Acta Cryst. (1983). C**39**, 1618–1620

Tris(phenylthio)arsine, $C_{18}H_{15}AsS_3$

BY G. C. PAPPALARDO

Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, Viale A. Doria 8, 95125 *Catania, Italy*

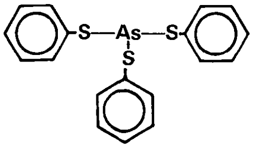
AND R. CHAKRAVORTY,* K. J. IRGOLIC AND E. A. MEYERS†

Department of Chemistry, Texas A & M University, College Station, Texas 77843, *USA*

(*Received* 1 *October* 1982; *accepted* 1 *June* 1983)

Abstract. $M_r = 402{\cdot}4$, rhombohedral, $R\bar{3}$, $a = 9{\cdot}706\,(1)$ Å, $\alpha = 82{\cdot}27\,(1)°$, $V = 891{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}95$ Mg m^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71073$ Å, $\mu = 2{\cdot}16$ mm^{-1}, $F(000) = 408$, $T = 296$ K. Final $R = 0{\cdot}033$ for 1125 observed reflections of which 989 were unique. The structure consists of discrete molecules of $(C_6H_5S)_3As$. The As atom is on a threefold axis, so the molecular symmetry in the crystal is C_3, with the C and As atoms on the same side of the plane through the S atoms. The three equivalent phenyl rings make angles of 95·6° to their As—S—C planes, and 90·5° to each other.

Introduction. Solid-state structures have been determined for relatively few organic compounds which possess As—S bonds. Moreover, the title compound shown below has been investigated in solution with a variety of physical techniques [^{1}H and ^{13}C NMR: Pappalardo, Irgolic, Pyles & Montoneri, 1982; dielectric constant and He(I) photoelectron spectroscopy: Distefano, Modelli, Grassi, Pappalardo, Irgolic & Pyles, 1981]. Thus it was of interest to determine the crystal structure of this material, both to measure the As—S bond distance and some related bond angles, and to compare the conformation of the molecule in the solid with that considered most likely in solution.



Experimental. X-ray data collected by the Molecular Structure Corporation, College Station, Texas. Colorless needle, 0·15 × 0·15 × 0·35 mm, mounted on a glass fiber. Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Hexagonal cell constants obtained by least-squares refinement of 2θ values for 25 reflections: $a = 12{\cdot}769\,(2)$, $c = 18{\cdot}939\,(4)$ Å. From systematic absences, $-h + k + l = 3n$, space group identified as rhombohedral, $V = 2674{\cdot}0$ Å^3, $Z = 6$, $D_x = 1{\cdot}95$ Mg m^{-3}; in structure determination cell converted to primitive rhombohedral; indices of reflections changed correspondingly and space group proved to be No. 148, $R\bar{3}$. Intensities of 1198 reflections (1050 were unique, 989 with $I > 0$; $-7 \le h \le 8$, $-6 \le k \le 8$, $1 \le l \le 11$) measured by scanning in 2θ ($2\theta_{\max} = 50°$); of these 1125 had $I > 0$, 1073 $F > 3\sigma(F)$. $R_{\rm int} = 0{\cdot}030$. No significant decline in intensities of three standard reflections, and empirical absorption correction small (min. transmission coefficient = 0·908, av. = 0·949). Corrections applied for Lorentz and polarization effects. *SHELX*76 (Sheldrick, 1976) modified for a DEC 1144 computer used in structure determination. A Patterson function yielded coordinates for As, and successive cycles of electron density and experimentally weighted least-squares calculations yielded coordinates and isotropic temperature factors for all As, S and C atoms in space group $R\bar{3}$. Positions of phenyl H atoms calculated, for C—H = 1·08 Å, and these atoms assigned temperature factors of C atoms to which they were attached. These parameters fixed for all later calculations. Weighted least-squares refinements of all As, S and C atomic parameters (isotropic thermal values) continued until all shifts $<0{\cdot}012\sigma$ for both the case in which 1125 reflections had $I > 0$, and for the case in which 1073 reflections had $F > 3\sigma(F)$. Although their final R values were considerably different, 0·0715 and 0·0751 respectively, none of the corresponding parameters differed by more than $0{\cdot}08\sigma$ from each other. Weighted least-squares refinement continued in $R\bar{3}$ with anisotropic temperature factors until all parameter shifts $<0{\cdot}07\sigma$. Quantity minimized $\sum w(|F_o| - |F_c|)^2$; $R = 0{\cdot}033$, $R_2 = 0{\cdot}042$, $S = 1{\cdot}6$, $w = 1/\sigma^2(F)$; $\sigma(I) = [\sigma^2 + (0{\cdot}05I)^2]^{1/2}$, with σ calculated from counting statistics. Scattering factors taken from Cromer & Liberman (1970), Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). A final difference electron density map was calculated, largest peak at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ 0·35 e Å^{-3}.

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* On leave from Rammohan College, Calcutta, India.

† To whom all inquiries should be directed.

