

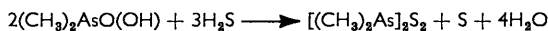
36. Stereochemistry of Arsenic. Part XI.¹ "Cacodyl Disulphide," Dimethylarsino Dimethyldithioarsinate.

By NORMAN CAMERMAN and JAMES TROTTER.

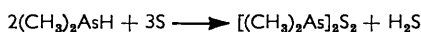
The molecular structure of "cacodyl disulphide," $(\text{Me}_2\text{AsS})_2$, has been determined by X-ray analysis of single crystals, which are triclinic, with $a = 6.34$, $b = 7.11$, $c = 11.35$ Å, $\alpha = 100^\circ 14'$, $\beta = 95^\circ 46'$, $\gamma = 89^\circ 55'$, $Z = 2$, space group $P\bar{1}$. The intensities were measured on a G.E. spectrogoniometer by using a scintillation counter and Mo- K_α radiation. The arsenic positions were determined by two-dimensional Patterson methods, and the other atoms (except hydrogen) were located on successive electron-density projections along the a - and the b -axis. The positional and isotropic thermal parameters of the arsenic, sulphur, and carbon atoms were then refined by four least-squares cycles on the full three-dimensional data. The final R value for 805 observed reflexions is 0.091.

The analysis reveals that the compound is dimethylarsino dimethyldithioarsinate (III) [not (I) or (II)], an unusual structure, having one tervalent and one quinquevalent arsenic atom in the molecule. The former atom has a trigonal-pyramidal configuration, with angles 96 – 99° ; the latter is tetrahedral (angles 101 – 116°). The As-S-As angle is $96.5^\circ \pm 0.3^\circ$. The shortest intermolecular contact is an $\text{As}^{\text{III}} \cdots \text{As}^{\text{III}}$ separation of 3.24 Å, considerably shorter than the normal van der Waals distance and suggesting charge-transfer bonding involving donation of lone-pair electrons on each As^{III} to vacant $4d$ -orbitals on the other As^{III} . The other intermolecular distances are normal.

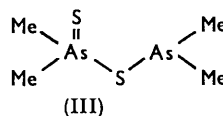
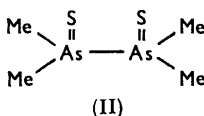
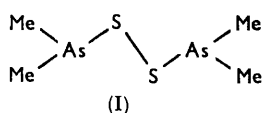
"CACODYL DISULPHIDE," $[(\text{CH}_3)_2\text{As}]_2\text{S}_2$, was first prepared by Bunsen² by passing hydrogen sulphide through a concentrated alcoholic solution of cacodylic acid:



and by reaction of cacodyl sulphide with sulphur. Dehn and Wilcox³ obtained cacodyl sulphide from dimethylarsine and sulphur, but found that the disulphide was formed when the arsine reacted with a greater amount of sulphur:



It appears to have been generally considered that the compound is a true disulphide and it is listed as a cacodyl derivative,⁴ so that structure (I) has been assumed. However its preparation from cacodyl sulphide and an excess of sulphur suggests that the disulphide contains quinquevalent arsenic, since tervalent arsines usually react with sulphur to give quinquevalent derivatives. This is substantiated by Bunsen's finding that the sulphide reacts with metal halides to yield salts of dimethyldithioarsinic acid, $(\text{CH}_3)_2\text{As}(\text{S})\cdot\text{SH}$. Formulations such as (II) or (III) are therefore possible.



The present analysis was undertaken to determine the structure of "cacodyl disulphide" by X-ray diffraction methods, and the results indicate that the compound is dimethylarsino dimethyldithioarsinate (III).

¹ Part X, *Acta Cryst.*, in the press.

² Bunsen, *Annalen*, 1843, **46**, 1.

³ Dehn and Wilcox, *Amer. Chem. J.*, 1906, **35**, 1.

