

Presumably the simultaneous rotation of *R*5 by 10° away from the equatorial plane allows for the closer approach of the equatorial rings *R*3 and *R*4. In the unsolvated (C₆H₅)₅Sb structure this same type of distortion is carried much further, and also involves displacement of the *R*1 and *R*2 rings away from *R*5 in the plane perpendicular to the original equatorial plane. Furthermore, in this final example the Sb–C(31) and Sb–C(41) bonds are significantly lengthened.

It could be argued that the distortions described above outline the mechanism of pseudo-rotation proposed by Berry (1960) for five-coordinate molecules. It has been suggested (Bürgi, 1973; Bürgi, Dunitz & Shefter, 1974) that an analysis of geometric parameters describing similar molecular units in a variety of environments can be used to experimentally map the minimum energy pathways involved in chemical transformations. In this study the pathway corresponds to a normal mode of the penta-aryl molecule. In any event, the energy changes required to distort the molecules in this way cannot be large since ¹³C NMR solution spectra (S. L. Smith & C. P. Brock, unpublished work) show the α -carbons of pentaphenylarsenic and pentaphenylantimony to be magnetically equivalent to 173 K. This equivalence implies rapid interconversion between axial and equatorial sites, presumably through an intermediate square-pyramidal geometry. It can thus be concluded that the first three molecules pictured in Fig. 2 define the preferred conformation of the penta-aryl Group V molecules, and that the last two show the types of distortions that are observed as a result of packing interactions.

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References

- BEAUCHAMP, A. L., BENNETT, M. J. & COTTON, F. A. (1968). *J. Amer. Chem. Soc.* **90**, 6675–6680.
 BERRY, R. S. (1960). *J. Chem. Phys.* **32**, 933–938.
 BRABANT, C., BLANCK, B. & BEAUCHAMP, A. L. (1974). *J. Organomet. Chem.* **82**, 231–234.
 BRABANT, C., HUBERT, J. & BEAUCHAMP, A. L. (1973). *Canad. J. Chem.* **51**, 2952–2957.
 BROCK, C. P. & IBERS, J. A. (1976). *Acta Cryst.* **A32**, 38–42.
 BÜRGI, H. B. (1973). *Inorg. Chem.* **12**, 2321–2325.
 BÜRGI, H. B., DUNITZ, J. D. & SHEFTER, E. (1974). *Acta Cryst.* **B30**, 1517–1527.
 BURNHAM, C. W. (1966). *Amer. Min.* **51**, 159–165.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.
 GILLESPIE, R. J. (1972). *Molecular Geometry*. London: Van Nostrand-Reinhold.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
 JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
 PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
 WHEATLEY, P. J. (1964a). *J. Chem. Soc.* pp. 2206–2222.
 WHEATLEY, P. J. (1964b). *J. Chem. Soc.* pp. 3718–3723.
 WHEATLEY, P. J. & WITTIG, G. (1962). *Proc. Chem. Soc.* pp. 251–252.
 WITTIG, G. & CLAUSS, K. (1952). *Liebigs Ann.* **577**, 26–39.

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The Crystal and Molecular Structure of the 2:1 Complex between Triphenylarsine Oxide and Selenous Acid

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(Ph₃AsO)₂H₂SeO₃ crystallizes in space group *Fdd*2, *a* = 20.59, *b* = 32.95, *c* = 10.05 Å, with eight formula units in the unit cell. The structure has been determined by three-dimensional X-ray methods from 959 visually estimated independent reflexions, and refined by full-matrix least squares; *R* = 0.11. The molecules of the complex are held together by hydrogen bonds; each hydrogen of the selenous acid is bonded to one triphenylarsine oxide.

Introduction

During an investigation into the reaction between selenium dioxide and triphenylarsine in various organic

solvents a colourless crystalline compound was obtained (El Sheikh, Patel, Smith & Waller, 1976). Since the chemical analysis and physical properties of this compound could not be explained in terms of a simple

adduct between the reacting species, the crystal structure has been determined.

Experimental

The crystals were provided by B. C. Smith, Birkbeck College, London.

