The structural evidence shows that $Hg_3(AlCl_4)_2$ is appropriately formulated as a molecular compound. The Hg–Cl bond distance of 2.54 Å is not much longer than 2.47 Å, the sum of the covalent radii according to Pauling;[23] in any case, it is much shorter than the distance of at least 3 Å to be expected on the basis of an ionic formulation of the compound, *i.e.*, $(Hg_3)^{2+}(AlCl_4^-)_2$. Since the distances from the Al atoms to the bridging Cl atoms are both significantly longer than those to nonbridging Cl atoms, it is clear that Hg competes effectively with Al for the valence electrons of Cl.

Two strong Raman lines have been reasonably assigned[2] to stretching vibrations involving the central Hg_3 group. The small departure of this group from linearity, while sufficient to permit the appearance of the two lines, may not completely explain their comparable intensity. It seems likely that the Hg_3 group interacts with the noncentrosymmetrically disposed terminal $AlCl_4$ groups to enhance the intensity of the line involving the pseudoantisymmetric vibration.

Significant contacts between molecules of $Hg_3(AlCl_4)_2$ are all between Hg and Cl atoms; each Hg is surrounded by five Cl atoms at distances of less than 4 Å. Hg(1), the central atom of the molecular skeleton, has five intermolecular contacts with Cl atoms ranging in length from 3.39 to 3.88 Å. Hg(2) and Hg(3) each have four intermolecular Cl contacts at distances of 3.21–3.84 Å; Hg(2) has in addition one intramolecular Cl contact at 3.52 Å, and Hg(3) has one at 3.40 Å. There are four intermolecular contacts between Cl atoms ranging in length from 3.51 to 3.60 Å; all other intermolecular Cl–Cl contacts are at distances greater than 3.7 Å. The arrangement of the molecules may be visualized as consisting of double chains along the crystal *a* axis, as illustrated in Figure 2. The chains are linked to neighboring chains by Hg···Cl contacts that form a net of molecules in the (102) planes of the crystal, as shown in Figure 3.

Acknowledgments.—The authors are indebted to Professor G. Mamantov[1c] for suggesting this crystal structure determination and for valuable discussions in connection with it.

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The Crystal and Molecular Structure of Diphenyldiarsenic Trisulfide. A Five-Membered Arsenic–Sulfur Ring Compound[1]

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The crystal and molecular structure of diphenyldiarsenic trisulfide, $As_2S_3(C_6H_5)_2$, was determined from three-dimensional X-ray data collected with a manual diffractometer using Mo Kα (λ 0.71069 Å) radiation. The compound crystallizes in the monoclinic space group $C2/c$, with $a = 15.966$ (3) Å, $b = 7.515$ (2) Å, $c = 12.465$ (2) Å, $\beta = 109.55$ (1)°, $Z = 4$, $d_{\text{measd}} = 1.88$ (2) g cm^{-3}, and $d_{\text{calcd}} = 1.87$ g cm^{-3}, at 23°. The structure was determined by Patterson and Fourier methods and refined with 532 observed reflections by full-matrix least squares to an R of 0.061. The molecule consists of a five-membered, nonplanar arsenic–sulfur ring with the sequence –As–S–As–S–S–. One phenyl ring is bonded to each arsenic atom. A crystallographic twofold rotation axis passes through the molecule. The As–S bond distances are 2.252 (5) and 2.253 (4) Å, the As–C bond length is 1.95 (1) Å, and the S–S bond length is 2.036 (6) Å. The bond angles around the arsenic are 98.4 (1), 99.7 (5), and 101.3 (4)°, the As–S–As bond angle is 107.47 (7)°, and the As–S–S bond angle is 101.1 (1)°. These parameters are interpreted to denote little or no π bonding in the As–S ring.

Introduction

The large variety of unique ring structures found in the nitrogen–sulfur system[3] has led us to undertake structural studies of what appears to be an equally varied system of arsenic–sulfur cyclic molecules. Crystal structures of five-, six-, and eight-membered arsenic–sulfur ring systems are being examined. The subject of this report, diphenyldiarsenic trisulfide ($As_2S_3(C_6H_5)_2$), contains a five-membered As–S ring. The compound was first reported almost 100 years ago[4] but it appears it was not considered a ring molecule prior to our structural study.

Data Collection and Reduction

$As_2S_3(C_6H_5)_2$ was prepared by the method of Schulte,[4] which involves successive treatment of a solution of phenylarsenic acid with aqueous ammonia, hydrogen sulfide gas, and concentrated hydrochloric acid. The clear, needlelike crystals were obtained by slow evaporation of a chloroform–octane mixed solvent; mp 130°. A mass spectrum confirmed the molecular formula. The measured density obtained by suspension in a mixture of tetrachloroethylene and 1,3-dibromopropane was 1.88 (2) g cm^{-3}, in agreement with the density of 1.87 g cm^{-3} calculated for four molecules per unit cell. Four molecules per unit cell in space group $C2/c$ implies the molecular centers must lie on a crystallographic center of symmetry or a twofold rotation axis.