⁴ See, e.g., Raiziss and Gavron, "Organic Arsenic Compounds," The Chemical Catalogue Co., Inc., New York, 1923.

EXPERIMENTAL

"Cacodyl disulphide" was prepared from cacodylic acid and hydrogen sulphide³ and by reaction of dimethylarsine with an excess of sulphur;³ X-ray powder photographs indicated that the two samples were identical.⁵ Crystals from ether are needles elongated along the *a*-axis. The unit-cell dimensions and space group were determined from rotation, Weissenberg, and precession photographs, and on the G.E. Spectrogonimeter. Efforts to measure the density by flotation were unsuccessful, since the crystal reacted with aqueous solutions and dissolved in organic liquids of suitable density; however, it appeared to be between about 1.5 and 2.0 g.cm.⁻³ and this sufficed to establish the number of molecules in the unit cell as two.

Crystal Data (Cu- K_{α} = 1.5418 Å, Mo- K_{α} = 0.7107 Å).—Dimethylarsino dimethyldithioarsinate, C₄H₁₂As₂S₂; *M*, 274.1. Triclinic, *a* = 6.34 ± 0.01, *b* = 7.11 ± 0.01, *c* = 11.35 ± 0.02 Å, α = 100° 14' ± 5', β = 95° 46' ± 5', γ = 89° 55' ± 5'. Volume of the unit cell = 500.4 Å³. *D_x* (with *Z* = 2) = 1.820 g.cm.⁻³. Absorption coefficient for X-rays, λ = 0.7107 Å, μ = 74 cm.⁻¹. *F*(000) = 268. No absent reflexions; space group *P*1 or $P\bar{1}$; $P\bar{1}$ from structure analysis.

The intensities of the reflexions were measured on a General Electric XRD-5 spectrogoniometer with single crystal orienter, with a scintillation counter and Mo- K_{α} radiation, an approximately monochromatic beam being obtained by use of a zirconium filter and a pulse-height analyser. The moving crystal-moving counter technique⁶ was used. All the reflexions in the range $0 < 2\theta \leq 40^{\circ}$ (corresponding to a minimum interplanar spacing $d = 1.04$ Å) were examined and 805 were measurable, 87% of the total number of reflexions in this range. All the intensities were corrected for background, which was found to be a function of θ only. The crystal used (mounted with *a** parallel to the ϕ -axis of the goniostat) was small and had cross-section 0.1 × 0.1 mm. perpendicular to *a* and length 0.5 mm. parallel to *a*; absorption was fairly low and no correction was applied. Lorentz and polarization corrections were made and the structure amplitudes derived.

STRUCTURE ANALYSIS

The largest peaks in the *0kl* and *h0l* Patterson projections could be interpreted in terms of two pairs of arsenic atoms related by a centre of symmetry. The co-ordinates derived for the arsenic atoms immediately eliminated structure (II), since no two arsenic atoms were close enough together to be directly bonded. Four-fold vector convergence (minimum) functions were then derived by placing the origins of the Patterson functions in turn at the four arsenic positions. The *0kl* map showed only three peaks; two of these were situated at arsenic, one being considerably higher than the other and probably corresponding to overlapping arsenic and sulphur atoms; the third peak could be ascribed to a single sulphur atom. The *h0l* map also had three significant peaks, and a smaller fourth peak adjacent to one of the arsenic atoms, but in such a position that it could not be involved in bonding with the second arsenic; the peaks at the arsenic positions were of equal height, and the third peak was about half this height. An effort was made to interpret both projections in terms of structure (I), and positions were derived for 2 arsenic and 2 sulphur atoms. Structure factors were calculated for the *0kl* and *h0l* reflexions by using standard scattering factors,⁷ with $B = 4.5$ Å² for all the atoms; the discrepancy factors were $R(0kl) = 33.4\%$, $R(h0l) = 38.9\%$. A similar calculation with arsenic atoms only gave $R(0kl) = 31.5\%$, $R(h0l) = 41.5\%$.

