The Crystal Structure of Triphenylarsine Sulphide

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Crystals of $AsPh_3S$ obtained from acetone solution are monoclinic, space group $P2_1/c$, $Z = 8$, with unit-cell dimensions $a = 18.523(8)$, $b = 9.642(4)$, $c = 18.140(8)$ Å, and $\beta = 105.93(4)°$. The compound is isomorphous with PPh_3S and PPh_3Se. The structure has been elucidated on the basis of this isomorphism, from 2 795 observed reflections and refined to R 0.042 2. The As=S bond is essentially a double bond, and in both molecules of the asymmetric unit one phenyl ring lies almost coplanar with the As–S bond, while the other rings have an average torsion angle of 53°. The molecular structure is compared with those of PPh_3S and PPh_3Se in an attempt to elucidate the reasons for the observed conformations.

THIS study is part of a structural investigation [1-3] of Group 5 chalcogenide ligands of the type $R_3M{=}Y$ ($M = P$, As, or Sb; $Y = S$ or Se; R = alkyl or aryl). It is directed at a better understanding of the behaviour of these molecules as ligands, the electronic structure of the M=Y bonds, and the factors affecting the conformation of the R groups.

Although there are now several *X*-ray determinations of the structures of phosphine sulphides and their complexes,[1-7] the only relevant study of an arsine sulphide is that of Hedberg and co-workers [8] who compared the structures of PMe_3O, PMe_3S, $AsMe_3O$, and $AsMe_3S$ by electron diffraction. The *X*-ray structure of $AsPh_3O{\cdot}H_2O$ was reported by Ferguson and Macaulay.[9]

In our previous investigations of triphenylphosphine sulphide and selenide [2,3] we were interested by the conformations of the phenyl rings with respect to the P=Y ($Y = S$ or Se) vector. In common with many similar structures in the crystalline state there is a departure from the C_3 symmetry normally assumed to be the ground state for molecules of this type. By comparing the interatomic distances in the present structure with those in related compounds it was hoped that some further insight into the causes of this lowering of symmetry could be obtained. An additional incentive for carrying out this study is the current interest in steric effects in co-ordination chemistry, largely instigated by Tolman's work on phosphines.[10] There is an obvious analogy between metal-complexed triphenylphosphine and triphenylarsine, and their chalcogenide derivatives.

EXPERIMENTAL

The sample was prepared from the reaction of triphenylarsine (Ventron) and elemental sulphur on hot toluene. Crystals suitable for single-crystal *X*-ray analysis were grown from acetone solution.

Weissenberg photographs indicated that the crystals were isomorphous with triphenylphosphine sulphide and selenide, and that the space group was $P2_1/c$, with systematic absences of the type $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. A crystal of dimensions $0.020 \times 0.020 \times 0.025$ mm was mounted in epoxy-resin and intensity data were collected on a Picker FACS-1 diffractometer with Mo-K_α radiation, and a graphite monochromator ($2\theta_m = 11.99°$). The unit-cell parameters were obtained from a least-squares refinement of the angular parameters of 12 reflections. The data were collected in the θ—2θ scan mode at an initial scan rate of 0.5° min^{-1} with a scan width of $\Delta 2\theta = (1.4 + 0.285 \tan \theta)°$. The scan rate was increased to 1° min^{-1} for the final two thirds of the data set. Background counts were measured for 20 s at either end of the scan. The data were measured to a maximum 2θ of 50°; of the 5 348 reflections measured, 2 795 had intensities greater than $3\sigma(I)$, where $\sigma(I) = [T + B + (0.02I)^2]^{\frac{1}{2}}$, T is the total count, and B is the total background count normalized to the time interval of the scan. Three standard reflections ($3\bar{6}2$, 206, $\bar{8}00$) were monitored every 50 reflections but no crystal deterioration was observed. Standard Lorentz and polarization corrections were applied, but the data were not corrected for absorption [μ(Mo-K_α) = 24.1 cm^{-1}].

Crystal Data.—$C_{18}H_{15}AsS$, $M = 338.3$, Monoclinic, $a = 18.523(8)$, $b = 9.642(4)$, $c = 18.140(8)$ Å, $\beta = 105.93(4)°$, $U = 3\,115.3$ Å^3, $D_m = 1.43$ g cm^{-3}, $Z = 8$, $D_c = 1.44$ g cm^{-3}, $F(000) = 1\,376$, λ(Mo-K_α) = 0.710 7 Å, space group $P2_1/c$.

