1980*b*), states that for intermetallic phases with a given structure formed by the like elements Ca, Sr and Ba or Sc, Y and La as one component, the cell dimension(s) is a linear function of the atomic numbers of the elements Ca, Sr and Ba or Sc, Y and La. This means that the cell dimension(s) cannot also be a linear function of the CN 12 diameters of these elements; the dimension(s) of the Ba or La phases must be too large to be collinear with those of the Ca and Sr, or Sc and Y phases. The *a* cell edge of $CaMg_2$, $SrMg_2$ and $BaMg_2$ is a strictly linear function of the atomic numbers of Ca, Sr, and Ba and, accordingly, as seen in Fig. 3, *a* for $BaMg_2$ is too large for it to be collinear with the (Y), Ca and Sr phases as a function of D_M. On the other hand, *c* for the four phases of Y, Ca, Sr and Ba is essentially a linear function of D_M, and so the atomic-number rule does not hold for the *c* dimension of the unit cell of these phases. Therefore, the decreased axial ratio of $BaMg_2$ relative to the other three phases results for the special adjustment of *a* that is required to satisfy the atomic-number rule. Whether or not the increase of c/a with D_M for the series of phases YMg_2, $CaMg_2$, $SrMg_2$ results from special relative changes in *a*, *c*, or both, there is no means of telling.

This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada. I am grateful to Miss M. G. Patterson for assistance with calculations.

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The Structure of Triphenylarsine Sulfide

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(*Received* 25 *March* 1980; *accepted* 29 *September* 1980)

Abstract

Crystals of $C_{18}H_{15}AsS$ are monoclinic, space group $P2_1/c$, with $a = 18{\cdot}426\ (4)$, $b = 9{\cdot}750\ (5)$, $c = 18{\cdot}582\ (4)$ Å, $\beta = 105{\cdot}74\ (6)°$, $Z = 8$, $\rho_c = 1{\cdot}40$, $\rho_m = 1{\cdot}38$ Mg m^{-3} and $\mu(\text{Cu } K\alpha) = 4{\cdot}127$ mm^{-1}. The two non-equivalent molecules in the asymmetric unit are nearly identical and lack C_{3v} symmetry because of the asymmetric orientation of their phenyl rings around the As—C bonds. The average of six As—C bonds is 1·949 Å, but one, As′—C(13′), is very short [1·854 (6) Å]. The final *R* factor was 0·086 ($R_w = 0{\cdot}092$) for 1675 visually estimated independent reflections. The structure is pseudo $P2_1/a$ type. The geometry at the As atom is approximately tetrahedral with an average As—S distance of 2·090 (6) Å.

Introduction

Krishnan, Datta & Narayana (1977) reported crystal data for compounds formed by the reaction of selenium sulfide, SeS_2, with triphenyl compounds of Group V elements, and started the structure determination of some of them. Meanwhile, Codding & Kerr (1978, 1979) reported the structures of triphenylphosphine sulfide and triphenylphosphine selenide. We now report the structure of triphenylarsine sulfide.

Experimental

A colorless crystal of dimensions 0·30 × 0·25 × 0·32 mm was obtained from benzene solution. Equi-inclination Weissenberg photographs were obtained using Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, covering lattice nets *h*0*l* to *h*6*l*, 0*kl* and 1*kl*. 1675 visually estimated intensities were corrected for Lorentz–polarization and spot-extension factors. Systematic absences confirmed the space group $P2_1/c$. Cell dimensions were measured from high-angle spots in Weissenberg photographs taken by the asymmetric mode of film loading (Straumanis & Ievins, 1935). Long exposure to X-rays (*ca* 100 h) turned the crystal light yellow without altering the relative intensities. Absorption corrections have not been applied. The intensities of *h*0*l* reflections

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with $h = 2n + 1$ were weak, indicating a pseudo-$P2_1/a$-type structure (non-space-group) with the two molecules related by a translation of approximately $a/2$ in the b-axis projection.

