

Crystal Structure of the Hydrogen-bonded Complex between Pentafluorophenol and Triphenylphosphine Oxide

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Pentafluorophenol forms a stable crystalline 1:1 hydrogen bonded complex with triphenylphosphine oxide. The crystals are triclinic, $a=8.293(2)$, $b=11.178(2)$, $c=11.340(5)$ Å, $\alpha=80.26(3)$, $\beta=86.73(3)$, $\gamma=85.05(1)^\circ$, $V=1031.1$ Å³, $M=462.36$, $Z=2$ and space group $P\bar{1}$. The structure was determined from 3697 independent reflections and refined to $R=0.050$. The molecules of a complex are joined together by a $P=O\dots H-O$ hydrogen bond. The $O\dots O$ distance is $2.645(2)$ Å while $\angle O\dots H-O$ is $174(5)^\circ$. The phosphorus atom is essentially tetrahedrally bonded with a $P=O$ distance of $1.496(2)$ Å and an average $P-C$ distance of $1.798(2)$ Å.

In a previous publication on complex formation between pentafluorophenol (PFP) and triphenylphosphine oxide (TPPO) in solution, it was suggested that a proton transfer reaction may have taken place.¹ With a stable crystalline 1:1 complex PFP and TPPO available, we undertook an X-ray crystallographic study of the complex to ascertain whether the association takes place by formation of a hydrogen-bonded complex, $P=O\dots H-O$, or a proton-transfer complex, $P=OH\dots O$.

Experimental

Preparation of the complex. Freshly recrystallized (from acetone/ether) TPPO (3.86 g, 0.014 mol) was dissolved in methanol (10 ml). To the resultant solution PFP (2.55 g, 0.014 mol) was added under stirring. The solvent was evaporated in vacuum and the crystalline residue was dissolved in a minimum of benzene. Upon addition of petrol ether (b.p. 60–80°C) colourless crystals deposited (yield, 5.96 g, 93%; m.p. 101–103°C; Equiv. 461.6; reg. 462.4). The equivalent weight was determined by titration with aqueous sodium hydroxide.

X-ray data. An Enraf-Nonius CAD4 diffractometer with graphite monochromated $MoK\alpha$ radiation was used for the determination of unit cell dimensions ($\lambda K\alpha_1=0.70926$, $\lambda K\alpha_2=0.710354$ Å) and the recording of intensity data ($\lambda K\alpha=0.70926$ Å). The temperature at the crystal site was -135°C . Unit cell parameters are based on least squares fits to the diffractometer settings of 22 general reflections with $9^\circ<\theta<13^\circ$. The space group is $P\bar{1}$ (No. 2) with $a=8.293(2)$, $b=11.178(2)$, $c=11.340(5)$ Å, $\alpha=80.26(3)$, $\beta=86.73(3)$, $\gamma=85.05(1)^\circ$, $V=1031.1$ Å³, $M=462.36$, $Z=2$, $d_{\text{calc}}=1.489$ g cm⁻³, $\mu(MoK\alpha)=1.904$ cm⁻¹. The crystal used had been cut to approximate cubical form *ca.* 0.25³ mm³. Intensity data were recorded using the ω scan technique, a constant scan rate of 4° min⁻¹, and a minimum scan angle of 1.5° including 0.25° background scans at the beginning and end of each reflection scan. Three standard reflections were remeasured every hour to check for possible decay and other causes for instability. Significant variation in their intensity was not observed. The orientation of the crystal was checked at intervals of 200 recordings. A total of 4947 crystallographically independent reflections were recorded ($\theta\leq 28^\circ$); of these 1250 had $I\leq 2\sigma(I)$ and were considered unobserved. The intensities were cor-

