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The first crystal and molecular structures of hydrated bis(n-perfluoroalkyl)phosphinic acids $[H_3O]^+[(R_f)_2PO_2]^-$ ($R_f = C_6F_{13}$, C_7F_{15} or C_8F_{17})

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Received 5th June 2000, Accepted 22nd September 2000
First published as an Advance Article on the web 30th October 2000

The first crystal and molecular structures of hydrated bis(n-perfluoroalkyl)phosphinic acids, $[H_3O]^+[(R_f)_2PO_2]^-$ ($R_f = C_6F_{13}$, C_7F_{15} or C_8F_{17}), have been determined by single crystal X-ray diffraction. $[H_3O]^+[(C_6F_{13})_2PO_2]^-$ **1** and $[H_3O]^+[(C_7F_{15})_2PO_2]^-$ **2** crystallize in the triclinic space group ($P\bar{1}$) and $[H_3O]^+[(C_8F_{17})_2PO_2]^-\cdot Me_2CO$ **3** crystallizes in the orthorhombic space group *Pca2*(1). In each case the phosphorus atom is tetrahedral and the perfluoroalkyl chains have a zigzag planar conformation. The structures consist of infinite sheets of the perfluoroalkyl phosphinate held together by hydrogen bonding with the counter ion H_3O^+. In compound **3** the additional solvent molecule participates in extended donor–acceptor bonding and helps to expand the three dimensional structure. Some close contacts between two atoms of two different molecules were also observed.

Introduction

Perfluoroalkyl phosphorus compounds have attracted attention due to their potential applications as electrolytes with good cell characteristics and in plastic optical fibers for data communications. Several surface and other applications of phosphinic acids have also been claimed.[1–4] Owing to non-polarizable properties that fluorine brings to chemical bonds, perfluoroalkyl compounds tend to display lower boiling and melting points compared to their corresponding non-fluorinated analogues. In general, solid compounds having longer perfluoroalkyl chains are difficult to crystallize. The non-fluorine-containing bis(n-alkyl)phosphinic acids have been known for a long time and their structures were investigated by X-ray crystallography.[5–7] As part of a series of investigations on bis(n-perfluoroalkyl)phosphinic acids we reported the synthesis of C_2 perfluoroalkyl-substituted phosphinic acids as well as new routes to the previously known C_1 and C_4 acids which are liquids.[8] Recently we achieved the synthesis of phosphinic acids with longer chain perfluoroalkyl groups (*e.g.* C_6F_{13}, C_7F_{15}, C_8F_{17}).[9] These compounds are high melting solids. Since there are no single crystal structures of bis(n-perfluoroalkyl)-phosphinic acids, we now report the first structures of these materials as hydrates, $[H_3O]^+[(R_f)_2PO_2]^-\cdot$solvent ($R_f = C_6F_{13}$, solvent = none **1**; $R_f = C_7F_{15}$, solvent = none **2**; $R_f = C_8F_{17}$, solvent = acetone **3**).

Results and discussion

Compounds **1**–**3** were prepared by the oxidation of $(R_f)_2PI$ ($R_f = C_6F_{13}$, C_7F_{15} or C_8F_{17}) with an excess of NO_2 and followed by aqueous hydrolysis.[9] They are colourless solids and are only slightly soluble in halogenated solvents. However, they are soluble in acetone and fluorinated solvents such as 1,1,2-trichlorotrifluoroethane and can be crystallized from a mixture of acetone and pentane. The hydrates are easily formed during the course of crystallization. The detailed synthetic procedure and spectral characterization data have been reported elsewhere.[9]