Structure analysis

The coordinates of the two As atoms were obtained from the Harker section $(u,\frac{1}{2},w)$ and a three-dimensional (3D) Patterson function (R = 0·39). The first 3D Fourier synthesis revealed all the non-hydrogen atoms. Three cycles of Fourier refinement of coordinates reduced R to 0·18. Three cycles of full-matrix least-squares refinement of coordinates and isotropic thermal parameters using the *XFLS* (W. R. Busing & H. A. Levy) computer program reduced R to 0·108. Finally, two cycles of refinement incorporating anisotropic thermal parameters reduced R_w to 0·096. Unit weights were used for the initial three cycles, where, as for the last two cycles, $\sqrt{w} = |F_o|/32{\cdot}8$ when $|F_o| < 32{\cdot}8$ and $\sqrt{w} = 32{\cdot}8/|F_o|$ when $|F_o| > 32{\cdot}8$. A final difference Fourier map revealed all the H positions, which were included in the model but were not refined owing to the low ratio of observations to parameters. The final R was 0·086 (R_w = 0·092).* The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1974).

Results and discussion

The numbering scheme used for the discussion and the atomic coordinates presented in Table 1 are based on the pseudo $P2_1/a$ symmetry (Fig. 2) present in the projection down the b axis. From the views of the molecules down their respective S—As bonds, rings (II) and (V), which make small angles with their respective S—As—C(Ph) planes, in contrast to other rings, are inferred to be equivalent. Also, rings (I) and (III) of molecule (1) are equivalent to rings (VI) and (IV), respectively, of molecule (2). Consequently, to obtain the average bond lengths and bond angles (Fig. 1) we note that atoms C(1), C(2) to C(6) are equivalent to C(13′), C(18′) to C(14′); C(7), C(8) to C(12) are equivalent to C(7′), C(12′) to C(8′); and C(13), C(14) to C(18) are equivalent to C(1′), C(6′) to C(2′) in the same order.

Table 1. *Final fractional coordinates and isotropic and equivalent isotropic thermal parameters of the non-hydrogen atoms with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}/B$ (Å^2)
As	0·5611 (1)	0·6589 (2)	0·6801 (1)	2·12 (8)
S	0·6038 (2)	0·4921 (3)	0·6342 (2)	3·74 (12)
C(1)	0·4517 (2)	0·6656 (5)	0·6459 (3)	4·36 (16)
C(2)	0·4100 (3)	0·6709 (6)	0·6963 (3)	5·78 (20)
C(3)	0·3304 (3)	0·6749 (6)	0·6699 (3)	6·16 (14)
C(4)	0·2948 (4)	0·6659 (6)	0·5941 (3)	6·74 (17)
C(5)	0·3365 (3)	0·6560 (5)	0·5430 (3)	6·17 (14)
C(6)	0·4144 (3)	0·6559 (6)	0·5699 (3)	4·99 (13)
C(7)	0·5915 (3)	0·6620 (5)	0·7883 (3)	4·51 (13)
C(8)	0·6272 (4)	0·5475 (5)	0·8264 (3)	5·39 (16)
C(9)	0·6522 (3)	0·5461 (5)	0·9043 (4)	6·29 (19)
C(10)	0·6413 (3)	0·6612 (5)	0·9452 (4)	6·99 (16)
C(11)	0·6060 (4)	0·7757 (5)	0·9088 (4)	6·51 (18)
C(12)	0·5811 (4)	0·7777 (6)	0·8309 (4)	5·19 (12)
C(13)	0·5974 (3)	0·8381 (6)	0·6531 (4)	4·91 (14)
C(14)	0·5443 (4)	0·9416 (6)	0·6394 (4)	5·82 (14)
C(15)	0·5744 (4)	0·0665 (5)	0·6235 (3)	7·22 (14)
C(16)	0·6514 (4)	0·0944 (6)	0·6297 (4)	7·40 (13)
C(17)	0·7026 (4)	0·9879 (6)	0·6536 (3)	7·21 (18)
C(18)	0·6750 (3)	0·8636 (6)	0·6695 (4)	6·14 (12)
As′	0·0564 (1)	0·5813 (2)	0·6676 (1)	2·19 (9)
S′	0·0957 (3)	0·7407 (4)	0·6122 (2)	3·70 (13)
C(1′)	0·9448 (3)	9·5756 (5)	0·6452 (3)	4·00 (14)
C(2′)	0·9032 (4)	0·5698 (7)	0·6963 (3)	5·66 (15)
C(3′)	0·8236 (3)	0·5738 (7)	0·6704 (4)	5·25 (13)
C(4′)	0·7879 (4)	0·5821 (7)	0·5946 (4)	6·26 (11)
C(5′)	0·8296 (3)	0·5887 (7)	0·5425 (4)	6·24 (12)
C(6′)	0·9075 (3)	0·5848 (6)	0·5681 (4)	5·07 (11)
C(7′)	0·0912 (3)	0·5803 (5)	0·7780 (3)	4·28 (11)
C(8′)	0·1268 (4)	0·6948 (6)	0·8161 (3)	5·74 (15)
C(9′)	0·1518 (3)	0·6962 (5)	0·8941 (4)	7·30 (16)
C(10′)	0·1409 (3)	0·5817 (6)	0·9336 (3)	7·19 (11)
C(11′)	0·1056 (3)	0·4677 (6)	0·8959 (3)	6·68 (13)
C(12′)	0·0806 (4)	0·4656 (6)	0·8180 (3)	5·59 (13)
C(13′)	0·0909 (4)	0·4104 (5)	0·6480 (3)	3·82 (10)
C(14′)	0·0417 (4)	0·3069 (6)	0·6148 (3)	5·58 (10)
C(15′)	0·0679 (3)	0·1795 (6)	0·5989 (3)	6·36 (14)
C(16′)	0·1447 (4)	0·1586 (6)	0·6149 (4)	6·57 (15)
C(17′)	0·1958 (4)	0·2616 (6)	0·6486 (4)	5·79 (15)
C(18′)	0·1681 (3)	0·3850 (5)	0·6644 (4)	5·43 (15)