0108-2701/83/121618-03$01.50

Table 1. *Fractional coordinates and equivalent isotropic temperature factors* (Å^2) *for non*-H *atoms*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j).$$

The e.s.d. of the last digit(s) is given in parentheses.

	x	*y*	*z*	U_{eq}
As	0·10460 (6)	0·10460	0·10460	0·0389
S	0·03998 (7)	0·33298 (7)	0·12177 (8)	0·0511
C(1)	−0·14536 (25)	0·33110 (22)	0·14979 (25)	0·0399
C(2)	−0·22085 (28)	0·34183 (27)	0·03628 (25)	0·0501
C(3)	−0·36472 (28)	0·34838 (29)	0·05761 (29)	0·0539
C(4)	−0·43480 (26)	0·34237 (26)	0·19082 (29)	0·0509
C(5)	−0·35891 (28)	0·33011 (28)	0·30441 (27)	0·0498
C(6)	0·21472 (26)	0·32388 (24)	0·28415 (25)	0·0454

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

As–S	2·243 (1)	S–C(1)	1·785 (3)
C(1)–C(2)	1·388 (4)	C(2)–C(3)	1·378 (4)
C(3)–C(4)	1·375 (4)	C(4)–C(5)	1·390 (4)
C(5)–C(6)	1·381 (4)	C(6)–C(1)	1·382 (3)
C(2)–H(2)	1·10	C(3)–H(3)	1·11
C(4)–H(4)	1·10	C(5)–H(5)	1·11
C(6)–H(6)	1·09	As···As	3·962 (1)

As···As–S	120·61 (3)	As–S–C(1)	98·8 (1)
S–C(1)–C(2)	120·0 (2)	S–C(1)–C(6)	120·2 (2)
C(2)–C(1)–C(6)	119·8 (2)	C(1)–C(2)–C(3)	120·0 (2)
C(2)–C(3)–C(4)	120·7 (3)	C(3)–C(4)–C(5)	119·3 (2)
C(4)–C(5)–C(6)	120·5 (2)	C(5)–C(6)–C(1)	119·8 (2)
S–As–S′	96·38 (3)		

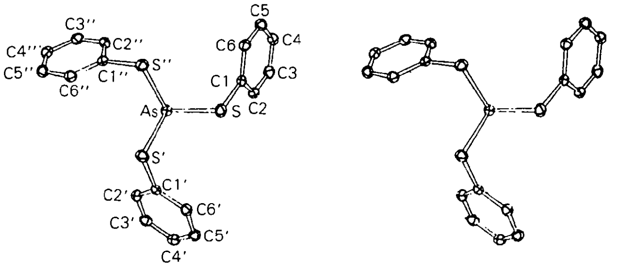

Fig. 1. Stereoscopic *ORTEP* drawing of $(C_6H_5S)_3As$. Primed atoms are related to the unprimed atoms by the crystallographic threefold rotational symmetry.

Discussion. Final parameters are given in Table 1.* An *ORTEP* drawing of the molecule is shown in Fig. 1 (Johnson, 1971) and some interatomic distances and angles are listed in Table 2. The weighted average of C–C distances is 1·382 (2)[2] Å and of C–C–C angles is 120·2 (2)[1]° (the e.s.d.'s in parentheses are calculated from the experimental deviations of the individual values from the weighted mean, and those in brackets from the e.s.d.'s of the individual values). The average C–C distance is approximately 0·01 Å shorter than expected, perhaps due to the uncorrected effect of thermal motion. There are only small deviations from 120·0° in the ring angles with apical atoms C(1), C(2), C(6) (α, β, β') but there are relatively large deviations at those with apical atoms C(3), C(4), C(5) (γ, δ, γ'). The analyses of Domenicano, Vaciago & Coulson (1975*a,b*) yield average values for substitution on the phenyl ring with bivalent sulfur of C–S = 1·781 (3) Å and α = 119·7 (3)°, in good agreement with the values found here, C(1)–S = 1·785 (3) Å and C(2)–C(1)–C(6) = 119·8 (2)°. More recently, Domenicano & Vaciago (1979) have attributed some of the observed deviations from 120° in γ, δ and γ' in substituted benzene as due to conjugation of the substituent with the ring.

The As atom lies in a special position, on the threefold axis in the crystal, and is 3·96 Å from the atom $\bar{\text{As}}$ at ($\bar{x}$, $\bar{x}$, $\bar{x}$). The sum of van der Waals radii is 4·0 Å. The As–S distance and S–As–S′ angle have been measured in various arsenic sulfides, As_mS_n. The As–S bond length appears to increase in a regular manner with an increasing ratio of S to As, from a short distance of 2·200 (8) Å in α-dimorphite, As_4S_3 (Whitfield, 1970) to a long distance of 2·293 (5) Å in orpiment, As_2S_3 (Mullen & Nowacki, 1972). The variation in the angle S–As–S′ is large in orpiment, 92·8 (2) to 105·0 (2)°. For comparison, As–S = 2·243 (1) Å, S–As–S′ = 96·38 (3)° in tris(phenylthio)arsine. In organic compounds that contain the As^{III}–S 'single' bond, this distance is reported as being as short as 2·228 (5) Å in 5,10-epithio-5,10-dihydroarsanthrene (Allen, Coppola, Kennard, Mann, Motherwell & Watson, 1970), and as long as 2·330 (6) Å in bis(*N*,*N*-diethyldithiocarbamato)phenylarsenic(III) (Bally, 1967). There is a variation in the angle S–As–S′ from 92·0 (5)° in arsenious ethylxanthate [tris(*O*-ethyl dithiocarbonato)arsenic(III), Carrai & Gottardi, 1960] to 104·0 (2)° in 5-chloro-l-oxa-4,6-dithia-5-arsocane (Drager, 1975). Finally, the angle As–S–C varies from 92 (1)° in arsenious ethylxanthate to 105·8 (2)° in dimethyl(thiourea)arsenic(III) chloride–thiourea (Javora, Zingaro & Meyers, 1975), compared to 98·8 (1)° in the present structure.