Crystal data

$C_{36}H_{32}As_2O_5Se$, $M=773.9$, orthorhombic, $a=20.59 \pm 0.01$, $b=32.95 \pm 0.01$, $c=10.050 \pm 0.007$ Å, $D_m=1.516$, D_c for $8[(Ph_3AsO)_2H_2SeO_3]=1.507$ g cm $^{-3}$, Cu $K\alpha$ radiation, $\mu=44.08$ cm $^{-1}$. Systematic extinctions: $hkl, h+k, k+l=2n+1$; $0kl (k, l=2n+1) k+l \neq 4n$; $h0l (h, l=2n+1) h+l \neq 4n$. Space group $Fdd2 (C_{2v}^{19}, \text{No. 43})$ or $Fddd (D_{2h}^{24}, \text{No. 70})$.

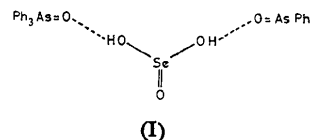
959 independent reflexions were visually estimated from equi-inclination Weissenberg photographs ($hk0-hk8$). The data were scaled on the exposure times for each layer which were proportional to $\sec^2\mu$.

Solution and refinement of structure

The normalized structure factors (E) were calculated and the distribution in the values of E suggested that the space group was the non-centrosymmetric $Fdd2$.

The unsharpened three-dimensional Patterson synthesis had only a single prominent feature which was consistent with a heavy atom in space group $Fdd2$. Successive F_o syntheses revealed a triphenylarsine oxide molecule with the As=O bond pointing in the direction of the twofold axis and with the O atom 3.7

Å from the axis. A difference Fourier synthesis was then calculated where the most prominent feature was a peak 0.44 Å from the twofold axis and it seemed likely that this represented a Se atom, disordered, with alternative positions on either side of the axis. From a sequence of least-squares refinements followed by difference Fourier syntheses it was established that there were only three atoms bonded to the Se atom; one near, and the other two somewhat away from the twofold axis. Each atom was disordered with an alternative position required by the axis, and for the two atoms away from the axis the position of one was only 1.1 Å from the alternative position of the other, Fig. 1. Since the difference Fourier synthesis showed no other significant features and as the weight of the contents of the unit cell now corresponds, within experimental error, to that calculated from the density of the crystal, it was assumed that the positions of all nonhydrogen atoms had been determined and that the molecular structure was as shown in (I).



The structure was refined with six cycles of least squares with anisotropic temperature factors on the As, Se and O atoms and isotropic temperature factors on all the C atoms. The SeO_3 group was placed in both positions with occupancy of one half in each.

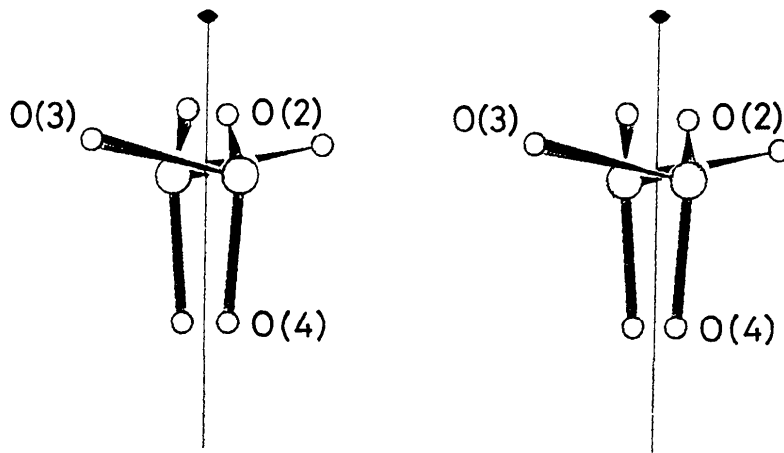


Fig. 1. A stereoscopic projection along a of the disordered SeO_3 group.

