

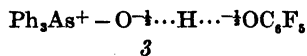
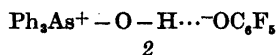
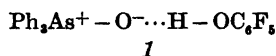
Crystal and Molecular Structure of the Hydrogen-bonded Adduct of Triphenylarsine Oxide with Pentafluorophenol

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The 1:1 triphenylarsine oxide (TPAO) adduct of pentafluorophenol (PFP) crystallizes in the monoclinic space group $P2_1/c$, with a unit cell of dimensions $a = 8.790(5)$ Å, $b = 15.617(7)$ Å, $c = 16.576(4)$ Å and $\beta = 105.26(3)^\circ$. There are 4 molecules in the unit cell. X-Ray data were collected on an off-line four-circle diffractometer. The structure was determined by three-dimensional Patterson and Fourier syntheses and refined by full-matrix least squares methods to a final R factor of 0.043. The arsenic atom is tetrahedrally coordinated with angles ranging from 107.2 to 112.3° . The adduct consists of TPAO and PFP moieties hydrogen-bonded together. The overall O—H...O distance is $2.599(5)$ Å and the hydrogen atom H(1) is located at the phenol oxygen.

The present structure determination was undertaken in order to ascertain whether the 1:1 triphenyl arsine oxide—pentafluorophenol adduct has the hydrogen-bonded structure (1) or the ionic structure (2) corresponding to a proton transfer, or if the adduct has crystallized in the form suggested by Jensen¹ (3).



This complex has previously been studied by means of infrared spectroscopy and NMR (^1H and ^{19}F).² The results from these experiments indicate a strong hydrogen bond and no proton transfer.

EXPERIMENTAL

The crystals used were prepared by mixing 1:1 mol ratios of TPAO to PFP in methanol solution. After evaporation the isolated crystals were recrystallized from a mixture of light petroleum and benzene. The crystal used throughout the data collection had the dimensions 0.7 mm \times 0.3 mm \times 0.3 mm and was mounted along the a axis.

The space group was determined from Weissenberg and precession photographs. Unit cell dimensions were derived from diffractometer measurements of 2θ values for 16 reflections using $\text{MoK}\alpha$ radiation.

3858 independent reflections with $2\theta \leq 50^\circ$ were recorded on a four-circle diffractometer using $\theta - 2\theta$ scan. 623 of these reflections had net counts less than twice the estimated error in measurements and were given zero weight in the calculations. Lp corrections and absorption corrections were applied, the latter according to a procedure described by Coppens *et al.*³

Approximate coordinates for the arsenic atom were found from a three-dimensional Patterson synthesis, and the positions of the remaining non-hydrogen atoms were found from a subsequent Fourier map. The phenyl-hydrogen positions were calculated from geometrical considerations. The atomic parameters were refined by full-matrix least squares procedures, minimizing the function $\sum \omega(|F_o| - |F_c|)^2$ where $\omega = 1/\sigma_F^2$. The final hydrogen atom H(1) was localized from a difference Fourier map. The refinement converged at an R of 0.043, the weighted R factor is 0.050, with no shift at that stage greater than the corresponding standard deviation.

Final atomic coordinates and temperature parameters are listed in Table 1. Lists of observed and calculated structure factors may be obtained from the author.

