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Synthesis of perfluorodiphenylphosphinic acid and its potassium and oxonium salts; crystal structure of oxonium perfluorodiphenylphosphinate

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Abstract

The syntheses of perfluorodiphenylphosphinic acid, oxonium perfluorodiphenylphosphinate (perfluorodiphenylphosphinic acid monohydrate), and the potassium salt are described. Crystals of $(C_6F_5)_2PO_2^- H_3O^+$ [$(C_6F_5)_2PO(OH)\cdot H_2O$] are monoclinic, $a=33.541(2)$ Å, $b=6.512(3)$ Å, $c=30.238(2)$ Å, $Z=16$, space group $C2/c$. The structure was solved by direct methods and was refined by full-matrix least-squares procedures to $R=R_w=0.037$ for 3792 reflections with $I \geq 3\sigma(I)$, respectively. The crystal structure contains H_3O^+ cations and $(C_6F_5)_2PO_2^-$ anions (two of each per asymmetric unit), linked by two strong, symmetrical hydrogen bonds ($O\cdots O \approx 2.4$ Å) and four more-normal hydrogen bonds ($O\cdots O \approx 2.6$ Å). P–C bonds are longer and P–O bonds shorter than in the perhydro analog. © 1997 Elsevier Science S.A.

Keywords: Perfluorodiphenylphosphinic acid; Oxonium perfluorodiphenylphosphinate; Synthesis; Crystal structure

1. Introduction

Although diphenylphosphinic acid, $(C_6H_5)_2PO(OH)$, has been known since before the turn of the century [1], and is available commercially, there seems to be no reference to the perfluorinated analog in the primary literature [2]. We report here the synthesis of $(C_6F_5)_2PO(OH)$, its potassium salt, and its monohydrate. The structure of the latter determined here by single crystal X-ray diffraction indicates that it is best described as oxonium perfluorodiphenylphosphinate, $(C_6F_5)_2PO_2^- H_3O^+$. A preliminary mention of this work was made previously [3]. Our interest in this acid stems from earlier studies on transition metal diphenylphosphinates, compounds which have extended-chain polymeric structures and which exhibit magnetic exchange effects in the solid state, providing examples of both ferromagnetically [4] and antiferromagnetically [5] coupled materials. To study the effects of fluorination on the magnetic properties of coordination polymers we are currently investigating some transition metal perfluorodiphenylphosphinates using the acid characterized in the work described here. Our studies on the metal systems will be presented elsewhere.

2. Results and discussion

$K(C_6F_5)_2PO_2$ was prepared by the hydrogen peroxide oxidation of perfluorotriphenylphosphine followed by hydrolysis of the oxide with aqueous KOH. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) showed the salt to be thermally stable to about 340 °C. Acidification of a solution of the salt with dilute HCl gave oxonium perfluorodiphenylphosphinate, $(C_6F_5)_2PO_2^- H_3O^+$. The anhydrous acid may be obtained by exposing the oxonium salt, under vacuum, to phosphorus(V) oxide for several hours or by heating the salt in a stream of dry nitrogen at 70 °C (as shown by thermogravimetric analysis, TGA). The DSC thermogram of the anhydrous acid shows an endothermic peak at 154 °C, corresponding to melting, and the onset of thermal decomposition at about 200 °C. The anhydrous acid is hygroscopic and should be handled in an inert atmosphere.

The crystal structure (Fig. 1 and Table 1) of oxonium perfluorodiphenylphosphinate, $(C_6F_5)_2PO_2^- H_3O^+$ contains two independent formula units in the asymmetric unit. Each H_3O^+ ion is linked to one phosphinate anion by a strong, nearly symmetric and linear hydrogen bond ($O\cdots O \approx 2.4$ Å, $H\cdots O \approx 1.2$ Å, $O\cdots H\cdots O \approx 174°$). More-normal hydrogen