For the least-squares plane through the C atoms of the phenyl ring the maximum deviation is 0·007 Å for C(1); S is 0·10 Å from this plane, and the *b* axis is nearly perpendicular to it, 84·3°. The angles between the axis As–$\bar{\text{As}}$ and the planes (I) [As, S, C(1)] and (II) [C(1), C(2), C(3), C(4), C(5), C(6)] are 55·6 and 55·1° respectively, and the angle between (I) and (II) is 95·6°. The angles between planes of the same kind in the same molecule are (I)/(I′) = 91·2 and (II)/(II′) = 90·5°. The molecule at room temperature possesses C_3 symmetry in the solid, not the (time-average) C_{3v} symmetry found from NMR studies of the compound in solution. It would be desirable to conduct a variable-temperature NMR study to lower temperatures.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38633 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure of tris(phenylthio)amine (Carruthers, Prout & Watkin, 1981) differs markedly from that of tris(phenylthio)arsine: (1) N lies nearly in the plane of its three S atoms with an average S—N—S angle of 119·5°; (2) one of the N—S distances is significantly shorter (1·67 Å) than the other two (1·70, 1·71 Å); and (3) the phenyl rings are disposed such that the molecule deviates drastically from C_3 symmetry.

Support of these investigations by NATO Research Grant No. 1659, CNR of Italy and the US National Science Foundation (Grant No. INT-7921544) through the US–Italy Cooperative Science Program is gratefully acknowledged. The investigations carried out at Texas A&M University were also supported by the Robert A. Welch Foundation of Houston, Texas.

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Acta Cryst. (1983). C**39**, 1620–1623

Diamminebis(2-sulfanilamidopyrimidinato)zinc(II), $[Zn(C_{10}H_9N_4O_2S)_2(NH_3)_2]$

BY N. C. BAENZIGER

Chemistry Department, University of Iowa, Iowa City, Iowa 52242, *USA*

AND S. L. MODAK AND CHARLES L. FOX JR

Department of Surgery, College of Physicians and Surgeons, Columbia University, New York, NY 10032, *USA*

(*Received* 9 *June* 1982; *accepted* 29 *June* 1983)

Abstract. $M_r = 597\cdot98$, orthorhombic, $Pn2_1a$, $a = 13\cdot894\ (1)$, $b = 14\cdot221\ (1)$, $c = 12\cdot608\ (1)$ Å, $V = 2492\cdot3$ Å^3, $Z = 4$, $D_x = 1\cdot59$, $D_m = 1\cdot59\ (1)$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1\cdot54052$ Å, $\mu = 32\cdot9$ cm^{-1}, $F(000) = 1232$, $T = 295$ K. Final $R_1 = 0\cdot040$ for 3485 observed independent reflections. The Zn atom is surrounded by four N atoms: two from the ammonia molecules [2·036 (4) and 2·050 (4) Å] and two from the sulfanilamidopyrimidine ligands in a distorted tetrahedral arrangement. The two pyrimidine-containing ligands are coordinated at different sites: one ligand through the imido N atom [2·166 (4) Å] and one ligand through an N atom in the pyrimidine ring [2·078 (4) Å]. No significant differences in the pyrimidine rings are apparent, but the imido N—C and N—S distances are significantly longer for the imido N atom which is coordinated to the Zn atom.

Introduction. The present structural investigation of the zinc sulfadiazine title complex was undertaken because of its effectiveness in preventing bacterial infection in burned animals (Fox, Modak & Stanford, 1978; Fox, Modak, Stanford & Fox, 1979). The related burn-treatment compound, (2-sulfanilamidopyrimidine)silver(I), commercially used for burn treatment in patients as Silvadene, has a polymeric structure (Baenziger & Struss, 1976; Cook & Turner, 1975) which allows for the slow release of the Ag^+ ion, the active bactericidal ingredient (Fox & Modak, 1974; Modak & Fox, 1973) in the vicinity of the burn. The effectiveness of the burn-treatment compound does not appear to depend solely on the presence of Ag^+ (or Zn^{2+}) *per se*, but depends strongly on the nature of the material to which the metal ion is bound. The structure of the zinc sulfadiazine complex was undertaken to see

0108-2701/83/121620-04$01.50