Both the dimensions and the conformations of the two molecules are almost similar, but in molecule (2) one As—C bond is rather short. The planes of the phenyl rings make different angles with each other: plane C(1)–C(6) with plane C(7)–C(12) 67·1°, plane C(1)–C(6) with plane C(13)–C(18) 80·8°, and plane C(7)–C(12) with plane C(13)–C(18) 85·8°. The corresponding values for the second molecule are 68·9, 73·8 and 81·2° respectively. In each molecule one phenyl ring (Table 2) is nearly parallel to the corresponding S—As—C(7) plane. A study of the similar compounds triphenylarsine sulfide, triphenylphosphine selenide (Codding & Kerr, 1978, 1979), triphenylarsine oxide monohydrate (Ferguson & Macauly, 1969), methylenetriphenylphosphorane (Bart, 1969) and triphenylphosphoranylidenethioketene (Daly, 1967) suggest that the rotations of the aromatic rings are determined to some extent by crystal forces, the common arrangement being the propeller-like structure, without attaining the C_{3v} symmetry due

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* Lists of structure factors, anisotropic thermal parameters, unrefined H-atom positions and bond lengths and angles in individual molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35443 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

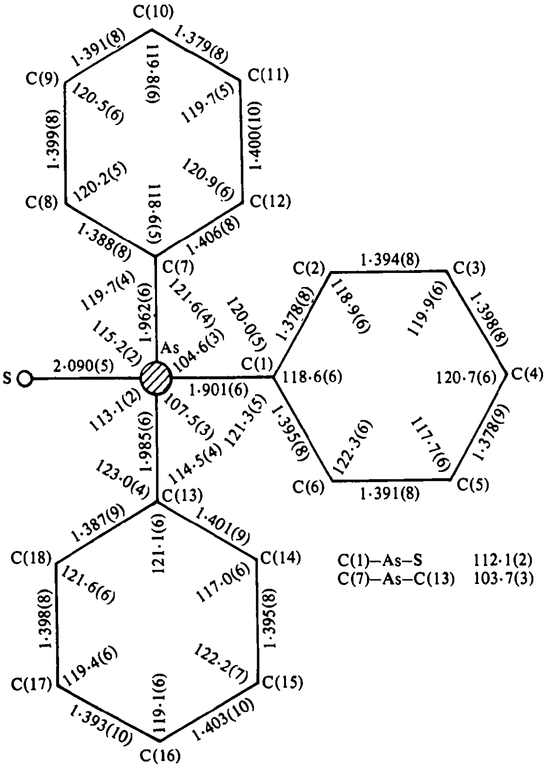

Fig. 1. Bond lengths (Å) and bond angles (°) involving non-hydrogen atoms in triphenylarsine sulfide.