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Table 1. Positional Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	B(A ²)
P	0.13981(7)	0.29171(6)	0.71468(5)	1.38(1)
F2	0.3276(2)	0.4301(2)	0.3910(1)	3.17(3)
F3	0.4730(3)	0.5546(2)	0.1976(2)	4.24(4)
F4	0.6862(2)	0.4385(2)	0.0552(2)	5.11(5)
F5	0.7542(2)	0.1923(2)	0.1139(2)	5.12(4)
F6	0.6047(2)	0.0660(2)	0.3067(2)	4.21(4)
O1	0.3857(2)	0.1764(2)	0.4452(2)	2.50(4)
O2	0.2790(2)	0.2892(2)	0.6250(1)	1.90(3)
C1	0.4618(3)	0.2447(2)	0.3527(2)	2.02(5)
C2	0.4327(3)	0.3689(2)	0.3237(2)	1.98(5)
C3	0.5066(3)	0.4339(3)	0.2244(2)	2.57(5)
C4	0.6143(3)	0.3756(3)	0.1522(2)	2.99(6)
C5	0.6473(3)	0.2522(3)	0.1814(3)	3.12(6)
C6	0.5720(3)	0.1876(3)	0.2800(3)	2.63(5)
C11	0.0698(3)	0.4453(2)	0.7311(2)	1.56(4)
C12	0.1100(3)	0.5386(2)	0.6392(2)	1.87(5)
C13	0.0552(3)	0.6584(2)	0.6466(2)	2.23(5)
C14	-0.0388(3)	0.6845(2)	0.7448(2)	2.20(5)
C15	-0.0788(3)	0.5915(2)	0.8370(2)	2.13(5)
C16	-0.0243(3)	0.4725(2)	0.8306(2)	1.85(5)
C21	-0.0310(3)	0.2205(2)	0.6754(2)	1.46(4)
C22	-0.0041(3)	0.1026(2)	0.6484(2)	1.79(4)
C23	-0.1303(3)	0.0457(2)	0.6130(2)	2.00(5)
C24	-0.2839(3)	0.1056(2)	0.6028(2)	2.05(5)
C25	-0.3112(3)	0.2222(2)	0.6288(2)	2.06(5)
C26	-0.1854(3)	0.2794(2)	0.6655(2)	1.75(4)
C31	0.1947(3)	0.2111(2)	0.8595(2)	1.50(4)
C32	0.3582(3)	0.1985(2)	0.8863(2)	1.98(5)
C33	0.4051(3)	0.1382(3)	0.9972(2)	2.31(5)
C34	0.2905(4)	0.0892(2)	1.0818(2)	2.36(5)
C35	0.1291(3)	0.1008(2)	1.0555(2)	2.01(5)
C36	0.0803(3)	0.1617(2)	0.9449(2)	1.71(4)
H	0.352(6)	0.218(4)	0.500(4)	10(1)

Hydrogen atoms were refined isotropically. For anisotropically refined atoms are given the equivalent isotropic thermal parameter.

rected for Lorentz- and polarization-, but not for absorption effects. The computer programs used throughout this investigation are supplied by ENRAF-NONIUS (SDP-plus 1983 and CAD4-OS11).

Structure determination. The structure was solved by direct methods (MULTAN) and refined by full matrix least squares, the function minimized was $\sum w(\Delta F)^2$, where the weights were calculated ac-

cording to $w = (\sigma(F)^2 + (0.01 F)^2 + 2)^{-1}$. The least squares iterations converged (max shift/error ≤ 0.01) giving $R = \sum |\Delta F| / \sum |F_o| = 0.050$, $R_w = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2} = 0.049$. $S = [\sum w(\Sigma F)^2 / (N - n)]^{1/2} = 1.25$. A final difference Fourier synthesis showed a maximum of 0.45 eÅ⁻³. Anisotropic thermal parameters were refined for non-hydrogen atoms. The hydrogen atoms were refined isotropically. Table 1 lists the coordinates for F-, O-, C-atoms and the H-atom involved in hydrogen bonding. Complete lists of atomic coordinates, thermal parameters and structure factors are available on request from one of the authors (K.M.-M.).

Results and discussion

Fig. 1 shows the structures of the PFP and TPPO molecules in the hydrogen bonded 1:1 complex. Interatomic distances and bond angles are listed in Tables 2a and 2b. There is no proton transfer. The hydrogen bond is relatively strong¹² with O1-H=0.86(5), H...O2=1.79(5), O1...O2=2.645(2) Å, $\angle C1-O1-H...O2=174^\circ(5)$, and $\angle P=O...H=141^\circ(2)$. These values agree with the corresponding values found in other hydrogen bonded P=O...H-O-systems,¹³⁻¹⁶ or systems involving PFP.^{2,10} The packing of the molecules, shown in Fig. 2, reveals several short intermolecular contacts between the individual complexes, notably some F...H contacts of about 2.5 Å, C...C contacts of 3.45-3.50 Å, and C...H contacts around 2.9 Å, all shorter than the corresponding sums of the van der Waals' radii.³ With a dihedral angle of 7.4°, the L.S. planes through F2-F6, C1-C6 and the phenyl group C11-C16 (-x, 1-y, 1-z) are almost parallel and as the atoms of the two moieties are partially overlapping, charge transfer may well be involved.

