

Hydrogen bonding and short contacts in [2,4,6-tris(trifluoromethyl)phenyl]phosphinic acid

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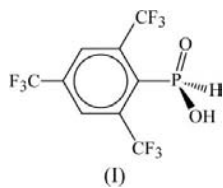
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In the title compound, C₉H₄F₉O₂P, molecules are linked by a single O—H···O hydrogen bond into chains related to those in phenylphosphinic acid. There are short intramolecular F···P contacts.

Comment

Several group 15 halides containing the 2,4,6-tris(trifluoromethyl)phenyl (*Ar*) ligand have been described, some of which have been characterized crystallographically, including phosphorus, arsenic, antimony and bismuth compounds (Batsanov *et al.*, 2002; Burford *et al.*, 2000; Whitmire *et al.*, 1991). Although the compound *Ar*PCL₂ has been synthesized and characterized by ³¹P and ¹⁹F NMR spectroscopy (Dillon *et al.*, 1988; Scholz *et al.*, 1989), single crystals have not been isolated so far; however, the hydrolysis product [2,4,6-tris(trifluoromethyl)phenyl]phosphinic acid, *Ar*P(O)H(OH), (I), has now been crystallized. This compound is believed to be formed by rearrangement of the initial phosphorus(III) hydrolysis product *Ar*P(OH)₂ to the more stable phosphorus(V) form, with a P=O double bond and a P—H bond as, for example, in phosphorous acid, H₃PO₃, which has the structure P(O)H(OH)₂ in solution and which behaves as a dibasic rather than as a tribasic acid.



Compound (I) (Fig. 1) crystallizes in the noncentrosymmetric space group *P*2₁ and shows signs of inversion twinning: the Flack *x* parameter (Flack, 1983) refined to 0.24 (16), although analysis of the Bijvoet differences using *PLATON*

(Spek, 2009) gave the Hooft *y* parameter as 0.16 (8), indicating that the probability that the configuration is correct is greater than 0.999 and the probability of an inversion twin is 8×10^{-4} (Hooft *et al.*, 2008). Each P—OH group is hydrogen bonded to the O=P group of an adjacent molecule (Table 1), forming a chain along [010] (Fig. 2). This hydrogen-bonding motif is similar to that seen in phenylphosphinic acid (Burrow *et al.*, 2000), although the chains in (I) propagate along a 2₁ screw axis, whereas in phenylphosphinic acid the chains are propagated along the *a* axis by glide planes. The chains in (I) pack together to form a herring-bone-type motif around the 2₁ axes, which leads to short intermolecular F···F contacts [2.870 (4)–2.926 (4) Å] and may perhaps explain why the *p*-CF₃ group, although displaying slightly elevated anisotropic displacement parameters, appears to be less mobile than observed in many related materials (Batsanov *et al.*, 2002, 2003; Cornet *et al.*, 2003).

The hydrogen-bonded O···O distance in (I) is comparable with those in phenylphosphinic acid, ethylenebis(phosphinic acid) and methylenebis(phosphinic acid), and also in the 1:1 mixture of [2-(diphenylphosphino)phenyl]phosphinic acid and its dimethylammonium salt (Table 2; Burrow *et al.*, 2000; Bruckmann *et al.*, 1999; King *et al.*, 1986; Kottsieper *et al.*, 2001), and corresponds to a strong hydrogen bond. Slightly

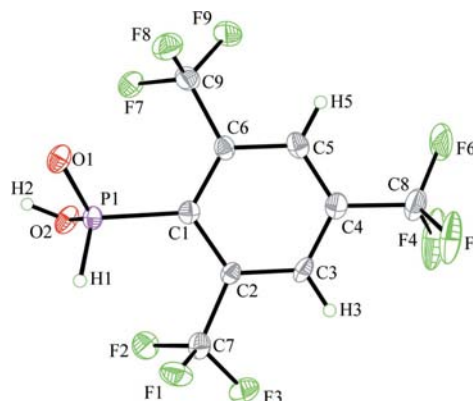


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

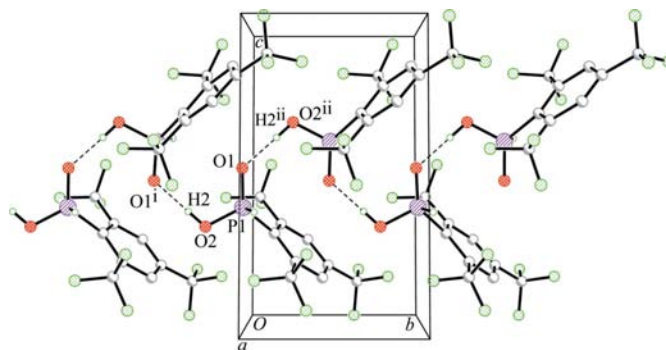
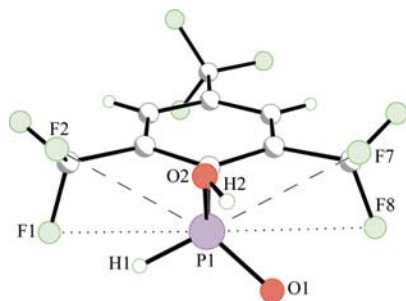