Fourier series were summed for both projections, by using as coefficients the measured structure amplitudes with signs based on the arsenic atoms only. The resulting electron-density maps showed the same features as the vector-convergence functions, including the fourth peak in the *b*-axis projection noted above, with much improved resolution, and there were in addition other smaller peaks. It was clear at this stage that neither structure (I) nor structure (II) could be fitted to these maps, but that the electron-density distributions corresponded to structure (III). Co-ordinates could be derived with confidence for 2 arsenic, 2 sulphur, and 2 carbon atoms; there were peaks which apparently corresponded to two other

⁵ Cullen, personal communication.

⁶ Furnas, "Single Crystal Orienter Instruction Manual," General Electric Company, Milwaukee, 1957.

⁷ "International Tables for X-Ray Crystallography," Volume III, Kynoch Press, Birmingham, 1962.

carbon atoms, but as there was some ambiguity they were omitted at this stage. Structure factors were recalculated, and the R values were reduced to 19.3% for $0kl$ and 25.8% for $h0l$ reflexions.

A second set of electron-density projections was then computed, and these maps showed good resolution of all the atoms. Inclusion of the two other carbon atoms in the structure factor calculations gave $R(0kl) = 13.2\%$, $R(h0l) = 23.4\%$. Examination of the structure-factor agreement suggested that the temperature factor was too high. B was therefore reduced to 3.0 \AA^2 , and structure factors were calculated for the complete three-dimensional data; $R(hkl)$, for the observed reflexions, was 18.2%.

Refinement.—The positional and isotropic thermal parameters of the arsenic, sulphur, and carbon atoms, together with an overall scale factor, were then refined by least squares, with a

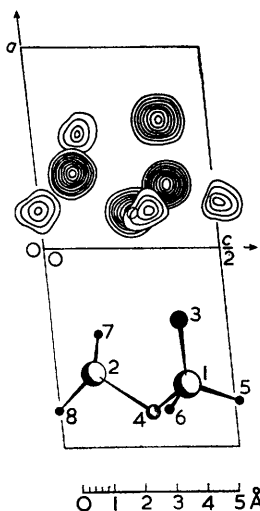


FIG. 1. Superimposed sections of the final three-dimensional electron-density distribution, through the atomic centres perpendicular to b ; contours at intervals of 2,3,4,5 $e\text{\AA}^{-3}$ for C; 2,4,6 . . . for S; and 5,10,15 . . . for As. A perspective drawing of the molecule is also shown.

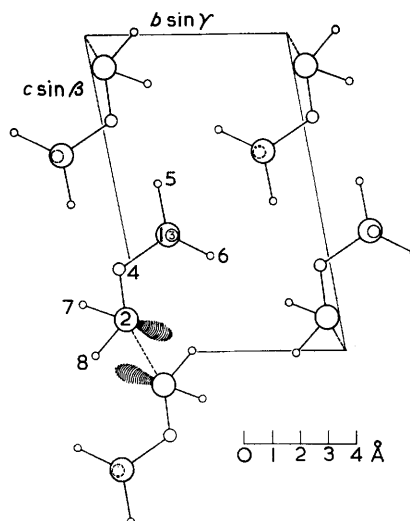


FIG. 2. Projection of the structure along $[100]$, illustrating the packing of the molecules. The short intermolecular contact is shown as a broken line, and the lone pairs are shown schematically.

programme previously described.⁸ The function minimized was $\sum w(F_o - F_c)^2$, with $\sqrt{w} = F_o/35$ when $F_o < 35$, and $\sqrt{w} = 35/F_o$ when $F_o \geq 35$. Refinement proceeded smoothly and was complete in four cycles, the maximum shift in the final cycle being about one-quarter of a standard deviation.