Table 1. Atomic parameters ($\times 10^4$)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As(1)	1267 (1)	798 (1)	0	265	402	345	0	0	-45
Se(1)	-125 (2)	107 (1)	3073 (7)	350	469	410	-40	72	-46
O(1)	697 (7)	450 (5)	368 (18)	424	430	128	-92	164	-280
O(2)	684 (17)	100 (18)	2399 (58)	315	1407	835	-984	48	-165
O(3)	-404 (24)	-412 (12)	2711 (54)	853	548	1048	328	-251	725
O(4)	-124 (11)	70 (19)	4584 (47)	245	889	459	-229	-36	50

Table 1 (cont.)

	x	y	z	U_{iso}
C(11)	1174 (11)	942 (9)	-1916 (35)	263
C(12)	787	701	-2761	280
C(13)	783 (16)	807 (11)	-4047 (46)	994
C(14)	1166	1154	-4483	717
C(15)	1554 (16)	1396 (10)	-3636 (42)	672
C(16)	1557	1290	-2352	483
C(21)	1178 (11)	1268 (8)	1033 (30)	275
C(22)	1701	1539	1271	509
C(23)	1602 (13)	1882 (9)	2137 (34)	393
C(24)	981	1954	2765	625
C(25)	458 (13)	1683 (9)	2527 (36)	614
C(26)	556	1340	1662	298
C(31)	2128 (12)	593 (7)	229 (29)	305
C(32)	2492	471	-920	441
C(33)	3095 (13)	270 (8)	-789 (36)	487
C(34)	3336	192	492	401
C(35)	2972 (13)	314 (9)	1641 (36)	599
C(36)	2369	515	1512	410

The three phenyl groups were refined with the rigid-body constraint for hexagonal rings (Sheldrick, 1972). The weighting scheme used was given by: $w = \{[(|F_o|_{lab} - 35)/30]^2\}^{-1}$ and the refinement converged at $R = 0.11$.* The final atomic parameters are given in

* A list of observed structure amplitudes and structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31677 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. The atomic scattering factors used were those published by Cromer & Waber (1965), and were corrected for the real part of the anomalous dispersion effect. The interatomic distances and bond angles are given in Table 2. Fig. 1 is a stereoscopic projection of the disordered SeO_3 group, Fig. 2 shows the unique molecule and Fig. 3 illustrates its packing in the unit cell. In both Figs. 2 and 3 only one of the two possible H_2SeO_3 positions is indicated. All calculations were computed on the New University of Ulster 1903A Computer with the Cameron (1973) *CRYSTAL* system. A routine specific to space group *Fdd2* was written for the Fourier calculations.

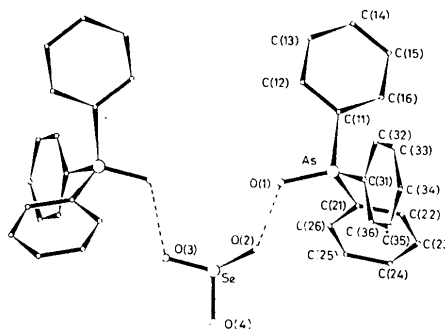


Fig. 2. A projection of the complex; the a axis has been rotated 40° from the perpendicular about the c axis.