to the unequal rotation of the phenyl rings about As–C bonds. Table 2 indicates a distinct departure of the conformation angles from the assumed C_3 symmetry of similar molecules. However, the conformation angles agree well with the results of energy calculations by Andose & Mislow (1974) in the investigation of a two-ring flip mechanism for stereoisomerization of trimesitylmethane. The average deviations of the atoms from the mean planes through their phenyl rings are negligible except for the ring C(13)–C(18) in molecule (1). The As–C bonds are tilted out of the planes of the phenyl rings, deviations of As atoms from the planes of the phenyl rings ranging from 0·002 to 0·09 Å.

The two As–S distances of 2·086 and 2·095 Å, with an average of 2·090 (5) Å, are shorter than the single-bond values of 2·22 Å reported by Pauling (1960) and 2·243 (9) Å by Porter & Sheldrick (1972) in β-As_4S_4, and 2·25 Å obtained by summing the covalent radii, indicating the π nature of this As–S bond. Although the average valence angle around As–S in Ph_3AsS at 109·3° is close to the tetrahedral value, the average of the three C(Ph)–As–C(Ph) angles (105·2°) is lower than the average S–As–C(Ph) angle (113·5°). Individual values of C(Ph)–As–C(Ph) and C(Ph)–As–S have a large spread, as is not uncommon in similar compounds (Codding & Kerr, 1978; Bart, 1969). The extent of π bonding in Ph_3AsS is independent of the bond angles around As. It can be seen that both the P–S bond in Ph_3PS and the As–S bond in Ph_3AsS are shorter by 0·18 Å than their single covalent bond value obtained from the covalent radii. Possible causes of the shortening have been discussed by Codding & Kerr (1978, 1979).

If the short As′–C(13′) bond [1·854 (6) Å] is included, the average of six As–C bonds at 1·949 Å is shorter than that in the trisubstituted derivative of arsenobenzene [1·966 (6) Å] (Hedberg, Hughes & Waser, 1961), but longer than that found in triphenylarsine oxide monohydrate (1·906 Å) (Ferguson & Macauly, 1969) and triphenylarsonium nitroprusside (1·923 Å) (Castellano, 1977). The deviations between equivalent As–C bond lengths in the two molecules have a minimum of 0·006 Å, a maximum of 0·095 Å and a mean of 0·042 Å. The corresponding results for C–C bonds are 0·000, 0·051 and 0·023 Å respectively. The average C(Ph)–C(Ph) distance of 1·393 Å agrees well with the standard value. The average of 36 C(Ph)–C(Ph)–C(Ph) angles is 119·9° and of 12 As–C(Ph)–C(Ph) angles is 120°.

Packing arrangement

Fig. 2 shows the packing arrangement as viewed down the *b* axis. The following notation is used: *A*, *B*, *C* and *D* denote generation of the first molecule of the asymmetric unit over the $P2_1/c$ equivalent positions. Similarly, *A′*, *B′*, *C′* and *D′* denote the second molecule. The structure may be described as a combination of $P2_1/c$ and pseudo $P2_1/a$. If the relationships were exact, a systematic non-space-group set of extinctions would occur (*h*0*l* for both *h* and *l* odd). Molecules such as *A*, *C* and *A′*, *C′* arranged around the pseudo center at $(\frac{1}{4},0{\cdot}6298,\frac{3}{4})$ as the new origin occupy a set of equivalent $P2_1/a$ positions, if one