The presence of the H_3O^+ group in addition to highly electronegative elements, such as F and O in bis(n-perfluoroalkyl)-phosphinic acids, gives rise to a variety of possible intermolecular hydrogen bonded structures. Prior infrared spectroscopic studies on the anhydrous phosphinic acids clearly show $\nu_{P=O}$ at ≈1365 cm^{-1}.[9] With compounds **1**–**3** the latter has decreased to 1283 cm^{-1}. This indicates a delocalization of the charge over the O–P–O array and the presence of hydrogen bonding. To clarify the extent and nature of this bonding we have used single crystal structure analysis to determine the exact conformation of the molecules in the solid state. The crystal structures of **1**–**3** are shown in Figs. 1–3 and selected bond lengths and angles are given in Table 1. In all the three cases the phosphorus configuration is tetrahedral as expected. The average P–C bond length is 1.87 Å and the P–O bond distances are approximately equal (*ca.* 1.48 Å). This is due to the delocalized nature of the negative charge. The perfluoroalkyl chains exhibit a common zigzag pattern. The mean C–C bond length is 1.53 Å and the mean C–C–C angle 116°. The O–P–O bond angle averages *ca.* 121°. Comparison of the X-ray crystallographic data with those of some non-fluorinated anhydrous phosphinic acids[6,7] such as $(CH_3)_2PO(OH)$ **4** and $(C_9H_{19})_2PO(OH)$ **5**, shows small but significant differences in the bond lengths and angles associated with the PO_2C_2 core (Table 2). In **1**–**3** the average P–O bond lengths are *ca.* 0.04 and 0.05 Å shorter than those in **4** (1.52) and **5** (1.53 Å). The average P–C bond length (ca. 1.87 Å) is larger than that found in **4** or **5** (1.77 Å). The average O–P–O bond angle (121°) is also greater than that in both **4** and **5** (112.7 and 113.1°, respectively). These differences can be attributed to the presence of hydrogen bonding and the high electronegativity of the perfluoroalkyl groups. The crystal structure of a perfluorinated aryl phosphinate, $[H_3O]^+[(C_6F_5)_2PO_2]^-$ **6**, has been reported[11] and the P–O and P–C bond distances are basically identical to those seen in compounds **1**–**3** (Table 2). The O–P–O bond angle in **6**, at 117°, is smaller than those in **1**–**3**. These results indicate the higher electronegativity of perfluoroalkyl *vs.* perfluoroaryl substituents. Bond distances and angles in **1**–**3** and the C-amino-substituted phosphaallyl compound, $[(Me_2N)_2C]_2PO_2$ **7** (P–O 1.48, P–C 1.88 Å and O–P–O 122.5°), are very similar (Table 2).[12]

In compounds **1**–**3** the crystals are built up from infinite chains of parallel molecules held together by O–H···O hydrogen bonds. Compound **1** crystallizes with two molecules in the asymmetric unit with two H_3O^+ molecules between the

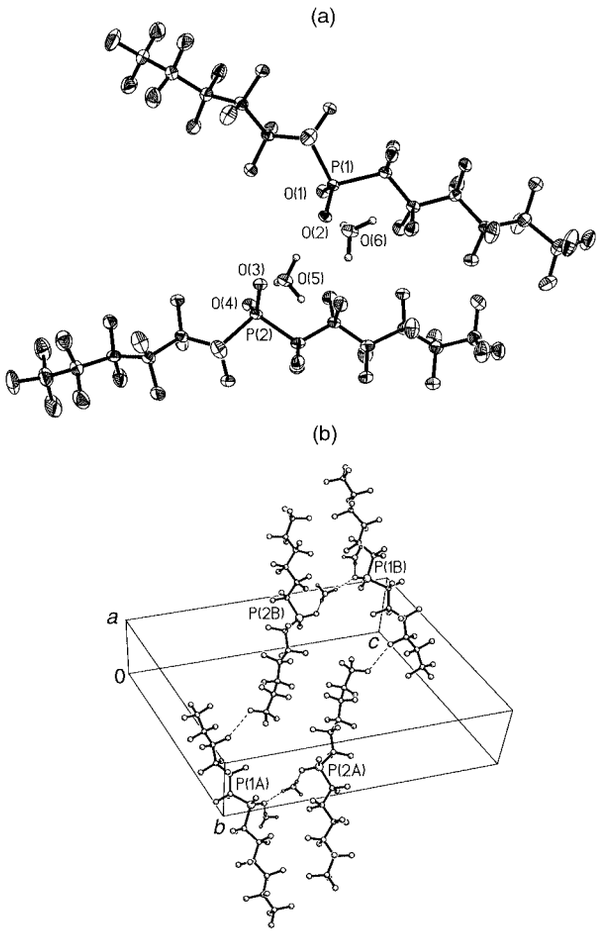

Fig. 1 (a) An ORTEP[10] drawing of compound **1** with thermal ellipsoids at 30% probability level; (b) crystal packing diagram for **1** showing intermolecular interactions.