Structural Determination.—Since the structure is isomorphous with PPh_3S and PPh_3Se the atomic co-ordinates of the latter compound were used to start the refinement. The positions and thermal parameters of the heavy atoms were refined in large blocks (1 molecule per block). The scattering factors were taken from ref. 11; anomalous-dispersion terms were included for all heavy atoms. The positions of the hydrogen atoms were calculated after two cycles of anisotropic refinement and although these atoms were included in the model they were not refined. No spurious electron-density peaks were located in a final difference-Fourier synthesis. The final R values are $R' = \{[\Sigma w(|F_o| - |F_c|)]^2/\Sigma w|F_o|^2\}^{\frac{1}{2}} = 0.042\,9$ for the 2 795 observed reflections; the conventional $R = 0.042\,2$ for these 2 795 reflections and 0.108 3 for all 5 348 reflections. The weighting scheme was $w = [\sigma^2(F) + 0.000\,3F^2]^{-1}$, where $\sigma(F)$ was derived from counting statistics. The standard deviation of an observation of unit weight was 1.31 and the average shift-to-error for the final cycle was 0.06. The final positions of the non-hydrogen atoms are given in Table 1, with the atoms labelled according to Figure 1. The anisotropic thermal parameters for the non-hydrogen atoms, the parameters for the hydrogen atoms, and the structure factors are contained in Supplementary Publication No. SUP 22529 (44 pp.).† Computer programs used include CUDLS (John Stevens), ORTEP (C. K. Johnson), and several programmes from the Los Alamos Scientific Laboratory System of Programmes (A. C. Larson).

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 1

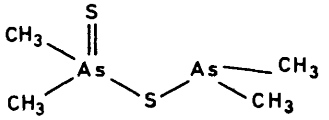
Fractional co-ordinates for the non-hydrogen atoms of $AsPh_3S$ with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
As	0.939 51(3)	0.158 53(7)	0.819 95(4)
S	0.896 0(1)	−0.009 8(2)	0.865 6(1)
C(1)	1.047 9(3)	0.162 7(6)	0.852 3(3)
C(2)	1.082 9(3)	0.144 2(7)	0.929 9(3)
C(3)	1.160 6(4)	0.142 1(8)	0.956 4(4)
C(4)	1.203 9(3)	0.160 1(7)	0.904 7(4)
C(5)	1.168 7(4)	0.176 1(7)	0.828 3(4)
C(6)	1.090 5(3)	0.178 7(7)	0.800 8(3)
C(7)	0.906 3(3)	0.336 3(6)	0.848 0(3)
C(8)	0.955 8(3)	0.436 9(7)	0.884 4(4)
C(9)	0.928 3(4)	0.563 1(8)	0.901 9(4)
C(10)	0.852 0(4)	0.585 3(8)	0.883 6(4)
C(11)	0.802 1(4)	0.484 2(8)	0.848 4(4)
C(12)	0.829 1(3)	0.359 9(7)	0.830 6(3)
C(13)	0.907 7(3)	0.161 0(7)	0.708 9(3)
C(14)	0.920 6(4)	0.274 7(7)	0.667 9(4)
C(15)	0.896 2(4)	0.273 0(8)	0.588 7(4)
C(16)	0.858 5(4)	0.159 5(10)	0.550 8(4)
C(17)	0.844 3(4)	0.048 0(8)	0.591 7(4)
C(18)	0.869 0(3)	0.047 6(7)	0.670 8(4)
As′	0.556 25(4)	0.580 63(7)	0.667 12(4)
S′	0.595 9(1)	0.742 7(2)	0.613 7(1)
C(1′)	0.447 8(3)	0.578 0(6)	0.642 2(3)
C(2′)	0.407 3(4)	0.591 7(7)	0.567 3(3)
C(3′)	0.329 4(4)	0.599 2(8)	0.547 3(4)
C(4′)	0.293 4(3)	0.591 6(7)	0.604 2(4)
C(5′)	0.333 0(4)	0.578 6(7)	0.678 7(4)
C(6′)	0.410 9(3)	0.570 9(7)	0.699 1(3)
C(7′)	0.587 8(3)	0.401 0(7)	0.642 1(3)
C(8′)	0.538 5(4)	0.296 6(7)	0.611 4(4)
C(9′)	0.565 7(4)	0.168 8(8)	0.596 5(4)
C(10′)	0.642 0(4)	0.148 2(8)	0.612 4(4)
C(11′)	0.691 1(4)	0.252 7(9)	0.641 3(4)
C(12′)	0.664 9(4)	0.379 0(7)	0.657 3(3)
C(13′)	0.593 0(3)	0.585 8(7)	0.777 3(3)
C(14′)	0.584 4(4)	0.474 9(7)	0.821 7(4)
C(15′)	0.611 0(4)	0.480 6(8)	0.900 5(4)
C(16′)	0.647 1(4)	0.598 3(9)	0.934 5(4)
C(17′)	0.655 5(4)	0.709 8(7)	0.890 9(4)
C(18′)	0.628 4(3)	0.704 0(7)	0.812 5(4)