Table 2. *Angles between different planes*

Plane	Atoms included in the plane	Average deviation	Angle to S–As–C	Angle to C(1)–C(7)–C(13)
(I)	C(1), C(2), C(3), C(4), C(5), C(6)	0·01 Å	51·6 (7)°	43·0 (6)°
(II)	C(7), C(8), C(9), C(10), C(11), C(12)	0·00	11·2 (6)	78·0 (5)
(III)	C(13), C(14), C(15), C(16), C(17), C(18)	0·040	47·1 (9)	50·8 (10)
(IV)	C(1′), C(2′), C(3′), C(4′), C(5′), C(6′)	0·000	42·4 (5)	56·1 (4)
(V)	C(7′), C(8′), C(9′), C(10′), C(11′), C(12′)	0·005	12·9 (6)	84·3 (6)
(VI)	C(13′), C(14′), C(15′), C(16′), C(17′), C(18′)	0·010	58·9 (6)	55·1 (7)

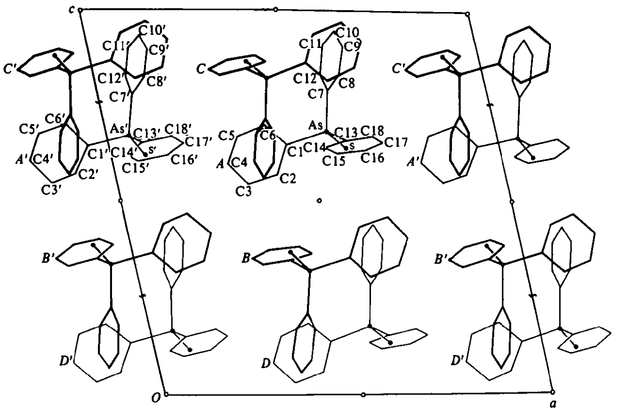

Fig. 2. Crystal packing of triphenylarsine sulfide as viewed down the short *b* axis.

disregards small deviations. Therefore, a pseudo glide plane is present at $y = 0\cdot379$, but only in the range $z = \frac{1}{2}$–1. Similarly *D*, *B*, *D'* and *B'* are related across a pseudo center at $(\frac{1}{4},0\cdot3704,\frac{1}{4})$ with a pseudo glide plane at $y = 0\cdot1201$ in the range $z = 0$–$\frac{1}{2}$. The distances between the alternating pseudo glide planes are thus about 0·241 (*ca* 2·35 Å) and 0·259 (*ca* 2·53 Å).

The structure is therefore built up from two non-identical layers of molecules stacked in alternate planes of the set (200). The interlayer distance is 8·87 Å. In these planes the stacking is through the screw axes and centers of symmetry. Because of the different positions of the molecules in the non-identical layers with respect to the center of symmetry the contacts between molecules *A* and *B* are not identical to those between *A'* and *B'*. There are no short (<3·0 Å) intermolecular contacts and the packing of the molecules involves mainly van der Waals forces.

We are grateful to Dr A. Datta for supplying the triphenylarsine sulfide and to Dr J. K. Suri for helping with the computation on the EC-1030 computer in IIT, Bombay. One of the authors (SVLN) is indebted to IIT, Bombay, for providing a scholarship.

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Acta Cryst. (1981). **B37**, 1189–1193

The Structure of *trans*-Dichlorobis[(+)-(*S*,*S*)-*trans*-1,2-diaminocyclopentane]cobalt(III) Chloride Hydrochloride Dihydrate, *trans*-$[CoCl_2\{(+)\text{-cptn}\}_2]Cl.HCl.2H_2O$

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(*Received* 5 *November* 1980; *accepted* 8 *December* 1980)

Abstract

Crystals of the title compound, $[Co(C_5H_{12}N_2)_2Cl_2]Cl.HCl.2H_2O$, $M_r = 438\cdot11$, are orthorhombic, space group $P22_12_1$, with $a = 9\cdot571$ (2), $b = 24\cdot541$ (3), $c = 8\cdot412$ (2) Å, $U = 1975\cdot9$ (7) Å^3, $Z = 4$, $D_x = 1\cdot47$, $D_m = 1\cdot47$ Mg m^{-3}, μ(Mo $K\alpha$) = 1·446 mm^{-1}. The crystal structure has been refined to give an *R* value of 0·044 for 2666 observed reflections collected by X-ray diffractometry. The complex cation has approximate D_2 symmetry, the Co atom being surrounded pseudo-octahedrally by the four N atoms of two (+)-cptn

0567-7408/81/061189-05$01.00