Table 1a. Fractional coordinates and thermal parameters for non-hydrogen atoms with standard deviations. Thermal parameters are of the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hkab^*c^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Atom	X/a	Y/b	Z/c	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	U ₁₃	U ₂₃	U ₁₃
As	.14386(4)	.37597(2)	.35559(2)	.0420(2)	.0413(2)	.0516(2)	-.0004(2)					
F2	.6140(4)	.1133(3)	.6416(3)	.091(2)	.164(3)	.181(3)	-.020(2)					
F3	.6205(4)	-.0492(2)	.6554(2)	.148(3)	.154(3)	.113(2)	.048(3)					
F4	.2508(5)	-.1078(2)	.5492(2)	.196(4)	.058(2)	.146(2)	-.026(2)					
F5	.0770(4)	-.0031(2)	.4325(2)	.110(2)	.116(2)	.107(2)	-.037(2)					
F6	.1654(4)	.1562(2)	.4170(2)	.098(2)	.106(2)	.107(3)	.015(2)					
O1	.2684(3)	.3365(2)	.4408(2)	.060(2)	.062(2)	.068(2)	.007(1)					
O2	.4484(5)	.2170(2)	.5245(4)	.100(3)	.058(2)	.252(6)	-.031(2)					
C1	.3903(6)	.1389(3)	.5292(3)	.075(3)	.054(2)	.132(4)	-.007(2)					
C2	.4771(6)	.0853(4)	.5894(4)	.069(3)	.093(4)	.118(4)	-.012(3)					
C3	.4327(6)	.0016(3)	.5975(3)	.094(4)	.084(3)	.072(3)	.020(3)					
C4	.2963(6)	-.0269(3)	.5446(3)	.113(4)	.049(2)	.080(3)	-.008(2)					
C5	.2111(5)	.0267(3)	.4865(3)	.076(3)	.071(3)	.078(3)	-.011(2)					
C6	.2572(5)	.1081(3)	.4790(3)	.063(3)	.058(2)	.102(3)	.009(2)					
C11	.1370(4)	.3084(2)	.2588(2)	.051(2)	.045(1)	.064(2)	-.002(2)					
C12	.2649(7)	.2562(4)	.2589(4)	.058(3)	.075(4)	.104(4)	.011(3)					
C13	.2598(9)	.2100(5)	.1877(5)	.091(5)	.098(5)	.128(6)	.018(4)					
C14	.1374(9)	.2121(4)	.1193(4)	.123(6)	.079(4)	.081(4)	-.009(4)					
C15	.0113(9)	.2643(4)	.1202(4)	.110(6)	.099(5)	.066(4)	.000(4)					
C16	.0079(7)	.3128(3)	.1900(3)	.079(4)	.073(3)	.055(3)	.002(3)					
C21	.2094(4)	.4891(2)	.3369(2)	.045(2)	.047(2)	.056(2)	-.003(2)					
C22	.3072(7)	.5318(3)	.4022(4)	.080(4)	.055(3)	.074(4)	-.011(3)					
C23	.3571(9)	.6135(4)	.3900(5)	.098(5)	.063(4)	.113(5)	-.022(3)					
C24	.3068(9)	.6524(4)	.3157(5)	.104(5)	.050(3)	.127(6)	-.016(3)					
C25	.2140(9)	.6093(4)	.2496(5)	.159(8)	.070(4)	.102(5)	-.015(4)					
C26	.1622(9)	.5271(4)	.2610(4)	.118(5)	.062(3)	.075(4)	-.024(4)					
C31	-.0665(4)	.3833(2)	.3665(2)	.050(2)	.044(2)	.054(2)	.001(2)					
C32	-.1345(6)	.3111(3)	.3884(3)	.054(3)	.047(3)	.090(4)	-.000(2)					
C33	-.2875(7)	.3139(4)	.3967(4)	.055(3)	.065(3)	.111(5)	.007(3)					
C34	-.3686(7)	.3886(4)	.3840(4)	.046(3)	.087(4)	.105(4)	.000(3)					
C35	-.3038(8)	.4604(4)	.3615(5)	.069(4)	.068(4)	.160(4)	.023(3)					
C36	-.1495(7)	.4585(4)	.3526(4)	.077(4)	.056(3)	.146(6)	.013(3)					

Table 1b. Fractional coordinates and thermal parameters for hydrogen atoms with standard deviations. Thermal parameters are of the form $T = \exp[-8\pi^2 U(\sin^2\theta)/\lambda^2]$.

Atom	X/a	Y/b	Z/c	U
H12	.356(7)	.247(3)	.309(3)	.074(16)
H13	.333(7)	.177(4)	.185(3)	.103(18)
H14	.127(6)	.179(4)	.069(3)	.090(16)
H15	-.070(8)	.273(4)	.073(4)	.121(20)
H16	-.077(6)	.348(3)	.189(3)	.150(15)
H22	.342(6)	.503(3)	.462(3)	.071(14)
H23	.429(9)	.641(4)	.437(4)	.131(25)
H24	.340(6)	.708(4)	.309(5)	.086(16)
H25	.183(9)	.627(4)	.192(5)	.144(28)
H26	.097(7)	.496(3)	.212(3)	.076(16)
H32	-.075(7)	.253(3)	.397(3)	.083(17)
H33	-.347(8)	.261(4)	.409(4)	.125(21)
H34	-.467(6)	.392(3)	.392(3)	.070(13)
H35	-.364(6)	.513(4)	.353(3)	.097(18)
H36	-.113(7)	.513(4)	.335(3)	.103(17)
H1	.388(9)	.246(4)	.491(4)	.17(3)

CRYSTAL DATA

$C_{24}H_{16}AsF_6O_4$ M.W. = 506.31
 Space group $P2_1/c$ (No. 14)
 $a = 8.790(5)$ Å, $b = 15.617(7)$ Å, $c = 16.576(4)$ Å,
 $\beta = 105.26(3)^\circ$
 $V = 2195(2)$ Å³, $Z = 4$.
 $D_c = 1.532$ g cm⁻³, $D_m = 1.50$ g cm⁻³.
 $\mu(\text{MoK}\alpha) = 16.7$ cm⁻¹.

RESULTS AND DISCUSSION

The structure, shown in Fig. 1, consists of TPAO and PFP moieties hydrogen-bonded together giving monomeric adducts. Some important bond distances are shown in the same figure in which the atomic numbering used in this paper is also given. The essential bond distances and bond angles are listed in Table 2.