The approximately parallelpiped crystal used for the diffractometer data collection measured 0.24 × 0.36 × 0.66 mm (all ±0.01 mm) in the [$\bar{3}$01], [101], and [010] directions. The crystal was mounted with b^* approximately parallel to the ϕ axis. The unit cell parameters at 23° are $a = 15.966$ (3), $b = 7.515$ (2), $c = 12.465$ (2) Å, and $\beta = 109.55$ (1)° as determined by a least-squares refinement[5] of the setting angles of

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[1] This work was supported by an NSF College Teacher Research Participation Program at the University of Arkansas and by the Petroleum Research Fund, administered by the American Chemical Society.

[2] Address correspondence to this author.

[3] O. Glemser, *Angew. Chem., Int. Ed. Engl.*, **2**, 530 (1963).

[4] C. Schulte, *Ber.*, **15**, 1955 (1882).

21 carefully centered reflections. The systematic absences (hkl, $h + k$ odd; $h0l$, l odd) imply either the centrosymmetric space group C_2/c ($C_{2h}{}^6$; no. 15) or the noncentrosymmetric space group Cc (C_s; no. 9). The structure was solved and refined in the centrosymmetric space group.

The diffractometer used was a G.E. XRD-5 manually operated quarter-circle system, with Mo Kα (λ 0.71069 Å) radiation filtered with 1-mil zirconium foil. A scintillation counter was used with a pulse height analyzer set for a 90% window.

Each reflection was scanned 2° in 2θ at a scan rate of 2°/min with a takeoff angle of 3°. Stationary-crystal, stationary-counter background readings were taken for 10 sec at each end of the scans. All peaks with $0° \leq 2\theta < 45°$ were scanned. There are 921 reflections in the Mo Kα sphere bounded by $2\theta < 45°$; 544 of these had intensities greater than two standard deviations. The latter reflections were used for the structure determination and refinement. The standard deviations were calculated by $\sigma_I = (S + BT^2 + 0.0064I^2)^{1/2}$ (where S = total scan count, B = sum of the background counts, T = scan time/total background time, and $I = S - BT$), except for a number of reflections for which the two background readings differed by more than twice the calculated σ due to tailing of the reflection peak. For the latter reflections the standard deviations were set equal to the deviation of the background readings from the mean background value.

An absorption correction was applied to each reflection using the program DEAR.[6] A 6 × 6 × 10 summation was employed. The linear absorption coefficient for Mo Kα is 35.8 cm^{-1}, and the range of transmission coefficients (for F) was 0.516–0.673. No correction was made for extinction.

Three standard reflections were measured periodically during the 4-day data collection, and their constancy provided evidence of crystal stability.

Scattering factors for neutral atoms were calculated from the analytical functions of Cromer and Waber,[7] and real and imaginary anomalous dispersion corrections were made for As and S using the values given by Cromer.[8]

The structure was solved by standard Patterson and Fourier techniques: the heavy-atom ring was located from analysis of the Patterson map, and the phenyl ring positions were determined from a subsequent Fourier map. Fourier and full-matrix least-squares refinement techniques led to an unweighted residual R_1 ($||F_o| - |F_c||/|F_o|$) of 0.094 and a weighted residual R_2 ($\{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, where $w = 1/\sigma$) of 0.102. The function minimized in the least squares was $\Sigma w(|F_o| - |F_c|)^2$. At this point all atoms had isotropic temperature factors. When the arsenic and sulfur atoms were refined with anisotropic thermal parameters R_1 became 0.061 and R_2 became 0.077, which is a significant improvement according to the R ratio test.[9]

In the final cycle of refinement no positional or thermal parameter was shifted more than 0.07 times its estimated standard deviation. The standard deviation of an observation of unit weight is 1.50.[10] A final difference Fourier map did not have any peaks which were chemically interpretable; the highest peaks were 22% of the value of a carbon peak on an electron density map. The positions of the phenyl group hydrogen atoms were calculated from the carbon positions and were included in the structure factor calculations but were not refined in the least-squares treatment. A final inspection of the $\Delta F/\sigma$ values did not show any apparent dependence on θ or F values. Twelve reflections were omitted because of an obvious error in recording the intensities. None of the reflections whose intensities were less than 2σ (the "unobserved" reflection) had F_o values more than 1σ greater than F_c.