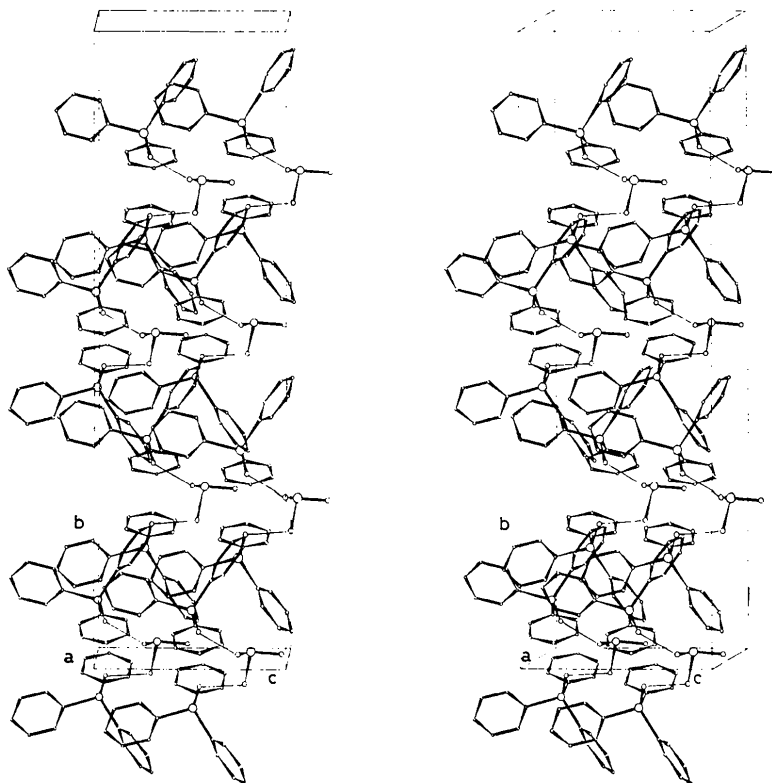


Fig. 3. Stereoscopic projection of the unit cell.

Table 2. *Interatomic distances and bond angles*

As(1)—O(1)	1.68 (1) Å	C(21)—C(22)	1.42 (2) Å
As(1)—C(11)	1.99 (2)	C(21)—C(26)	1.45 (2)
As(1)—C(21)	1.88 (1)	C(22)—C(23)	1.44 (2)
As(1)—C(31)	1.91 (1)	C(23)—C(24)	1.45 (2)
Se(1)—O(2)	1.80 (3)	C(24)—C(25)	1.42 (2)
Se(1)—O(3)	1.84 (2)	C(25)—C(26)	1.44 (2)
Se(1)—O(4)	1.52 (3)	C(31)—C(32)	1.43 (2)
C(11)—C(12)	1.41 (2)	C(31)—C(36)	1.40 (2)
C(11)—C(16)	1.46 (2)	C(32)—C(33)	1.41 (2)
C(12)—C(13)	1.34 (3)	C(33)—C(34)	1.40 (2)
C(13)—C(14)	1.46 (2)	C(34)—C(35)	1.43 (2)
C(14)—C(15)	1.41 (2)	C(35)—C(36)	1.41 (2)
C(15)—C(16)	1.34 (3)	O(1)—O(3)	2.43 (3)
		O(1)'—O(2)	2.34 (3)
O(1)—As(1)—C(11)	107.9 (6)°	As(1)—C(21)—C(22)	123 (1)°
O(1)—As(1)—C(21)	111.9 (5)	As(1)—C(21)—C(26)	118 (1)
O(1)—As(1)—C(31)	112.3 (6)	C(22)—C(21)—C(26)	120 (1)
C(11)—As(1)—C(21)	109.2 (7)	C(21)—C(22)—C(26)	119 (1)
C(11)—As(1)—C(31)	106.9 (6)	C(22)—C(23)—C(24)	121 (1)
C(21)—As(1)—C(31)	108.5 (5)	C(23)—C(24)—C(25)	120 (1)
O(2)—Se(1)—O(3)	104 (3)	C(24)—C(25)—C(26)	119 (1)
O(2)—Se(1)—O(4)	109 (3)	C(25)—C(26)—C(21)	121 (1)
O(3)—Se(1)—O(4)	98 (3)	As(1)—C(31)—C(32)	119 (1)
As(1)—C(11)—C(12)	120 (1)	As(1)—C(31)—C(36)	120 (1)
As(1)—C(11)—C(16)	115 (1)	C(32)—C(31)—C(36)	120 (1)
C(12)—C(11)—C(16)	124 (2)	C(31)—C(32)—C(33)	121 (2)
C(11)—C(12)—C(13)	116 (2)	C(32)—C(33)—C(34)	119 (2)
C(12)—C(13)—C(14)	120 (2)	C(33)—C(34)—C(35)	120 (1)
C(13)—C(14)—C(15)	124 (2)	C(34)—C(35)—C(36)	121 (2)
C(14)—C(15)—C(16)	116 (2)	C(35)—C(36)—C(31)	119 (2)
C(15)—C(16)—C(11)	120 (2)		
As(1)—O(1)⋯O(2)	122 (1)		
As(1)'—O(1)'⋯O(3)	115 (1)		
Se(1)—O(2)⋯O(1)	108 (1)		
Se(1)—O(3)⋯O(1)'	110 (1)		

A prime indicates an atom related by the twofold axis.