The final measured and calculated structure factors, calculated from the parameters output from the fourth least-squares cycle ($R = 9.1\%$ for the 805 observed reflexions), are listed in Table 1. A three-dimensional Fourier series was summed, and superimposed sections of the resulting electron-density distribution taken through the atomic centres are shown in Fig. 1.

Co-ordinates and Molecular Dimensions.—The final positional and thermal parameters are listed, with their standard deviations, in Table 2; x , y , and z are fractional co-ordinates referring to the triclinic cell axes. No effort was made to determine positions of the hydrogen atoms. The bond distances and valency angles are given, with their standard deviations, in Table 3. The shorter intermolecular contacts are listed in Table 4, and the packing of the molecules is shown in Fig. 2.

DISCUSSION

The analysis has established that the compound called "cacodyl disulphide" is dimethylarsino dimethyldithioarsinate (III) (Figs. 1 and 3). It therefore contains one

⁸ Camerman and Trotter, *Acta Cryst.*, in the press.

TABLE I.

Measured and calculated structure factors.

(Unobserved reflexions, for which F_o is listed as 0·0, have threshold values in the range 4—8.)

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	
0	0	1	9.4	-11.2	1	2	9	10.5	10.1	3	1	1	39.4	-34.0	-1	1	5	28.2	26.6	
0	0	2	10.0	-13.0	1	3	0	62.1	61.0	3	1	2	52.4	53.9	-1	1	6	37.2	39.8	
0	0	3	45.2	50.0	1	3	1	45.2	-42.7	3	1	3	24.9	-27.2	-1	1	7	44.1	-43.4	
0	0	4	66.5	-79.5	1	3	2	35.0	-31.8	3	1	4	52.7	-58.4	-1	1	8	9.4	-9.3	
0	0	5	29.3	-24.6	1	3	3	17.0	-19.1	3	1	5	13.0	11.1	-1	1	9	11.9	-6.6	
0	0	6	17.7	-12.3	1	3	4	43.3	-43.9	3	1	6	20.2	-24.7	-1	1	10	35.8	-34.9	
0	0	7	27.8	-31.1	1	3	5	6.1	-2.6	3	1	7	0.0	-4.2	-1	2	1	50.6	-51.5	
0	0	8	47.3	53.7	1	3	6	5.1	4.5	3	1	8	21.3	25.0	-1	2	2	4.3	0.9	
0	0	9	15.5	4.3	1	3	7	5.4	3.6	3	2	0	20.2	-14.3	-1	2	3	11.2	12.2	
0	0	10	7.9	1.5	1	3	8	35.0	36.0	3	2	1	27.8	25.3	-1	2	4	4.0	-5.1	
0	1	0	80.9	89.5	1	4	0	42.3	39.3	3	2	2	58.5	57.3	-1	2	5	75.9	75.0	
0	1	1	5.1	-1.8	1	4	1	13.0	-12.0	3	2	3	48.0	-45.7	-1	2	6	6.5	6.5	
0	1	2	97.2	102.5	1	4	2	0.0	0.1	3	2	4	0.0	-3.9	-1	2	7	16.6	-16.2	
0	1	3	35.0	-34.2	1	4	3	35.4	-33.0	3	2	5	11.9	-14.4	-1	2	8	13.4	16.4	