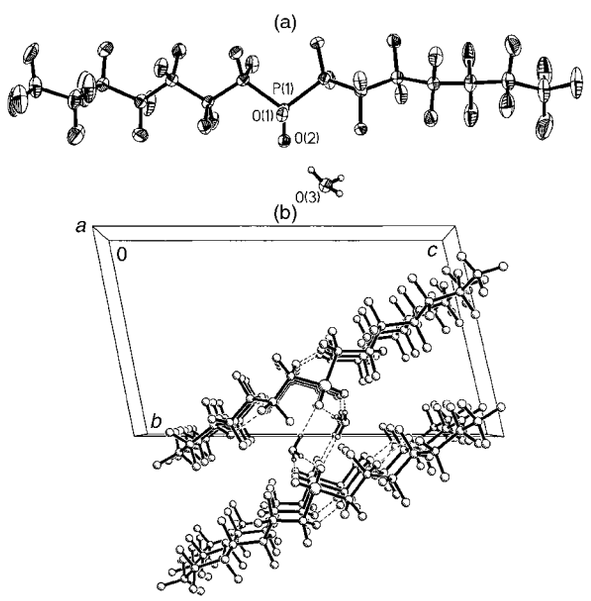

Fig. 2 (a) An ORTEP drawing of compound **2**; (b) crystal packing diagram for **2**. Details as in Fig. 1.

perfluorophosphinates. Hydrogen bonding links two groups of perfluorophosphinate molecules perpendicular to the *a* axis with an average O–H · · · O distance of *ca.* 1.68 Å forming an infinite one dimensional chain. There is considerable space between these two molecules. The packing diagram (Fig. 1b) shows that the perfluorophosphinate molecules of another linked unit interpenetrate giving rise to F · · · F close contacts (2.697(6) to 3.133(5) Å). Compound **2** crystallizes in the same space group as that of **1**; however, it has only one molecule of the perfluorophosphinate and one H_3O^+ in the asymmetric unit. In spite of this the packing diagram (Fig. 2b) shows that **2** also has the same structural motif displayed by **1**, *i.e.* two layers of perfluorophosphinates linked by hydrogen bonding to form an infinite chain perpendicular to the *a* axis. The average

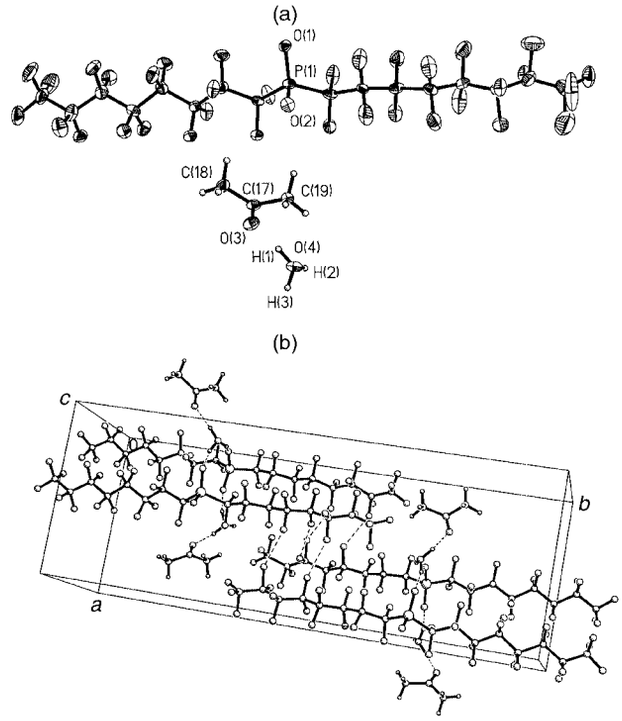

Fig. 3 (a) An ORTEP drawing of compound **3**; (b) crystal packing diagram for **3**. Details as in Fig. 1.