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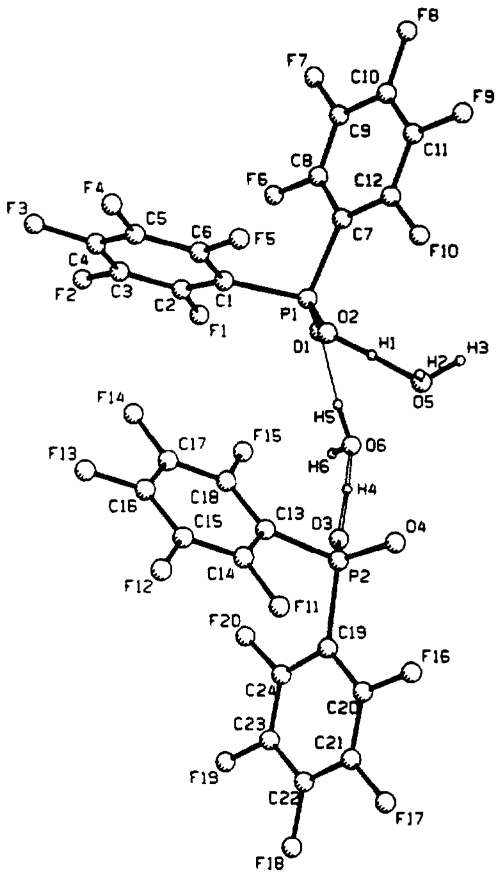

Fig. 1. Structure of $(C_6F_5)_2PO_2^-H_3O^+$ showing the atom numbering scheme.

bonds involving the other two hydrogens on each $(C_6F_5)_2PO_2^-H_3O^+$ unit form an extended hydrogen-bonded motif best described as involving chains of these units linked together into groups of four chains (O···O ≈ 2.6 Å, H···O ≈ 1.7 Å, O···H···O = 148–174°) (Fig. 2).

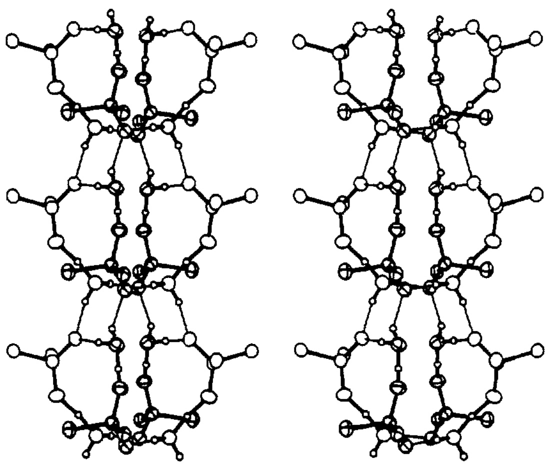

Fig. 2. Stereoview of $(C_6F_5)_2PO_2^-H_3O^+$ showing the H-bonding network. The perfluorophenyl groups are omitted for clarity.

The perfluorophenyl groups exhibit normal bond parameters [6]. Comparison of the structure reported here with that of the perhydro analog, $(C_6H_5)_2PO(OH)$ [7], however, reveals small but significant differences in the bond lengths and angles associated with the PO_2C_2 entities in the two compounds. In the perfluoro derivative the average P–C distance is longer (1.816(3) Å vs. 1.786(6) Å), the average C–P–C angle is smaller (102.6(1)° vs. 107.7(3)°), the average P–O distance is shorter (1.485(2) Å vs. 1.506(6) Å) and the average O–P–O angle is marginally larger (117.4(1)° vs. 116.6(3)°). These differences, which may arise partly from hydrogen bonding effects, also suggest that the greater electronegativity of the perfluorophenyl group compared to phenyl leads to weaker P–C bonds and a concomitant increase in the strength of the P–O bonds. This latter effect has been previously ascribed to an increase in dπ–pπ bonding between phosphorus and oxygen on increasing the electronegativity of X in X_2PO_2 structures generally [8].