0	1	4	39.4	-40.2	1	4	4	14.1	-14.6	3	2	6	23.8	-27.1	-1	2	9	21.7	-23.4	
0	1	5	9.8	12.4	1	4	5	0.0	-1.6	3	2	7	15.9	17.0	-1	3	1	41.2	-38.8	
0	1	6	82.4	-90.1	1	4	6	24.2	-23.1	3	3	0	14.1	-7.4	-1	3	2	26.0	24.4	
0	1	7	0.0	-2.3	1	4	7	18.1	17.9	3	3	1	68.3	66.9	-1	3	3	32.1	-29.0	
0	1	8	26.4	27.9	1	5	0	13.0	11.3	3	3	2	0.0	-1.7	-1	3	4	22.8	21.0	
0	1	9	10.8	-13.8	1	5	1	24.9	23.7	3	3	3	5.1	0.8	-1	3	5	61.4	56.8	
0	1	10	23.8	25.0	1	5	2	4.3	-3.3	3	3	4	6.1	5.7	-1	3	6	5.1	-4.0	
0	2	0	42.3	-35.2	1	5	3	28.2	-26.1	3	3	5	42.3	-43.7	-1	3	7	22.4	21.6	
0	2	1	96.4	96.3	1	5	4	0.0	2.1	3	3	6	0.0	-0.4	-1	3	8	0.0	-0.7	
0	2	2	27.1	29.6	1	5	5	0.0	-14.3	3	4	0	30.7	29.5	-1	4	1	7.2	7.8	
0	2	3	44.1	-41.4	1	6	0	17.3	15.4	3	4	1	19.5	20.0	-1	4	2	20.6	-19.2	
0	2	4	50.9	52.8	1	6	1	35.8	33.6	3	4	2	5.1	-1.5	-1	4	3	41.9	-39.2	
0	2	5	37.9	-37.7	1	6	2	17.3	-14.8	3	4	3	43.7	41.5	-1	4	4	35.0	33.8	
0	2	6	71.2	-71.6	2	0	0	73.3	-68.7	3	4	4	24.9	-23.0	-1	4	5	13.7	11.3	
0	2	7	11.2	14.1	2	0	1	37.9	43.8	3	4	5	24.9	-23.8	-1	4	6	22.4	18.7	
0	2	8	23.5	-23.5	2	0	2	32.1	36.5	3	5	0	25.3	23.3	-1	4	7	21.3	18.8	
0	2	9	0.0	4.1	2	0	3	28.5	34.3	3	5	1	19.5	-14.8	-1	5	1	0.0	-1.4	
0	3	0	11.9	0.5	2	0	4	26.7	30.5	3	5	2	6.5	29.5	-1	5	2	48.0	-45.8	
0	3	1	98.2	95.7	2	0	5	25.3	-25.4	3	5	3	25.6	23.2	-1	5	3	8.7	-6.4	
0	3	2	24.6	-21.9	2	0	6	5.4	-1.3	4	0	0	45.9	-47.1	-1	5	4	0.0	-2.3	
0	3	3	32.9	29.6	2	0	7	9.4	-9.4	4	0	1	24.2	-29.2	-1	5	5	0.0	-5.7	
0	3	4	40.8	39.1	2	0	8	40.1	-48.4	4	0	2	14.1	16.7	-1	6	1	27.8	-34.7	
0	3	5	46.6	-44.6	2	0	9	5.4	4.7	4	0	3	27.5	-30.6	-1	6	2	14.1	-11.9	
0	3	6	5.8	-0.4	2	1	0	12.3	-10.1	4	0	4	22.8	28.6	-1	6	3	0.0	-1.9	
0	3	7	26.4	-24.3	2	1	1	40.1	33.2	4	0	5	33.2	41.6	-2	1	1	17.0	21.3	
0	3	8	23.5	-23.0	2	1	2	7.2	3.3	4	0	6	7.2	-7.7	-2	1	2	49.5	-51.8	
0	4	0	55.3	53.5	2	1	3	74.4	80.1	4	0	7	9.4	8.3	-2	1	3	51.7	-51.9	
0	4	1	28.9	27.4	2	1	4	19.9	21.0	4	1	0	54.9	-54.2	-2	1	4	13.4	-12.1	
0	4	2	4.3	3.1	2	1	5	13.7	-15.1	4	1	1	0.0	-2.8	-2	1	5	35.0	-35.2	
0	4	3	53.1	50.6	2	1	6	22.8	26.8	4	1	2	22.4	-22.7	-2	1	6	31.8	33.0	
0	4	4	0.0	-2.0	2	1	7	24.2	-25.7	4	1	3	26.0	-30.4	-2	1	7	15.9	16.1	
0	4	5	9.8	3.5	2	1	8	18.4	-21.1	4	1	4	24.6	30.0	-2	1	8	0.0	0.0	
0	4	6	0.0	4.0	2	1	9	0.0	-4.1	4	1	5	6.9	9.4	-2	1	9	35.4	34.4	