Figure 2

A hydrogen-bonded chain in (I). For the sake of clarity, H atoms bonded to C atoms have been omitted, but the H atom bonded to P is included. [Symmetry codes: (i) $1 - x, -\frac{1}{2} + y, 1 - z$; (ii) $1 - x, \frac{1}{2} + y, 1 - z$.]


Figure 3

The intramolecular F...P interactions in (I). The stronger interactions are shown with broken lines and the longer distances are shown with dotted lines.

longer O...O contacts, between 2.62 and 2.69 Å, were found in $\{[C_5H_5NH]^+[PhP(O)(H)O]^- \}_2 \cdot 3F_3CC(OH)_2CF_3$ (Goerlich *et al.*, 1995); the P=O and P—O bond lengths are also comparable with those in these phosphinic acids (Table 2).

Another interesting feature of the structure is the existence of short intramolecular contacts between two F atoms, in particular (F2 and F7) of the *o*-CF₃ groups, and the P atom, at distances of 2.922 (2) and 2.915 (2) Å, respectively (Fig. 3). This is appreciably shorter than the sum of the empirical van der Waals radii of P (1.91 Å) and F (1.40 Å) (Zefirov & Zorkii, 1989), as well as of the theoretical radii, estimated as 2.05 and 1.42 Å, respectively (Franck *et al.*, 1984). The next nearest F atoms, F1 and F8, are at 3.356 (2) and 3.5341 (2) Å, respectively, from the P atom and would thus not appear to have significant interactions. Short P...F contacts, between 2.843 and 3.250 Å, have been found previously in other arylphosphorus compounds with one or two *o*-CF₃ groups on the aromatic ring (see Table 3).

Similar short E—F distances have been reported in the 2,4,6-(CF₃)₃C₆H₂ (*Ar*), 2,6-(CF₃)₂C₆H₃ (*Ar'*) and 2,4-(CF₃)₂-C₆H₃ [*Ar''*; *o*-(CF₃) group only] derivatives of elements in group 14 (Si, Ge, Sn and Pb; Grützmacher *et al.*, 1991, 1992, 1994; Brooker *et al.*, 1991; Lay *et al.*, 1992; Buijink *et al.*, 1993; Grützmacher & Pritzkow, 1993; Vij *et al.*, 1994; Van der Maelen Uría *et al.*, 1994; Braddock-Wilking *et al.*, 1995; Freitag *et al.*, 1995; Bender *et al.*, 1997, 1998, 1999; Klinkhammer *et al.*, 1998), group 15 (As and Sb, as well as P; Burford *et al.*, 2000; Batsanov *et al.*, 2002; Cornet *et al.*, 2004), group 16 [Se and Te (Voelker *et al.*, 1999); Zn, Cd and Hg (Brooker *et al.*, 1992); Li (Stalke & Whitmire, 1990); B (Toyota *et al.*, 2000; Cornet *et al.*, 2003)].

They have also been reports of similar derivatives of V (Gibson *et al.*, 1996), Cr (Batsanov, Dillon *et al.*, 2001), Mo (Dillon *et al.*, 1997; Batsanov, Dillon *et al.*, 2001) and Ni (Benedikt *et al.*, 2001), although the M—F distances in Pd^{II} derivatives (Bartolomé *et al.*, 1996), and in Au^I and Au^{III} compounds (Espinet *et al.*, 2000) were considered to be essentially nonbonding. In systems where such short contacts have been found, they have generally been regarded as contributing to the overall stabilities of the species concerned, and that is expected to be true for the title compound. There are also the following short contacts in the title

compound: F1...H1 [2.46 (4) Å], F2...H1 [2.44 (3) Å], F2...O2 [2.944 (3) Å], F7...O1 [2.766 (3) Å] and F7...O2 [2.978 (4) Å].