Table 1
Selected bond lengths and angles for $(C_6F_5)_2PO_2^-H_3O^+$

P(1)–O(1)	1.490(2)	P(2)–O(4)	1.490(2)
P(1)–O(2)	1.477(2)	P(2)–O(3)	1.481(2)
P(1)–C(1)	1.811(3)	P(2)–C(13)	1.820(3)
P(1)–C(7)	1.818(3)	P(2)–C(19)	1.813(3)
O(2)–H(1)	1.11(4)	O(3)–H(4)	1.25(4)
O(5)–H(1)	1.30(4)	O(6)–H(4)	1.18(5)
O(5)–H(2)	0.81(5)	O(6)–H(5)	0.95(4)
O(5)–H(3)	0.91(4)	O(6)–H(6)	0.90(4)
C–F	1.329(4)–1.348(4)	C–C	1.359(5)–1.384(4)
O(1)–P(1)–O(2)	117.2(1)	O(3)–P(2)–O(4)	117.6(1)
O(1)–P(1)–C(1)	110.3(1)	O(3)–P(2)–C(13)	110.1(1)
O(1)–P(1)–C(7)	108.3(1)	O(3)–P(2)–C(19)	106.8(1)
O(2)–P(1)–C(1)	106.3(1)	O(4)–P(2)–C(13)	108.4(1)
O(2)–P(1)–C(7)	111.5(1)	O(4)–P(2)–C(19)	110.0(1)
C(1)–P(1)–C(7)	102.3(1)	C(13)–P(2)–C(19)	102.9(1)
P(1)–O(2)–H(1)	139(2)	P(2)–O(3)–H(4)	136(2)
H(1)–O(5)–H(2)	110(3)	H(4)–O(6)–H(5)	121(3)
H(1)–O(5)–H(3)	118(3)	H(4)–O(6)–H(6)	110(3)
H(2)–O(5)–H(3)	90(4)	H(5)–O(6)–H(6)	106(3)

3. Experimental details

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were made using a TA Instruments 2000 system with a DSC 910S cell and a TGA 51 unit. Powdered samples of 10–20 mg were heated at 10 °C min^{-1} in an atmosphere of dry nitrogen at a flow rate of 40–100 ml min^{-1}. Infrared spectra were recorded using a Bomem MB 102 Fourier-transform infrared spectrometer. Samples were mulled in Nujol and pressed between KRS-5 plates (Harshaw Chemical Co.). Frequencies are considered accurate to about 2 cm^{-1}. Bands observed over the range 450–1350 cm^{-1} are listed below (s = strong, m = medium, w = weak, sh = shoulder). Carbon and hydrogen analyses were performed by P. Borda at the University of British Columbia.

3.1. Synthesis of $(C_6F_5)_2PO_2K$, $(C_6F_5)_2PO_2^- H_3O^+$ and $(C_6F_5)_2PO(OH)$

The Grignard reagent, C_6F_5MgBr, was prepared from 62.5 ml (0.50 mol) of pentafluorobromobenzene and 12.0 g (0.49 mol) of magnesium turnings in 50 ml of anhydrous ether with cooling in an ice bath [9]. To this was added 21 ml (0.24 mol) of freshly distilled PCl_3 in 80 ml of anhydrous ether [10]. The reaction mixture, under a nitrogen atmosphere, was maintained at −6 °C with a salt/ice bath. After the addition was complete, the reaction mixture was hydrolyzed by pouring over ice (600 ml) that had been acidified with 3 ml conc. HCl. After allowing the mixture to evaporate overnight, approximately 66 g of a dark brown solid, identified as crude $(C_6F_5)_3P$ by infrared spectroscopy [11], was isolated from the aqueous layer. Extraction of the aqueous layer with ether yielded no additional product. The crude phosphine was ground, suspended in a minimum amount of water and 175 ml of hydrogen peroxide (30%) was added. The mixture was stirred with heating until the excess peroxide had decomposed. A fine white solid which settled out on standing was removed by filtration. Infrared spectroscopy [11] indicated the material to be largely perfluorotriphenylphosphine oxide; yield 68 g (in the subsequent reaction it was determined that 19 g of this was unoxidized $(C_6F_5)_3P$).