Discussion

The final positional and thermal parameters are given in Tables I and II, and Figure 1 gives an ORTEP drawing. Table III lists the derived bond distances and angles. The As–S bond distances of 2.252 (5) and 2.253 (4) Å in

TABLE I

FINAL ATOMIC POSITIONS AND ISOTROPIC THERMAL PARAMETERS FOR $As_2S_3(C_6H_5)_2$[a]

	x	y	z	B, Å^2
As	0.0549 (1)	0.1243 (2)	0.4033 (1)	...
S(1)	0.0	0.3016 (8)	0.25	...
S(2)	0.0116 (2)	−0.1313 (6)	0.1745 (3)	...
C(1)	0.174 (1)	0.079 (2)	0.401 (1)	3.5 (3)
C(2)	0.206 (1)	0.134 (2)	0.314 (1)	4.7 (4)
C(3)	0.294 (1)	0.094 (2)	0.326 (1)	5.7 (4)
C(4)	0.347 (1)	0.011 (2)	0.419 (1)	6.1 (5)
C(5)	0.319 (1)	−0.042 (2)	0.507 (1)	5.4 (4)
C(6)	0.232 (1)	−0.005 (2)	0.498 (1)	4.4 (4)
H(2)	0.162	0.203	0.238	5.0
H(3)	0.319	0.132	0.259	5.0
H(4)	0.415	−0.016	0.425	5.0
H(5)	0.362	−0.111	0.582	5.0
H(6)	0.208	−0.043	0.566	5.0

[a] Numbers in parentheses are the standard deviations for the last digit given. The hydrogen atom positions were calculated from the carbon atom positions and were not refined.

TABLE II

FINAL ANISOTROPIC THERMAL PARAMETERS FOR $As_2S_3(C_6H_5)_2$[a]

A. β Values × 10^4

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As	39 (1)	227 (4)	57 (1)	−10 (2)	28 (1)	−13 (2)
S(1)	51 (3)	167 (13)	92 (6)	0	26 (4)	0
S(2)	41 (2)	130 (9)	76 (4)	14 (4)	23 (2)	−22 (5)

B. Root-Mean-Square Amplitudes of Vibration (Å) along the Principal Axis of the Ellipsoids

	Major	Intermed	Minor
As	0.26	0.22	0.16
S(1)	0.25	0.24	0.22
S(2)	0.25	0.22	0.18

[a] Numbers in parentheses are standard deviations for the last digit given. The thermal correction was of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

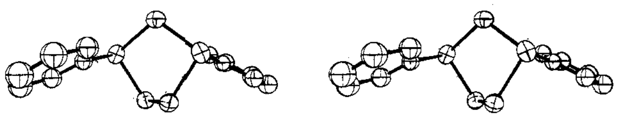

Figure 1.—An ORTEP Drawing of $As_2S_3(C_6H_5)_2$.

TABLE III

BOND DISTANCES (Å) AND BOND ANGLES (DEG) FOR $As_2S_3(C_6H_5)_2$[a]

As–S(1)	2.253 (4)	As–S(1)–As′	107.47 (7)
As–S(2)′	2.252 (5)	S(1)–As–S(2)′	98.4 (1)
S(2)–S(2)′	2.036 (6)	As–S(2)′–S(2)	101.1 (1)
As–C(1)	1.95 (1)	S(1)–As–C(1)	101.3 (4)
C(1)–C(2)	1.41 (2)	S(2)′–As–C(1)	99.7 (5)
C(2)–C(3)	1.40 (3)	C(1)–C(2)–C(3)	118 (1)
C(3)–C(4)	1.34 (3)	C(2)–C(3)–C(4)	122 (2)
C(4)–C(5)	1.39 (3)	C(3)–C(4)–C(5)	122 (2)
C(5)–C(6)	1.38 (3)	C(4)–C(5)–C(6)	118 (1)
C(6)–C(1)	1.40 (2)	C(5)–C(6)–C(1)	121 (1)
		C(6)–C(1)–C(2)	120 (1)
		As–C(1)–C(2)	124.8 (8)
		As–C(1)–C(6)	115 (1)

[a] Primed atoms are related to the positions given in Table I by $(-x, y, 0.5 - z)$.

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(5) Program ANGSET by A. Foust, University of Wisconsin, 1969.

(6) A general absorption program from the University of Wisconsin which utilizes the method of W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

(7) D. T. Cromer and J. T. Waber, Los Alamos Scientific Laboratory, private communications.

(8) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(9) W. C. Hamilton, *ibid.*, **18**, 502 (1965).