0	4	7	45.5	-40.5	2	2	0	17.0	16.7	4	1	6	13.0	16.0	-2	1	10	0.0	0.9	
0	5	0	20.6	16.2	2	2	1	58.2	-57.7	4	2	0	23.5	-23.8	-2	2	1	7.6	7.0	
0	5	1	19.9	-18.7	2	2	2	31.8	33.3	4	2	1	5.4	3.5	-2	2	2	28.5	-25.0	
0	5	2	44.8	42.0	2	2	3	72.2	72.9	4	2	2	35.4	-37.5	-2	2	3	18.4	-18.0	
0	5	3	17.0	16.4	2	2	4	0.0	-2.6	4	2	3	0.0	-5.1	-2	2	4	50.6	-49.4	
0	5	4	0.0	-3.8	2	2	5	22.0	22.1	4	2	4	0.0	-0.7	-2	2	5	15.2	-12.5	
0	5	5	35.8	30.2	2	2	6	10.8	13.0	4	2	5	6.5	6.1	-2	2	6	33.2	32.4	
0	5	6	41.2	-37.8	2	2	7	20.6	-22.5	4	2	6	26.0	30.2	-2	2	7	9.4	-12.0	
0	6	1	5.8	2.7	2	2	8	0.0	-2.1	4	3	0	5.1	7.1	-2	2	8	32.1	28.7	
0	6	2	31.1	26.5	2	3	0	36.5	-36.0	4	3	1	20.9	-20.6	-2	2	8	19.9	20.7	
0	6	3	15.9	-12.2	2	3	1	65.7	-63.4	4	3	2	16.6	-18.8	-2	3	1	6.9	-5.1	
1	0	0	70.8	-69.0	2	3	2	36.5	34.6	4	3	3	4.3	0.8	-2	3	2	12.3	12.7	
1	0	1	71.2	-87.2	2	3	3	7.2	7.9	4	3	4	20.6	-22.3	-2	3	3	15.5	-13.4	
1	0	2	6.9	-8.7	2	3	4	19.9	21.7	4	3	5	15.5	14.5	-2	3	4	62.1	-59.6	
1	0	3	19.1	-25.9	2	3	5	30.7	33.2	4	4	0	5.4	-1.6	-2	3	5	0.0	1.4	
1	0	4	33.2	35.1	2	3	6	11.2	-12.6	4	4	1	23.5	-24.9	-2	3	6	0.0	-2.2	
1	0	5	25.6	23.9	2	3	7	9.0	8.6	4	4	2	7.2	5.5	-2	3	7	4.3	-3.6	
1	0	6	7.6	5.8	2	4	0	56.7	-54.2	4	4	3	22.0	-20.8	-2	3	8	24.2	21.3	
1	0	7	54.2	62.8	2	4	1	19.9	-18.0	5	0	0	5.8	5.9	-2	4	1	9.0	9.2	
1	0	8	5.8	-3.8	2	4	2	11.6	-12.2	5	0	1	34.7	42.9	-2	4	2	38.6	36.2	
1	0	9	17.7	-18.2	2	4	3	6.5	-5.1	5	0	2	9.8	9.9	-2	4	3	25.6	-25.2	
1	0	10	0.0	7.9	2	4	4	40.8	39.2	5	0	3	0.0	-4.5	-2	4	4	37.2	-34.4	
1	1	1	0	56.0	-51.6	2	4	5	4.3	3.6	5	0	4	16.3	21.8	-2	4	5	8.7	-7.2
1	1	1	1	5.1	-6.2	2	4	6	0.0	4.5	5	0	5	15.9	-19.4	-2	4	6	23.5	-21.8
1	1	1	2	83.1	-90.6	2	5	0	22.4	-21.4	5	1	1	34.7	34.4	-2	4	7	0.0	4.8
1	1	1	3	18.8	-21.2	2	5	1	0.0	-0.1	5	1	2	5.4	-3.5	-2	5	1	30.0	28.6
1	1	1	4	34.7	37.2	2	5	2	6.1	-37.3	5	1	3	17.7	22.9	-2	5	2	18.8	17.3
1	1	1	5	10.1	-13.3	2	5	3	15.9	11.9	5	1	4	9.4	7.6	-2	5	3	13.4	-10.8
1	1	1	6	29.6	30.7	2	5	4	21.7	18.3	5	2	0	16.3	13.3	-2	5	4	0.0	-2.0
1	1	1	7	48.8	50.2	2	6	0	17.3	15.1	5	2	1	6.1	5.5	-2	5	5	28.9	-25.0
1	1	1	8	5.1	-6.1	2	6	1	24.6	-22.1	5	2	2	0.0	7.2	-2	6	1	20.6	19.4
1	1	1	9	7.2	9.1	3	0	0	60.0	57.0	5	2	3	23.1	24.1	-2	6	2	8.3	6.0
1	1	2	0	48.0	45.5	3	0	1	4.3	-2.9	5	3	0	0.0	-2.1	-3	1	1	5.4	6.2
1	1	2	1	32.1	-29.2	3	0	2	22.8	-23.4	5	3	1	5.8	-8.8	-3</				