DISCUSSION

The important bond lengths and angles are given in Table 2. The average values for the two molecules per asymmetric unit are shown in Figure 1, and a stereodrawing of the asymmetric unit is in Figure 2. The arsenic atom is approximately tetrahedrally co-ordinated, but the possibility of C_3 molecular symmetry is not realized, due to unequal rotations of the phenyl groups about the C–As bonds (Table 3) and a significant distortion in the C–As–C angles from an ' averaged ' structure. In both molecules the C(7)–As–C(13) angle is smaller than the other two C–As–C angles. In contrast, the S–As–C angles are approximately the same.

The As–S bond lengths [average 2.079(2) Å] can be compared with the two values quoted by Camerman and Trotter [12] for the following structure:



The terminal sulphur–arsenic bond was found to be 2.07 Å, and the bridging As–S 2.21 and 2.29 Å. The As=S bond length in $Me_3As=S$ of 2.059(3) Å was obtained from an electron-diffraction study [8] and is thus not strictly comparable with the X-ray results since the two experiments measure different averages. In view of the extensive arguments in the literature concerning the nature of the M–Y (Group 5 element–chalcogenide) bond,[8] we are tempted to comment on the significance of the As–S bond length. Vibrational spectra usually indicate a strengthening of the M–Y bond with increasing electron-withdrawing character of the R group attached to M. Thus we would expect from this reasoning that the As–S bond should be shorter in $AsPh_3S$ [ν(As–S) at 490 cm^{-1}] [13] than in $AsMe_3S$ [ν(As–S) at 473 cm^{-1}].[13] Zingaro *et al.*[13] showed that from Pauling's arguments [14] the length of a ' pure ' As=S double bond would be 2.05 Å whereas that for a single bond would be 2.25 Å. Hedberg and co-workers [8] used their electron-diffraction data to ascribe a Pauling bond order of 1.94 to the As–S bond in $AsMe_3S$. An extension

TABLE 2

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

As–S	2.082(2)	As′–S′	2.076(2)
As–C(1)	1.931(5)	As–C(1′)	1.935(6)
As–C(7)	1.936(6)	As′–C(7′)	1.922(6)
As–C(13)	1.937(6)	As′–C(13′)	1.926(6)
Average C–C (phenyl)	1.38(1)		
S–As–C(1)	112.3(2)	S′–As′–C(1′)	112.3(2)
S–As–C(7)	113.6(2)	S′–As′–C(7′)	113.5(2)
S–As–C(13)	112.5(2)	S′–As′–C(13′)	113.3(2)
C(1)–As–C(7)	106.3(2)	C(1′)–As′–C(7′)	107.3(2)
C(1)–As–C(13)	108.1(2)	C(1′)–As′–C(13′)	106.9(3)
C(7)–As–C(13)	103.6(2)	C(7′)–As′–C(13′)	103.0(2)
As–C(1)–C(2)	117.6(5)	As′–C(1′)–C(2′)	118.9(5)
As–C(1)–C(6)	122.3(4)	As′–C(1′)–C(6′)	121.3(4)
As–C(7)–C(8)	122.2(5)	As′–C(7′)–C(8′)	123.1(5)
As–C(7)–C(12)	117.7(4)	As′–C(7′)–C(12′)	116.9(4)
As–C(13)–C(14)	121.4(4)	As′–C(13′)–C(14′)	121.5(5)
As–C(13)–C(18)	118.6(5)	As′–C(13′)–C(18′)	119.3(5)
C–C–C (Average internal phenyl)	120.0(6)		

TABLE 3

Interplanar angles (°). The angles refer to the angle between the normals of the respective planes. The S–As–S planes include the leading carbon of the corresponding phenyl ring

Plane	σ (plane)	Atoms in plane	Angle to S–As–C	Angle to hub	Δ(Å) of As out of plane
Phenyl 1	0.006	C(1), C(2), C(3), C(4), C(5), C(6)	48.6	46.1	+0.046
Phenyl 2	0.006	C(7), C(8), C(9), C(10), C(11), C(12)	56.2	40.4	+0.028
Phenyl 3	0.007	C(13), C(14), C(15), C(16), C(17), C(18)	9.0	80.6	+0.025
Phenyl 1′	0.002	C(1′), C(2′), C(3′), C(4′), C(5′), C(6′)	49.1	44.2	−0.117
Phenyl 2′	0.007	C(7′), C(8′), C(9′), C(10′), C(11′), C(12′)	56.4	41.1	−0.040
Phenyl 3′	0.005	C(13′), C(14′), C(15′), C(16′), C(17′), C(18′)	12.3	78.1	−0.011