$(C_6F_5)_3PO$ was converted to potassium perfluorodiphenylphosphinate by a method adapted from the solid state reaction of KOH with tribenzylphosphine oxide [12]. Crude $(C_6F_5)_3PO$ (68 g) was suspended in 600 ml of water and aqueous KOH (9.3 g in 200 ml of water) was added in 10 ml aliquots. The mixture was heated to 65–70 °C with stirring and the pH was allowed to return to approximately neutral before the addition of the next aliquot of base. During the course of the reaction the amount of insoluble phosphine oxide in the suspension decreased noticeably as conversion to the soluble salt occurred. When about 70% of the KOH solution (140 ml) had been added (after two days of slow addition) the solution remained basic although there was still unreacted solid in the mixture. The solid was removed by filtration and identified by infrared spectroscopy as unoxidized $(C_6F_5)_3P$ (19 g). The filtrate was evaporated yielding a tan solid which was taken up in a minimum of water/acetone (40/60 by volume). With the addition of ether and vigorous stirring, a pure white solid formed at the interface between the aqueous and the ether layers. The solid was removed by filtration, more ether was added to the filtrate and the process was repeated until no more solid formed with ether addition. Analysis: Calc. for $C_{12}F_{10}PO_2K$: C, 33.04. Found: C, 33.14%; H, trace. Yield: 20 g. IR (cm^{-1}): 479s, 537s, 547sh, 588, 637s, 727m, 732sh, 758w, 768w, 833w, 841sh, 977s, 1033w, 1076sh, 1092sh, 1111s, 1136sh, 1255s, 1277s, 1298s.

The oxonium salt was obtained as follows. Crude $(C_6F_5)_3PO$ (3.53 g) was treated with aqueous KOH as described above. A small amount of unreacted solid was removed by filtration and the filtrate was acidified with dilute HCl. After evaporation the solid residue was taken up in ether and filtered to remove KCl. The addition of a large volume of *n*-heptane (4:1 heptane:ether) with cooling and triturating resulted in the precipitation of fine white needles which were separated by filtration. Crystals suitable for X-ray crystallography were formed by slow evaporation of the *n*-heptane–ether filtrate. Analysis: Calc. for $C_{12}H_3F_{10}PO_3$: C, 34.64; H, 0.73. Found: C, 34.84; H, 0.79%. Yield: 2.4 g. IR (cm^{-1}): 481m, 532m, 550m, 589m, 642m, 732m, 764w, 845w, 859w, 981s, 1032sh, 1074sh, 1097sh, 1117s, 1301m.

The anhydrous acid was obtained by drying the oxonium salt over phosphorous pentoxide in an inert atmosphere for 12 h. Analysis: Calc. for $C_{12}HF_{10}PO_2$: C, 36.21; H, 0.25. Found: C, 36.60; H, 0.40%. IR (cm^{-1}): 475m, 517w, 544s, 590m, 641s, 731s, 765w, 845w, 890w, 979s, 1009m, 1031w, 1110s, 1150w, 1252m, 1302m, 1307m.

3.2. X-ray crystallographic analysis of $(C_6F_5)_2PO_2^- H_3O^+$

Crystallographic data are given in Table 2. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with $2\theta = 55.5–71.0°$. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, showed only small random variations. The data were processed [13], corrected for Lorentz and polarization effects, and absorption (empirical, based on azimuthal scans for three reflections).

The structure was solved by direct methods. The analysis was initiated in the centrosymmetric space group *C*2/*c* on the basis of the *E*-statistics and the appearance of the Patterson function. This choice was confirmed by subsequent calculations. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were refined with isotropic thermal parameters. A correction for secondary extinction was applied (Zachariasen isotropic type I), the final value of the extinction coefficient being

$2.27(13)\times10^{-7}$. Neutral atom scattering factors [14] and anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography [14].