TABLE I. (Continued.)

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c
-3	2	1	54.5	52.4	1	-3	3	55.3	57.7	3	-1	5	34.7	-38.6	0	1	-8	20.2	18.1
-3	2	2	52.7	55.1	1	-3	4	52.4	51.9	3	-1	6	32.5	39.7	0	1	-9	36.8	39.8
-3	2	3	4.3	4.3	1	-3	5	7.6	-9.4	3	-1	7	7.6	7.8	0	1	-10	5.8	-10.1
-3	2	4	44.1	43.4	1	-3	6	41.2	47.9	3	-1	8	0.0	-2.1	0	2	-1	39.0	41.4
-3	2	5	32.9	-30.5	1	-3	7	4.7	0.8	3	-2	0	53.8	-52.1	0	2	-2	69.0	-62.4
-3	2	6	14.4	-13.0	1	-3	8	38.6	-42.3	3	-2	1	23.1	24.6	0	2	-3	56.7	-61.2
-3	2	7	0.0	4.5	1	-3	9	0.0	-0.5	3	-2	2	14.8	-14.3	0	2	-4	22.0	22.0
-3	2	8	40.5	-39.1	1	-3	10	13.4	-16.1	3	-2	3	73.0	-79.2	0	2	-5	74.4	-80.8
-3	3	1	30.3	29.2	1	-4	0	76.6	-75.8	3	-2	4	21.7	21.4	0	2	-6	10.8	-13.6
-3	3	2	9.8	-8.0	1	-4	1	12.3	9.3	3	-2	5	0.0	2.3	0	2	-7	50.2	56.3
-3	3	3	56.0	52.5	1	-4	2	40.8	41.2	3	-2	6	0.0	2.3	0	2	-8	10.1	-13.5
-3	3	4	25.6	25.3	1	-4	3	5.1	7.0	3	-2	7	34.0	40.0	0	2	-9	26.7	27.6
-3	3	5	31.1	-30.0	1	-4	4	49.5	49.6	3	-2	8	0.0	-4.2	0	2	-10	14.4	17.6
-3	3	6	21.3	19.7	1	-4	5	12.3	11.2	3	-3	0	14.8	-13.7	0	3	-1	40.8	-41.5
-3	3	7	23.8	-21.0	1	-4	6	9.4	-5.9	3	-3	1	51.3	-50.6	0	3	-2	14.8	-14.2
-3	4	1	33.2	-32.2	1	-4	7	13.0	14.9	3	-3	2	17.7	17.8	0	3	-3	73.3	-71.9
-3	4	2	0.0	3.5	1	-4	8	35.8	-41.8	3	-3	3	48.8	-53.0	0	3	-4	19.5	-21.8
-3	4	3	56.3	54.0	1	-4	9	9.8	-9.4	3	-3	4	11.6	-11.2	0	3	-5	5.4	6.0
-3	4	4	13.0	-12.3	1	-5	0	14.4	-13.9	3	-3	5	36.5	43.0	0	3	-6	38.6	-42.4