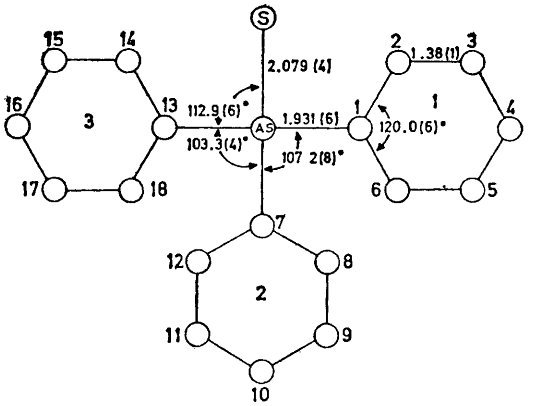


FIGURE 1 Average molecular dimensions of the two molecules in the asymmetric unit

of these arguments by Zingaro *et al.*[13] through application of Gordy's rule led to the calculated results: $\nu(As{=}S)$ at 555 cm^{-1}; $\nu(\overset{+}{As}-\overset{-}{S})$ at 372 cm^{-1}. Clearly the As–S bond length we report here is consistent with the predictions based on spectroscopic data, *viz.* there is approximately a double bond. However, our earlier studies of P–S bond lengths in phosphine sulphides [1,2] showed that anomalies in bond length–stretching frequency correlations can occur for P=S bonds:

	PMe_3S	$P(C_6H_{11})_3S$	PPh_3S
$\tilde{\nu}(PS)/cm^{-1}$	570 [a]	619 [a]	637 [a]
$d(P-S)/Å$	1.959(2) [b]	1.966(2) [c]	1.950(3) [d]

[a] Ref. 15. [b] Ref. 4. [c] Ref. 1. [d] Ref. 2.

Tricyclohexylphosphine sulphide exhibits an anomalously high stretching frequency, but has the longest observed P–S bond.

There is clearly a need for further high-precision *X*-ray structural studies of the Group 5 chalcogenides before the subtle interplay between electronic and steric influences on the M–Y bond can be fully appreciated.

The isostructural series PPh_3S, PPh_3Se, and $AsPh_3S$ does enable us to make some pertinent comments on the conformational aspects of these structures. One of the striking aspects of the series is the maintenance of the molecular conformation with substitution of Se for S, and As for P. The torsion angles for the phenyl rings [2,3] (Table 3) and close intermolecular distances (Table 4) are comparable in the three structures. This is a rather surprising result since the M–Y bond changes by 0.165 Å and the M–C bond lengthens by 0.114 Å through the series. A lack of C_3 symmetry, as observed here, is noted in many structures of $Ph_3M{=}Y$ molecules [9] and in metal complexes of the MPh_3 ligand.[16] Furthermore, in many instances the conformations involve one phenyl ring lying within 10° of planarity with the M–Y (M = P or As; Y = S or Se) or phosphorus–metal bond.[5,9,16] This conformation places the sulphur atom in van der Waals contact with the *ortho*-hydrogen atom of that 'parallel' phenyl ring in PPh_3S,[2] and similarly for Se in PPh_3Se,[3] yet does not appear to distort the molecule.

In this series of structures the conformation does not appear to be due to unusually short intermolecular distances. The pattern of intermolecular contacts given in Table 4 shows that the molecules do not pack in any special manner. Although ring 2 and ring 2′ of the asymmetric unit are nearly parallel, as seen in Figure 3, the close approach is edge to edge, C(11′) to C(12), and C(12′) to C(12) and C(11) rather than quasi-graphitic stacking reported in similar structures.[17] This particular packing arrangement seems to accommodate the enlargement of the structure through the isostructural series without any markedly shorter intermolecular contraction. The $AsPh_3S$ structure does show some strain but it seems to arise from intramolecular interactions. For each phenyl ring the two As–C–C angles (Table 2) are significantly different from one another and from the unstrained value of 120°. In each case the angle distal to the sulphur atom is larger than the proximal angle. A trend in the same direction and of similar magnitude has been observed for both PPh_3S and PPh_3Se.