Table 2
Crystallographic data for $(C_6F_5)_2PO_2^- H_3O^+$ [a]

Compound	$(C_6F_5)_2PO_2^- H_3O^+$
Formula	$C_{12}H_3F_{10}O_3P$
FW	416.11
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	33.541(2)
b (Å)	6.512(3)
c (Å)	30.238(2)
β (deg)	118.014(5)
V (Å^3)	5831(2)
Z	16
ρ_{calc} (g cm^{-3})	1.896
$F(000)$	3264
Radiation (λ (Å))	Cu (1.54178)
μ (cm^{-1})	29.90
Crystal size (mm)	0.15×0.18×0.40
Transmission factors	0.77–1.00
Scan type	ω–2θ
Scan range (deg in ω)	$1.15+0.20 \tan\theta$
Scan speed (deg/min)	32 (up to eight rescans)
Data collected	$+h, +k, \pm l$
$2\theta_{max}$ (deg)	155
Crystal decay (%)	negligible
Total reflections	6708
Total unique reflections	6593
R_{merge}	0.018
Reflections with $I\geq3\sigma(I)$	3792
No. of variables	494
R	0.037
R_w	0.037
GOF	2.21
Max Δ/σ (final cycle)	0.08
Residual density (e Å^{-3})	−0.23 to 0.25

[a] Temperature 294 K, Rigaku AFC6S diffractometer, graphite monochromator, takeoff angle 6.0°, aperture 6.0×6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma^2(F^2)=[S^2(C+4B)]/\mathrm{Lp}^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\Sigma w(|F_o|-F_c|)^2$ where $w=4F_o^2/\sigma^2(F_o^2)$, $\mathrm{R}=\Sigma\|\mathrm{F_o}|-|\mathrm{F_c}\|/\Sigma|\mathrm{F_o}|$, $\mathrm{R_w}=(\Sigma\mathrm{w}(|\mathrm{F_o}|-|\mathrm{F_c}|)^2/\Sigma\mathrm{w}|\mathrm{F_o}|^2)^{1/2}$, and $\mathrm{GOF}=[\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$. Values given for R, R_w, and GOF are based on those reflections with $I\geq3\sigma(I)$.

4. Supplementary material available

Tables of final atomic coordinates, equivalent isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, bond lengths and angles involving hydrogen atoms, torsion or conformation angles, intermolecular distances involving non-hydrogen atoms, intermolecular distances involving hydrogen atoms, least-squares planes and structure factor amplitudes are available from the authors.

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References

[1] H. Gotter, A. Michaelis, Ber. Chem. Dtsh. Ges. 11 (1878) 885.
[2] R. Kurpat, Ph.D. dissertation, Technische Universitat Braunschweig, (1977).
[3] R.C. Thompson, J. Fluorine Chem. 71 (1995) 191.
[4] J.-L. Du, K.W. Oliver, R.C. Thompson, Inorg. Chim. Acta 141 (1988) 19.
[5] J.-L. Du, S.J. Rettig, R.C. Thompson, J. Trotter, Can. J. Chem. 69 (1991) 277.
[6] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. II (1987) S1–S19.
[7] D. Fenske, R. Mattes, J. Lons, K.-F. Tebbe, Chem. Ber. 106 (1973) 1139.
[8] E.A. Robinson, Can. J. Chem. 41 (1963) 3021.
[9] W.J. Pummer, L.A. Wall, J. Res. Natl. Bur. Stand. 63A (1959) 167.
[10] L.A. Wall, R.E. Donadio, W.J. Pummer, J. Am. Chem. Soc. 82 (1960) 4846.
[11] M. Fild, I. Hollenberg, O. Glemser, Z. Naturforsch. 22b (1967) 248.
[12] L.P. Zhuravleva, M.I. Zola, M.G. Suleimanova, A.V. Kirsanov, Zh. Obshch. Khim. 38 (1968) 342. Eng. translation: J. Gen. Chem. USSR. 38 (1968) 341.
[13] TEXSAN. Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985.
[14] International Tables for X-Ray Crystallography, Vol. IV. Kynoch Press, Birmingham, UK, 1974. pp. 99–102, 149.