Experimental

Crystals of the title compound were obtained by slow hydrolysis of a solution of *Ar*PCL₂ (Dillon *et al.*, 1988; Scholz *et al.*, 1989) in a CH₂Cl₂/CDCl₃ mixture in an NMR tube. NMR: δ(H) 8.21 (*s*, aromatic C—H), 8.06 (*d*, ¹J_{PH} = 618 Hz, H—P), 5.90 (*s, br*, HO—P); δ(F) −55.9 (*d*, ⁴J_{PF} = 6.4 Hz, *o*-CF₃), −64.1 (*s, p*-CF₃); δ(P) 14.0 (*d*, ¹J_{PH} = 625 Hz). The ³¹P NMR data are very similar to those recorded for 2,6-(CF₃)₂C₆H₃PH(O)OH [δ(P) 9.50 (*d*, ¹J_{PH} = 600 Hz); Karlstedt *et al.*, 1992]; comparable values have also been reported for MePH(O)OH [δ(P) 35.0 (*d*, ¹J_{PH} = 557 Hz); Gallagher, 1991], PhPH(O)OH [δ(P) 20 (*d*, ¹J_{PH} = 560 Hz); Gallagher, 1991] and 2,4,6-^tBu₃C₆H₂PH(O)OH [δ(P) 25.7 (*d*, ¹J_{PH} = 576 Hz); Yoshifuji *et al.*, 1983].

Crystal data

C ₉ H ₄ F ₉ O ₂ P	V = 582.60 (12) Å ³
M _r = 346.09	Z = 2
Monoclinic, P2 ₁	Mo Kα radiation
a = 8.3240 (10) Å	μ = 0.36 mm ^{−1}
b = 6.3744 (8) Å	T = 120 (2) K
c = 11.0384 (13) Å	0.49 × 0.12 × 0.06 mm
β = 95.898 (2)°	

Data collection

Bruker SMART CCD 1K area-detector diffractometer	6410 measured reflections
Absorption correction: integration (XPREP in SHELXTL; Sheldrick, 2008)	2828 independent reflections
T _{min} = 0.874, T _{max} = 0.978	2293 reflections with I > 2σ(I)
	R _{int} = 0.041

Refinement

R[F ² > 2σ(F ²)] = 0.051	H atoms treated by a mixture of independent and constrained refinement
wR(F ²) = 0.107	Δρ _{max} = 0.48 e Å ^{−3}
S = 1.05	Δρ _{min} = −0.54 e Å ^{−3}
2828 reflections	Absolute structure: Flack (1983), 1258 Friedel pairs
199 parameters	Flack parameter: 0.24 (16)
1 restraint	

Table 1

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O2—H2...O1 ⁱ	0.84 (5)	1.68 (5)	2.509 (4)	168 (5)

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

Table 2

Selected distances with literature values (Å).

Compound	O...O	P=O	P—O
<i>Ar</i> P(O)H(OH), (I)	2.509 (4)	1.482 (2)	1.541 (3)
Phenylphosphinic acid ^a	2.513 (3)	1.4933 (19)	1.556 (2)
Ethylenebis(phosphinic acid) ^b	2.511 (3)	1.4871 (16)	1.5501 (18)
Methylenebis(phosphinic acid) ^c	2.512 (2)	1.488 (1)	1.547 (1)
	2.508 (2)	1.492 (1)	1.542 (1)
[2-(Diphenylphosphino)phenyl]-phosphinic acid ^d	2.430	1.470 (2)	1.514 (2)

Notes: literature data from (a) Burrow *et al.* (2000); (b) Bruckmann *et al.* (1999); (c) King *et al.* (1986); (d) Kottsieper *et al.* (2001).

Table 3

Short P...F contacts (Å).

P1 and P2 are the P atoms from the two independent molecules in the asymmetric unit.

Compound	Range	No. of contacts
$ArPBr_2^a - P1$	2.865–3.208	3
$ArPBr_2^a - P2$	2.877–3.217	3
Ar_2PCl^a	2.843–3.111	5
$Ar^*_2PCl^a$	2.874–3.124	3
$Ar^*_2PBr^a$	2.887–3.122	3
$Ar^*Ar^*PCl_2^b$	2.890–3.250	4

Notes: literature data from (a) Batsanov *et al.* (2002); (b) Batsanov, Cornet *et al.* (2001).

H atoms bonded to C atoms were treated as riding atoms, with C–H distances of 0.93 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. The two other H atoms were freely refined, giving distances O–H = 0.84 (5) Å and P–H = 1.28 (4) Å.

Data collection: *SMART-NT* (Bruker, 2000); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3280). Services for accessing these data are described at the back of the journal.

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