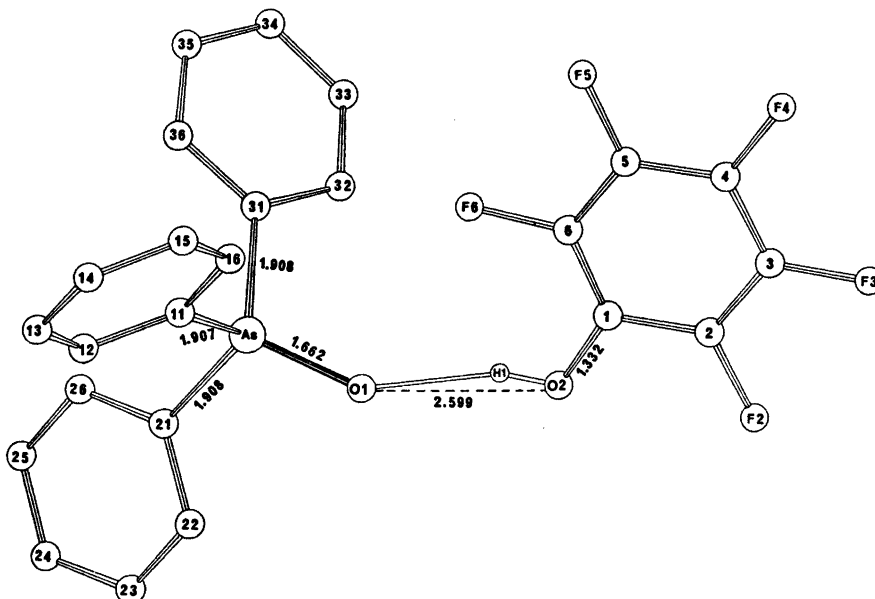


Fig. 1. TPAO-PFP with numbering of atoms and a few parameters.

Table 2. Selected bond distances and bond angles with corresponding standard deviation in parentheses.

	(Å)	Angle	(°)
As—O(1)	1.662(2)	O(1)—As—C(11)	112.2(1)
As—C(11)	1.907(4)	O(1)—As—C(21)	108.8(1)
As—C(21)	1.908(3)	O(1)—As—C(31)	112.3(1)
As—C(31)	1.908(4)	C(11)—As—C(21)	108.7(1)
C(1)—O(2)	1.332(6)	C(11)—As—C(31)	107.2(1)
O(1)—O(2)	2.599(5)	C(21)—As—C(31)	107.5(1)
O(1)—H(1)	0.80(6)	As—O(1)—O(2)	153.2(2)
O(2)—H(1)	1.83(7)	O(1)—O(2)—C(1)	120.0(3)
		H(1)—O(2)—C(1)	111(5)
		O(1)—H(1)—O(2)	162(5)

Table 3. Some average bond angles and bond distances in triphenylarsine oxide complexes.

Compound	Average C—As—C (°)	Average C—As—O (°)	As—O (Å)	Average* O...O (Å)
Ph ₃ AsO.H ₂ O ⁴	108.0	110.9	1.644	2.800*
Ph ₃ AsO.C ₆ H ₅ Cl ₄ O ₃ ⁵	108.4	110.6	1.694	2.616*
(Ph ₃ AsO.HgCl ₂) ₂ ⁶	108.9	110.1	1.66	
(Ph ₃ AsO) ₂ .HgCl ₂ ⁷	107.7	111.2	1.69	
Ph ₃ AsO.C ₆ F ₅ OH	107.8	111.1	1.662	2.599

The mean C—C bond distance in the phenyl groups are 1.369(4) Å, while the C—H distances range from 0.84 to 1.04 Å. Standard deviations of the individual C—H bond distances are approximately 0.06 Å. In the PFP moiety the mean C—C bond distance is 1.373(3) Å and the mean C—F bond distance 1.346(3) Å. The bond distances have not been corrected for rigid-body libration.

The geometry around the arsenic atom is essentially tetrahedral with angles ranging from 107.2 to 112.3°. The average C—As—C and C—As—O angles, 107.80(6) and 111.10(6)° respectively, are comparable with corresponding values in analogous complexes⁴⁻⁷ (see Table 3). The TPAO moiety as a whole possesses no symmetry because of unequal rotations of the phenyl groups about the As—C bonds. The twist angles between the planes through the benzene rings and the planes containing As, O(1) and C(11), C(21) and C(31), respectively, are 22, 20, and 54°. The three phenyl rings are planar within experimental error.