Results and discussion

The crystal contains isolated units with two triphenylarsine oxide fragments, related by the twofold axis, each hydrogen-bonded to one selenous acid molecule (I). The triphenylarsine oxide molecules pack in planes approximately parallel to (040) with a phenyl group from each fitting into the cavity behind the As=O bond of the adjacent molecule. The As=O bonds of alternate molecules point to opposite sides of the plane (Fig. 3).

The dimensions of the triphenylarsine oxide molecule resemble those observed for the triphenylarsine oxide hydrate, $\text{Ph}_3\text{AsO} \cdot \text{H}_2\text{O}$, by Ferguson & Macaulay (1969). The As=O bond length, 1.68 (1) Å, may just be significantly longer than that [1.644 (7) Å] in the hydrate and this would be consistent with the significantly shorter O—O hydrogen-bond contacts in the present compound [2.43 (3) and 2.34 (3) compared with 2.819 and 2.780 Å]. A similar lengthening of the P—O bond length was observed in $(\text{Ph}_3\text{POH})^+$ (Cameron & Prout, 1969). The As—C bond lengths are 1.99 (2), 1.91 (1) and 1.88 (1) Å. This significant difference in length (and possibly the long C—C bonds) might well be a consequence of the partial rigid-body refinement that was necessary to make the least-squares procedure

converge. However the two short As—C bond lengths are at the phenyl groups where there is a short intermolecular contact to the C atom *para* to the arsenic, C(21)—As 1.88 (1), C(24)—O(2) 3.46 (3) and C(31)—As 1.91 (1), C(34)—O(4) 3.37 (3) Å. These short contacts are in such a direction (Fig. 3) as to exert a compression force along the As—C bond and it has been shown in substituted phenylphosphines that such compression forces cause a shortening of the P—C bond length (Cameron & Dahléen 1975). It is possible that a similar compression is shortening these two As—C bonds.

With the Se atom so close to the axis and with two alternative positions also for the three O atoms there are eight chemically plausible combinations of O and Se atoms to make the SeO_3 fragment. The combination that was chosen gives a structure where the Se=O(4) bond length of 1.58 (3) compares with that of 1.61 (1) Å in gaseous SeO_2 (*International Tables for X-ray Crystallography*, 1968) and the Se—O(2) and Se—O(3) bond lengths, 1.81 (3) and 1.84 (2) Å respectively, compare with the reported range of Se—O distances (1.72–1.76 Å) in the extended layer lattice of selenous acid (Wells & Bailey 1949) and the mean length of 1.76 (2) Å in the H_3SeO_3^+ ion (Vijayan 1968). The SeO_3 group is pyramidal with Se at the apex and with a mean O—Se—O interbond angle of 104°.

Clearly the H_2SeO_3 fragment of the complex is just too small for the cavity in the structure between the arsine oxide molecules and while this permits it to adopt one of two positions and noticeably to librate [see the temperature factors of O(2)—O(4)], it is not so small as to allow the structure to accommodate a solvent molecule.

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References

- CAMERON, T. S. (1973). New Univ. of Ulster Internal Report I.
 CAMERON, T. S. & DAHLÉN, B. (1975). *J. Chem. Soc. Perkin II*, pp. 1737–1751.
 CAMERON, T. S. & PROUT, C. K. (1969). *J. Chem. Soc. (C)*, pp. 2289–2291.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 105–109.
 EL SHEIKH, S. I. A., PATEL, M. S., SMITH, B. C. & WALLER, C. B. (1976). To be published.
 FERGUSON, G. & MACAULAY, E. W. (1969). *J. Chem. Soc. (A)*, pp. 1–7.
International Tables for X-ray Crystallography (1968). Vol. III, p. 267. Birmingham: Kynoch Press.
 SHELDRIK, G. M. (1972). Personal communication.
 VIJAYAN, M. (1968). *Acta Cryst.* **B24**, 1237–1241.
 WELLS, A. F. & BAILEY, M. (1949). *J. Chem. Soc.* pp. 1282–1288.