From Table 3 it can be seen that the bond lengths and angles in the TPPO molecule, as observed in this study, conform with the tabulated and referred results. That the C-P-O angles are significantly greater than the C-P-C angles follows from the VSEPR-theory. The torsional angles of the P-C bonds, *i.e.*, O-P-C(Ph) (see Table 4) are close to those found in orthorhombic TPPO and in several other hydrogen bonded TPPO complexes, and in the arsenic analog.² The PFP molecule, as observed in this analysis, shows no differences of importance from earlier studies.^{2,10} As frequently found in ortho-substituted

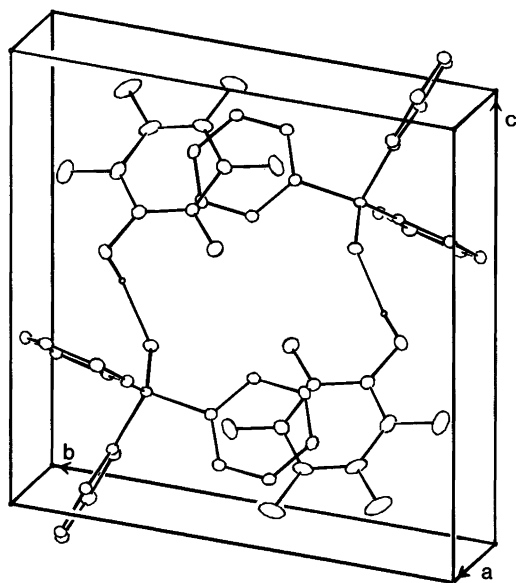


Fig. 2. The molecular packing of the complex in the unit cell.

phenols the bond angles O1-C1-C2 and O1-C1-C6 (see Table 2b) differ. This may be related to the intramolecular F2-H distance, 2.48 Å.^{2,10,11}

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Table 4. Selected least-squares planes, interplanar and torsional angles.

No. of plane	Atoms included	Maximum deviation of atoms (Å)
1	C1-C6, F2-F6, O1	0.05 (O1)
2	P, C11-C16	0.02 (P)
3	P, C21-C26	0.03 (P)
4	P, C31-C36	0.006 (C32)

Interplanar angles (°).

2-3 72.2; 2-4 71.6; 3-4 81.3

Distances of atoms from plane no. 1 (Å), esd. in parenthesis.

H: 0.26(5); O2: 0.930(2); P: 0.675(1)

Torsional angles (°).

H-O1-C(phenyl)-24.1 O2-P-C21(phenyl)53.5
O2-P-C11(phenyl)19.5 O2-P-C31(phenyl)24.0

Table 3. Selected interatomic distances (Å) and angles (°) in Ph₃P=O and some of its complexes with hydrogen-bond donors. (The compound Ph₃As=O, C₆F₅OH is included for comparison).

Compound	P=O	O...O	P-C _{ave}	<O-P-C _{ave}	<C-P-C _{ave}	Torsional angles O=P-C (Phenyl)	Ref.
Ph ₃ P=O (Monocl.)	1.483(2)	-	1.792	112.3	106.5	11.4; 76.9; 18.7	4
Ph ₃ P=O (Orthorh.)	1.46(1)	-	1.76	111.7	107.1	21.1; 59.3; 24.1	5
Ph ₃ P=O, C ₆ F ₅ OH	1.496(2)	2.645(2)	1.798	111.9	106.9	20.0; 52.0; 24.1	
Ph ₃ P=O, HF	1.495(4)	2.384(5) ^a	1.787	111.1	107.8	20.8; 59.3; 28.6	6
Ph ₃ P=O, HCl ^b	1.517(2)	2.747(2) ^c	1.782	110.1	108.8	15.6; 103.3; 28.1	7
(Ph ₃ P=O) ₂ , HBr, H ₂ O	1.480(3)	2.470(1)	1.790	111.0	107.8	10.9; 56.22; 21.4	8
[(Ph ₃ P=O) ₂ H] ⁺ AuCl ₄ ⁻	1.526(8)	2.39	1.777	110.0	108.6		9
Ph ₃ As=O, C ₆ F ₅ OH ^d	1.662(2)	2.599(5)	1.908	111.7	107.1	20, 54, 22	2

^aO...F distance. ^bProton is transferred to oxygen. ^cO...Cl distance. ^dWhen reading table, replace P by As for this compound.

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