Table 1 Selected bond lengths (Å) and bond angles (°) for compounds **1**–**3**

	1	**2**	**3**
P(1)–O(1)	1.481(3)	1.485(3)	1.471(7)
P(1)–O(2)	1.495(3)	1.487(3)	1.471(7)
P(1)–C(1)	1.886(5)	1.872(4)	1.870(10)
F(1)–C(1)	1.352(5)	1.339(5)	1.373(11)
F(2)–C(1)	1.358(5)	1.347(5)	1.352(11)
C(1)–C(2)	1.539(6)	1.530(6)	1.522(14)
O(1)–P(1)–O(2)	119.56(18)	121.73(7)	123.0(4)
O(2)–P(1)–C(1)	107.8(2)	105.94(18)	107.9(4)
O(1)–P(1)–C(1)	109.26(19)	108.55(17)	107.0(4)
F(2)–C(1)–C(2)	108.4(4)	108.8(3)	109.4(8)
F(1)–C(1)–C(2)	108.9(4)	108.5(3)	108.3(8)
F(2)–C(1)–P(1)	109.5(3)	108.8(3)	110.0(6)
F(1)–C(1)–P(1)	109.9(3)	109.6(3)	109.9(6)
C(2)–C(1)–P(1)	112.6(3)	112.9(3)	114.0(7)
C(1)–C(2)–C(3)	117.1(4)	116.5(3)	116.0(9)
C(2)–C(3)–C(4)	113.2(4)	114.5(4)	113.2(9)

Table 2 Comparison of selected bond lengths (average) and angles of compounds **1**–**3** with those of other phosphinic acids

Compound	P–O/Å	P–C/Å	O–P–O/°
1 [a]	1.48	1.88	119.56
2 [a]	1.48	1.87	121.73
3 [a]	1.47	1.86	122.9
4 [b]	1.52	1.77	112.7
5 [c]	1.53	1.77	113.1
6 [d]	1.48	1.81	117.2
7 [e]	1.48	1.88	122.5

[a] This work. [b] Reference 5. [c] Reference 6. [d] Reference 11. [e] Reference 12.