(10) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

the arsenic–sulfur ring are comparable to other values available for ring and nonring compounds: 2.25 Å in the AsS_3^{3-} ion,[11] 2.23 and 2.21 Å for the gas-phase[12] and crystal[13] values for As_4S_4, and 2.25 Å for the As–S bonds in the gas phase of As_4S_6.[12] The S–S distance of 2.036 (6) Å is equal to the 2.037 (5) Å value reported for the S_8 molecule.[14] The SAsS and AsSAs angles in $As_2S_3(C_6H_5)_2$ are within several standard deviations of the values reported in the electron diffraction studies of As_4S_4 and As_4S_6.[7] The As–C distance of 1.95 (1) Å for this structure is within the range of values commonly found for this linkage.

The close comparisons of the $As_2S_3(C_6H_5)_2$ bond distances with a variety of As–S compounds, along with the S–S bond which is equal to the S_8 value, suggests that the As–S ring system does not have appreciable π bonding above that found in the average As–S and S–S bonds. The approximately tetrahedral angles of the ring atoms, giving a highly puckered ring, also support this conclusion. The arsenic atoms are 1.09 Å above and below the plane of the three sulfur atoms, the S(2) and S(2)′ sulfur atoms are 0.61 Å above and below the plane of As(1)–S(1)–As(1)′, and the As atom and its phenyl ring are coplanar within 0.03 Å.

The crystal packing is illustrated in Figure 2, which shows the contents of one unit cell projected on the xz plane. There are only two intermolecular distances less than Pauling's[15] nonbonding radii values: there is an As–S distance (As(1) with S(2) in the position related to the table value by x, $-y$, $0.5 + z$) of 3.671 (5) Å compared to the sum of the van der Waals radii of 3.85 Å, and there is an As–As contact (As(1) with As(1) at $-x$, $-y$, $1 - z$) of 3.901 (5) Å compared to the van der Waals sum of 4.0 Å. No special significance is attributed to these values.

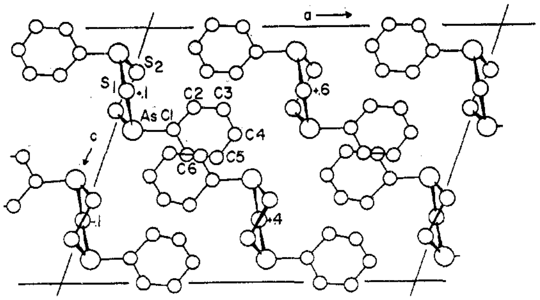

Figure 2.—The contents of the unit cell projected on the xz plane. The y values for the ring centers are given.

The five-membered ring compound of known structure which is most closely related chemically to the present ring is $S_3N_2Cl_2$.[16] The ring structures are quite different, however, in that the S_3N_2 ring is nearly planar and has S–N distances appreciably shorter than the value usually accepted for a single S–N bond. The planarity and shortened bonds apparently reflect $p\pi-d\pi$ bonding in the N–S system which is not present in the As–S ring of $As_2S_3(C_6H_5)_2$.

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The Crystal and Molecular Structure of the Tetranuclear Ruthenium Carbonyl Hydride α-$H_2Ru_4(CO)_{13}$

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A single-crystal X-ray structural analysis has established the structure of one of two reported forms of the tetranuclear ruthenium carbonyl hydride $H_2Ru_4(CO)_{13}$. This compound crystallizes in space group $P2_1/c$ of the monoclinic system, with eight molecules in a cell of dimensions $a = 9.534$ (10), $b = 9.032$ (9), $c = 47.44$ (4) Å, and $\beta = 90° 29'$ (3′). The structural determination was based upon 1134 independent counter data; a blocked full-matrix, least-squares refinement converged to a conventional R factor of 0.059. The two crystallographically independent $H_2Ru_4(CO)_{13}$ molecules have similar configurations, with the metal atoms tetrahedrally disposed. Eleven of the thirteen carbonyl groups are terminally bound; the other two form asymmetric Ru–C···Ru bridges with average Ru–C and Ru···C distances of 1.94 (5) and 2.40 (6) Å, respectively. Two different metal–metal distances are observed; each molecule has two long Ru–Ru distances of mean value 2.93 (1) Å and four shorter distances averaging to 2.78 (2) Å. Indirect evidence implies that the hydrogen atoms are situated in bridging configurations on the two long Ru–Ru edges.

Introduction

The tetranuclear ruthenium carbonyl hydride $H_2Ru_4(CO)_{13}$ is obtained from $Ru_3(CO)_{12}$ under a variety of conditions including reduction with $NaBH_4$ in THF,[1] treatment with OH^- in methanol followed by acidification,[1] reflux in various solvents,[2-4] and reaction with alcohols, aldehydes, and ketones.[5] Two distinct

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