewed along the [001] axis. The weak C–H···O interactions between the sheets are represented by dashed lines. H atoms not involved in these interactions have been omitted for clarity. [Symmetry codes: (i)  $x, -y + \frac{1}{2}, z$ ; (vi)  $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$ ; (vii)  $-x, y + \frac{1}{2}, -z + 1$ .]

## Experimental

All manipulations were performed under an inert atmosphere of dinitrogen. A solution of tetramethyldiphosphine (126 mg, 1 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 ml) was added to a  $\text{CH}_2\text{Cl}_2$  solution (3 ml) of 1,3-bis(2,6-dimethylphenyl)-2,4-ditriflato-1,3,2,4-diazadiphosphetidine (300 mg, 0.5 mmol), leading to the formation of a bright-yellow solution. Addition of  $\text{Et}_2\text{O}$  resulted in the formation of a bright-yellow precipitate. Compound (I) was obtained as colorless needles from vapor diffusion of  $\text{Et}_2\text{O}$  into a  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  solution of the yellow precipitate amidst copious amounts of an oily yellow material of unknown constitution. The analytical data are in agreement with those reported previously (Burford *et al.*, 2005).

### Crystal data

$\text{C}_6\text{H}_{18}\text{P}_3^+\cdot\text{CF}_3\text{SO}_3^-$	$V = 3043.9$ (2) Å <sup>3</sup>
$M_r = 332.19$	$Z = 8$
Orthorhombic, <i>Pnma</i>	Mo $K\alpha$ radiation
$a = 23.5972$ (7) Å	$\mu = 0.55$ mm <sup>-1</sup>
$b = 10.7419$ (4) Å	$T = 123.1$ K
$c = 12.0086$ (4) Å	$0.40 \times 0.17 \times 0.12$ mm

### Data collection

Rigaku R-AXIS diffractometer	2682 reflections with $F^2 > 2\sigma(F^2)$
25123 measured reflections	$R_{\text{int}} = 0.080$
6230 independent reflections	

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	193 parameters
$wR(F^2) = 0.063$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\text{max}} = 1.08$ e Å <sup>-3</sup>
2682 reflections	$\Delta\rho_{\text{min}} = -0.62$ e Å <sup>-3</sup>

**Table 1**  
Selected geometric parameters (Å, °).

P1–P2	2.190 (2)	P4–P5	2.211 (2)
P2–P3	2.214 (1)	P6–C6	1.828 (4)
P1–C1	1.842 (4)	P5–C5	1.797 (4)
P2–C2	1.793 (3)	P4–C4	1.839 (4)
P3–C3	1.830 (4)	F1–C7	1.313 (8)
P5–P6	2.187 (2)	F2–C7	1.299 (7)
P1–P2–P3	108.77 (6)	P4–P5–P6	108.17 (7)
P1–P2–C2	107.3 (1)	C5–P5–P6	107.6 (1)
P2–P3–C3	100.2 (1)	C4–P4–P5	100.1 (1)
C1–P1–P2	98.4 (1)	P5–P6–C6	98.1 (1)
C2–P2–P3	113.2 (1)	P4–P5–C5	113.2 (1)
C1 <sup>i</sup> –P1–C1	100.3 (2)	C6 <sup>i</sup> –P6–C6	101.6 (2)
C2 <sup>i</sup> –P2–C2	106.9 (2)	C5 <sup>i</sup> –P5–C5	106.7 (2)
C3 <sup>i</sup> –P3–C3	100.4 (2)	C4 <sup>i</sup> –P4–C4	101.5 (2)

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

**Table 2**  
Hydrogen-bond 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>
C2–H4···O3	0.95	2.56	3.380 (5)	145
C2–H5···O4 <sup>ii</sup>	0.95	2.27	3.222 (5)	177
C2–H6···O1 <sup>iii</sup>	0.95	2.46	3.402 (4)	173
C5–H13···O1 <sup>iv</sup>	0.95	2.31	3.258 (5)	173
C5–H14···O2	0.95	2.60	3.429 (5)	146
C3–H8···F2	0.95	2.77	3.491 (5)	134
C6–H16···F2 <sup>v</sup>	0.95	2.73	3.295 (5)	119

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

H atoms were located in a difference Fourier map and their coordinates were refined as riding [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ]. The data set for (I) was truncated at  $2\theta = 60^\circ$  as only statistically insignificant data were present above this limit.

Data collection: *PROCESS* (Rigaku, 1996); cell refinement: *PROCESS*; data reduction: *CrystalStructure* (Rigaku/MSK, 2004); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *CrystalStructure*.

We thank the Natural Sciences and Engineering Research Council of Canada, the Killam Foundation, the Canada Research Chairs Program and the Alexander von Humboldt-Stiftung (Humboldt Fellowship for JJW, Lynen program) for funding.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3074). Services for accessing these data are described at the back of the journal.

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