It is interesting to note that the conformation of the TPAO moiety is practically the same in the present study as in triphenylphosphine oxide.⁸ The average C—P—C and C—P—O angles are 107.1(5) and 111.7(4)°, respectively, and the twist angles of the phenyl groups are 24.7, 21.1, and 59.3°. In the analogous arsenic compounds⁴⁻⁷ one also finds one large twist angle and two smaller ones; however, the values of the angles differ from those already mentioned.

The spectroscopic data⁸ on this compound indicate a strong hydrogen bond. The overall O...O distance of 2.599(5) Å found in the present X-ray diffraction study supports the spectroscopic evidence for a strong bond.

In X-ray work on analogous triphenylarsine oxide complexes⁴⁻⁷ no evidence for proton transfer is found, indicating that these complexes belong to the hydrogen-bonded structure (I).

In the present case the structure (I) is supported by the location of the hydrogen atom

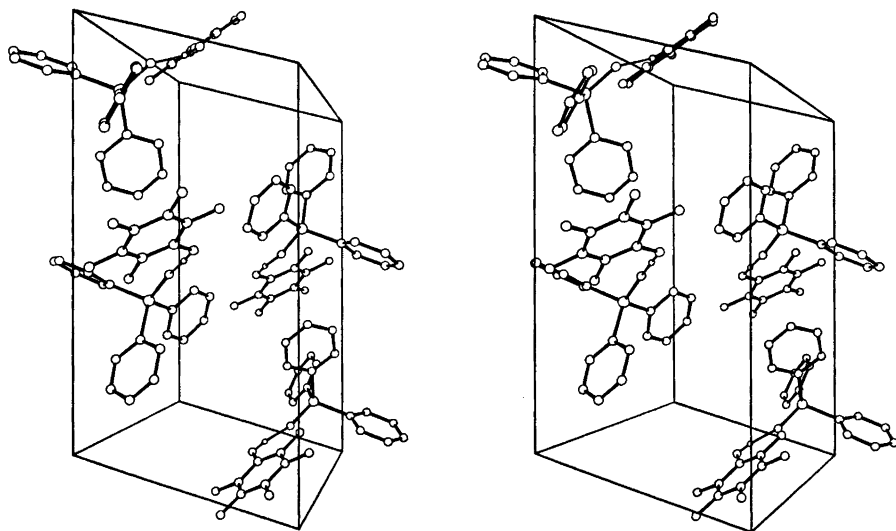


Fig. 2. Stereo drawing showing the packing of the molecules in the unit cell. The *b*-axis is pointing away from the viewer, the *c*-axis is running vertically, bottom to top, and the *a*-axis diagonally left to right. Figs. 1 and 2 were drawn by use of the ORTEP program.¹²

H(1) in the difference Fourier map and also by consideration of the bond distances As—O(1) and C(1)—O(2) found. The As—O(1) bond distance of 1.662(2) Å is appreciable shorter than the As—O bond distance of 1.87 Å calculated from covalent bond radii, and also significantly shorter than the calculated As—O double distances of 1.73 Å.⁹ Similar shortening effects are found in analogous compounds of phosphorus and sulfur. Cruickshank¹⁰ has explained this shortening by overlap between the filled *p* π -orbitals of the oxygen atom and the unfilled 3*d* π -orbitals of the phosphorus and sulfur atoms. In the present case the unfilled 4*d* π -orbitals of the arsenic atom are presumably involved.

The C(1)—O(2) bond distance of 1.332(6) Å is comparable to the C—O bond distance of 1.33 Å in pentachlorophenol.¹¹

A stereo drawing of the molecular packing in the unit cell is shown in Fig. 2. There are no intermolecular contacts shorter than the corresponding van der Waals distances.

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REFERENCES

1. Jensen, K. A. *Z. Anorg. Allg. Chem.* **250** (1943) 268.
2. Dale, A. *To be published.*
3. Coppens, P., Leiserowitz, L. and Rabinovitch, D. *Acta Crystallogr.* **18** (1965) 1035.
4. Ferguson, G. and Macaulay, E. W. *J. Chem. Soc. A.* (1969) 1.
5. Farris, F. F. and Robinson, W. R. *J. Organomet. Chem.* **31** (1971) 375.
6. Brandén, C. I. *Ark. Kemi* **22** (1964) 485.
7. Brandén, C. I. *Acta Chem. Scand.* **17** (1963) 1363.
8. Bandoli, G., Bortolozzo, G., Clemente, D. A., Croatto, U. and Panattoni, C. *J. Chem. Soc. A* (1970) 2778.
9. Gillespie, R. J. *Molecular Geometry*, Van Nostrand Reinhold Company, London 1972, p. 18.
10. Cruickshank, J. *J. Chem. Soc. A* (1961) 5487.
11. Sakurai, T. *Acta Crystallogr.* **15** (1962) 1164.
12. Johnson, C. K. *ORTEP, A Fortran Thermal Ellipsoid Program for Crystal Structure Analysis*, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee 1970.

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