TABLE 4

Closest contacts (Å) to phenyl-ring carbon atoms. Superscripts refer to equivalent positions listed at the end of the Table

		PPh_3S	PPh_3Se	$AsPh_3S$
Ring 1	C(2)–H(15)$^{(1)}$	2.769	2.742 [a]	2.756
	C(3)–H(15)$^{(1)}$	2.960	2.952 [a]	2.984
	C(4)–H(17)$^{(2)}$	3.048	3.118	3.040 [b]
	C(5)–H(18)$^{(2)}$	2.891	2.897	2.823 [b]
	C(6)–H(18)$^{(2)}$	2.964	2.991	2.879 [b]
Ring 2	C(9)–H(6)$^{(2)}$	2.939	2.918 [a]	2.950
	C(10)–H(16)$^{(3)}$	3.183	3.194	3.101 [b]
	C(10)–N(5)$^{(2)}$	3.215	3.172 [a]	3.156 [b]
	C(11)–H(16)$^{(3)}$	2.920	2.866 [a]	2.835 [b]
	C(11)–H(12′)	3.090	2.982 [a]	3.103
	C(12)–H(16)$^{(3)}$	2.962	2.907 [a]	2.849 [b]
	C(12)–H(12′)	3.245	3.160 [a]	3.220
Ring 3	C(15)–H(9)$^{(1)}$	3.000	3.155	2.950 [b]
	C(16)–H(9)$^{(1)}$	3.138	3.230	3.166
	C(17)–H(8)$^{(1)}$	2.827	2.834	2.857
	C(18)–H(8)$^{(1)}$	3.085	3.029 [a]	3.050

(1) $2 - x, -\frac{1}{2} + y, \frac{3}{2} - z$
(2) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$
(3) $x, \frac{1}{2} - y, \frac{1}{2} + z$

[a] Contact shorter in PPh_3Se than in PPh_3S. [b] Contacts shorter in $AsPh_3S$ than in either PPh_3Se or PPh_3S.

The frequent occurrence of the molecular conformation with one ring 'parallel,' and its maintenance

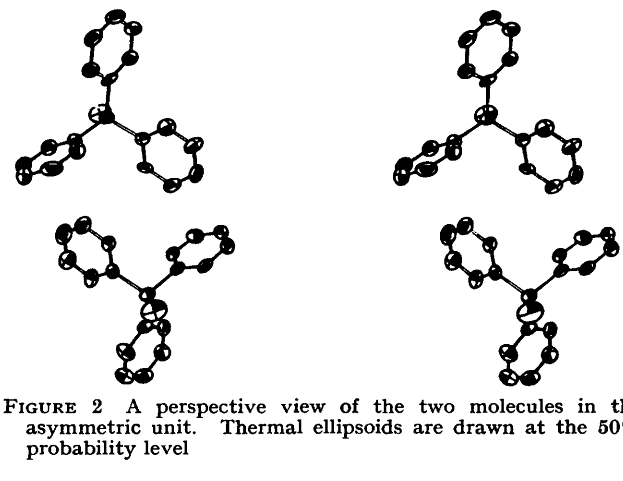


FIGURE 2 A perspective view of the two molecules in the asymmetric unit. Thermal ellipsoids are drawn at the 50% probability level

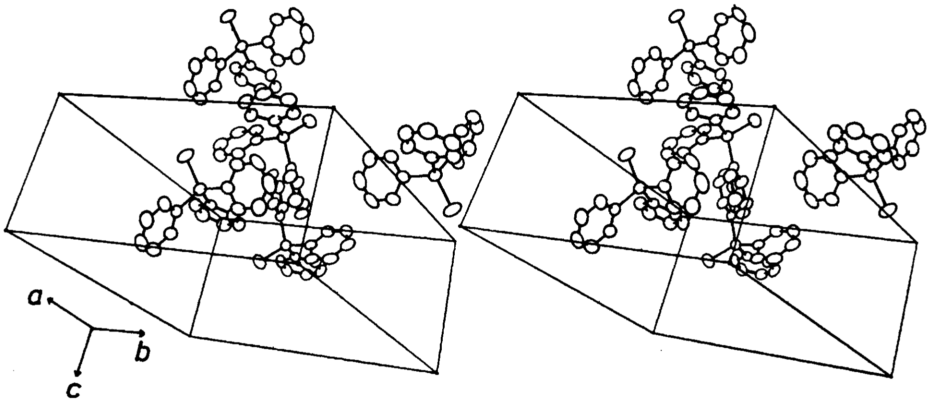


FIGURE 3 Packing diagram showing the two molecules whose co-ordinates are listed in Table 1 and those molecules in closest contact with them

throughout the isostructural series we have reported, suggest that this is a low-energy conformation. We are attempting molecular-mechanics calculations to test this hypothesis.

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