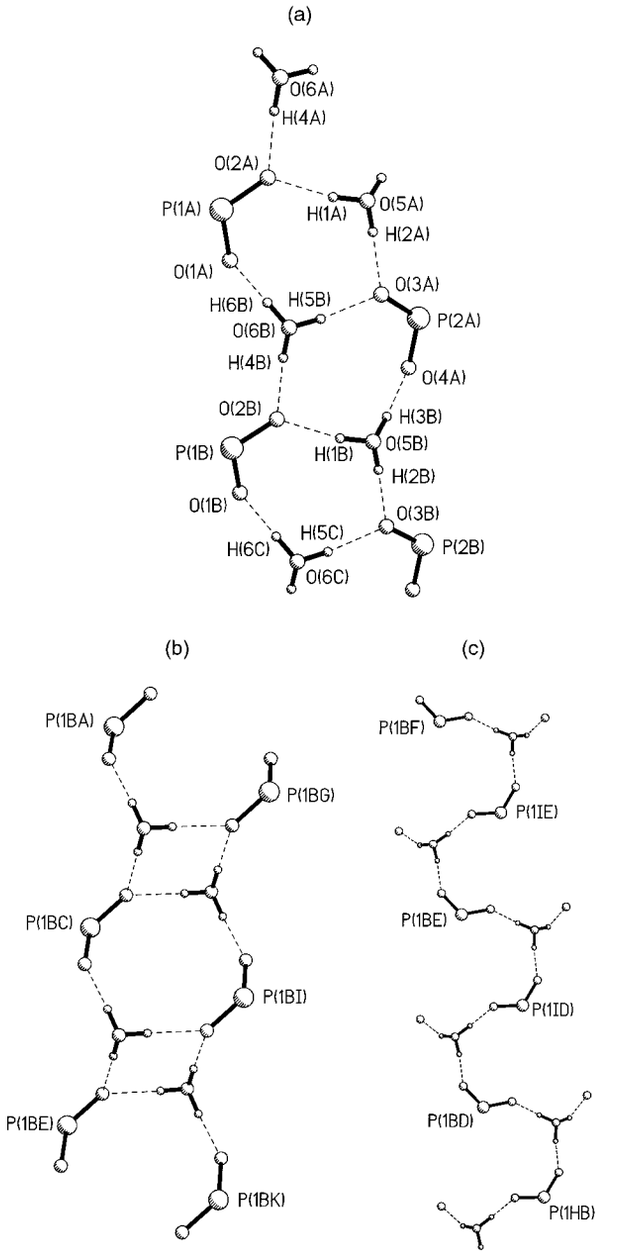

Fig. 4 (a) Hydrogen bonding network in compound **1** O5b–H1b···O2b 1.74(2), O5b–H2b···O3b 1.73(2), O5b–H3b···O4a 1.59(2), O6b–H4b···O2b 1.71(2), O6b–H5b···O3a 1.73(2) and O6b–H6b···O1a 1.59(2) Å. (b) Hydrogen bonding network in **2**: O3–H3···P2bi 1.55(2), O3–H2···O1bg 1.77(2) and O3–H1···O1bc 1.81(2) Å. (c) Hydrogen bonding network in **3**: O4–H3···O1be 1.540(19), O4–H2···O2id 1.67(3) and O4–H1···O3 1.70(3) Å.

O–H···O bond distance is *ca.* 2.23 Å. The void between the molecules of **2** is less than that in **1** allowing a more regular packing and more F···F interactions ranging from 2.788(3) to 3.137(2) Å. Compound **3** is different from both **1** or **2** in that the solvent of crystallization is also present and is hydrogen bonded to the H_3O^+ ion. Unlike **1** and **2**, **3** propagates perpendicular to the *c* axis in an 'S-shaped' fashion with an average O–H···O bond distance of 1.73 Å. This can be seen clearly in Fig. 4(c). The presence of acetone between the repeating units enlarges the distances between each perfluoroalkylphosphinate moiety. The molecules of the adjacent infinite chains penetrate these voids, as seen in **1**, in a 'zipper-like' fashion, giving rise to F···F close contacts of 2.733(17) to 3.133(11) Å. Compound **3** is also an infinite chain, however, it consists of only one layer of phosphinates unlike both **1** and **2**. This probably arises from the presence of acetone, which is hydrogen bonded to H_3O^+ thus preventing further association.

Table 3 Selected crystallographic data for compounds **1**–**3**

	1	**2**	**3**
Formula	$C_{24}H_6F_{52}O_6P_2$	$C_{14}H_3F_{30}O_3P$	$C_{19}H_9F_{34}O_4P$
Formula weight	1440.23	820.13	978.23
T/K	183(2)	203(2)	183(2)
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	*Pca*2(1)
a/Å	6.3795(2)	6.1951(2)	10.7873(6)
b/Å	17.5638(5)	11.1604(3)	30.1060(16)
c/Å	20.9551(7)	18.7348(5)	9.7817(5)
α/°	76.1780(10)	78.0740(10)	
β/°	88.2640(10)	89.2660(10)	
γ/°	81.768(5)	82.5320(10)	
V/Å^3	2256.48(12)	1256.48(6)	3176.7(3)
Z	2	2	4
μ/mm^{-1}	0.352	0.353	0.317
No. of reflections	21499	12430	20576
Independent reflections	7670	4329	4113
R_{int}	0.0509	0.0379	0.0829
Final $R(I > 2\sigma(I))$	0.0708	0.0641	0.0800
*wR*2 (all data)	0.1196	0.1567	0.1861

Conclusion

We report the first single crystal structures of bis(n-perfluoroalkyl)phosphinic acids, $[H_3O]^+[(C_6F_{13})_2PO_2]^-$, $[H_3O]^+[(C_7F_{15})_2PO_2]^-$, and $[H_3O]^+[(C_8F_{17})_2PO_2]^-\cdot Me_2CO$. These complexes have intermolecular hydrogen bonds. Several intermolecular close contacts are observed between fluorine atoms. In the three cases the two P–O distances are very similar. The presence of two highly electronegative perfluoroalkyl substituents on the phosphorus atom enhances the acidic nature of the compounds. They are stabilized by an H_3O^+ cation which leads to the formation of crystalline solids.

Experimental

Materials

Perfluoroalkyliodophosphines, $(R_f)_2PI$ ($R_f = C_6F_{13}$, C_7F_{15} or C_8F_{17}) were prepared by the reaction of red phosphorus with perfluoroalkyl iodide according to literature procedures.[13–15] Bis(n-perfluoroalkyl)phosphinic acids $(R_f)_2P(O)OH$ ($R_f = C_6F_{13}$, C_7F_{15} or C_8F_{17}) were also prepared according to a literature procedure by the oxidation of $(R_f)_2PI$ with an excess of NO_2 followed by hydrolysis.[9]

Single crystal X-ray measurements

Single crystals of compounds **1**–**3** suitable for X-ray analysis were grown by slow evaporation of an acetone–hexane solution. They were removed from the flask and covered with a layer of hydrocarbon oil.[16] A suitable crystal was selected, attached to a glass fiber and placed in a low-temperature nitrogen stream. Data were collected using a Siemens SMART 1000 instrument (Mo-Kα radiation, $\lambda = 0.71073$ Å) equipped with a Siemens LT-2A low temperature device. The SHELXTL program package was used for structure solution and refinement.[17] An absorption correction was applied using SADABS.[18] The structures were solved by direct methods and refined by full matrix least squares procedures. All non-hydrogen atoms were refined anisotropically. Some fluorine groups were disordered in **3** but these could be modeled successfully at half occupancy. Except for the hydrogen atoms of the acetone molecule in **3**, all hydrogen atoms in **1**–**3** were located on the Fourier difference maps and refined. The hydrogen atoms of the acetone molecule in **3** were included in the refinement at calculated positions using a riding model included in the SHELXTL program. Some details of the data collection and refinement are given in Table 3.

CCDC reference number 186/2195.

Acknowledgements

This work was supported by National Science Foundation grant (CHE-9720635), the American Chemical Society Petroleum Research Fund, and the NASA Idaho Space Grant Consortium. We are thankful to Photon-X, Inc. for reagents and Dr. Gary Knerr for measuring GCMS.

References

1 H. Brechi and H. Hoffmann, *Ger. Offen.*, 2,110,767, Sept. 28, 1972.
2 H. Brechi, *Ger. Offen.*, 2,110,769, Sept. 28, 1972.
3 H. Christian, H. Dieter and P. Johannes, *Ger. Offen.*, 2,233,941, Jan. 31, 1994.
4 M. Mori and O. Sakurai, *Jpn. Kokai Tokkyo Koho Jp*, 06, 199,061, July 19, 1994.
5 F. Giordano and A. Ripamonti, *Acta Crystallogr.*, 1967, **22**, 678.
6 P. Bello, *Gazz. Chim. Ital.*, 1973, **103**, 537.
7 V. Giancotti, F. Giordano, L. Randaccio and A. Ripamonti, *J. Chem. Soc.*, 1968, 757.
8 T. Mahmood and J. M. Shreeve, *Inorg. Chem.*, 1986, **25**, 3128 and references therein.
9 R. P. Singh and J. M. Shreeve, *Inorg. Chem.*, 2000, **39**,1787.
10 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
11 K. W. Oliver, S. J. Retting, R. C. Thompson, J. Trotter and S. Xia, *J. Fluorine Chem.*, 1997, **83**, 47.
12 A. Schmidpeter, K. H. Zirzow, A. Willhalm, J. M. Holmes and R. R. Holmes, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 457.
13 F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1565.
14 A. H. Cowley, T. A. Furtsch and D. S. Dierdorf, *Chem. Commun.*, 1970, 523.
15 H. G. Ang, M. E. Redwood and B. O. West, *Aust. J. Chem.*, 1972, **25**, 493.
16 H. Hope, *Prog. Inorg. Chem.*, 1995, **41**, 1.
17 SHELXTL, Version 5.10 PC/NT, Bruker AXS, Madison, WI, 1998.
18 SADABS, Siemens Area Detector Absorption Correction Program, Siemens Analytical Instrument Division, Madison, WI, 1996.