-3	4	5	13.0	12.0	1	-5	1	25.6	-24.4	3	-3	6	8.7	-7.8	0	3	-7	57.8	61.2
-3	4	6	14.4	12.7	1	-5	2	56.7	58.1	3	-3	7	18.1	20.1	0	3	-8	22.4	23.9
-3	5	1	34.0	-33.0	1	-5	3	11.9	10.2	3	-3	8	15.2	20.5	0	3	-9	7.6	-12.5
-3	5	2	25.6	24.0	1	-5	4	0.0	1.3	3	-4	0	16.6	15.3	0	3	-10	20.9	24.6
-3	5	3	10.5	11.2	1	-5	5	25.3	26.2	3	-4	1	33.3	-39.7	0	4	-1	81.6	-77.7
-3	5	4	0.0	2.5	1	-5	6	20.6	-21.6	3	-4	2	20.2	-22.1	0	4	-2	8.7	-8.5
-4	1	1	36.1	-38.2	1	-5	7	8.7	-6.9	3	-4	3	6.1	-1.4	0	4	-3	0.0	0.8
-4	1	2	35.0	-35.2	1	-5	8	10.8	-12.1	3	-4	4	23.1	-23.6	0	4	-4	59.2	-59.6
-4	1	3	44.8	45.8	1	-6	0	17.0	15.4	3	-4	5	28.9	33.4	0	4	-5	25.6	27.1
-4	1	4	0.0	0.6	1	-6	1	5.4	-7.1	3	-4	6	14.1	16.0	0	4	-6	17.3	18.2
-4	1	5	17.7	19.5	1	-6	2	23.8	23.8	3	-4	7	6.9	-10.0	0	4	-7	14.8	14.4
-4	1	6	35.4	36.0	1	-6	3	29.3	29.0	3	-5	0	9.0	-8.4	0	4	-8	40.5	42.7
-4	1	7	0.0	-2.9	1	-6	4	17.0	-18.5	3	-5	1	0.0	2.0	0	4	-9	10.5	-12.5
-4	1	8	0.0	2.9	1	-6	5	11.2	11.6	3	-5	2	39.0	-41.2	0	5	-1	29.6	-27.5
-4	2	1	67.2	-66.3	2	-6	6	0.0	0.9	3	-5	3	13.0	10.9	0	5	-2	58.2	-56.4
-4	2	2	7.6	-6.5	2	-1	0	29.3	-27.7	3	-5	4	5.8	6.0	0	5	-3	23.1	21.0
-4	2	3	8.3	6.7	2	-1	1	10.1	11.4	3	-5	5	0.0	6.3	0	5	-4	16.3	-15.2
-4	2	4	11.9	-13.8	2	-1	2	74.4	81.9	4	-1	0	0.0	-2.2	0	5	-5	13.0	-9.5
-4	2	5	35.8	33.2	2	-1	3	6.1	7.1	4	-1	1	36.5	-35.1	0	5	-6	49.5	52.0
-4	2	6	10.1	10.9	2	-1	4	11.2	9.7	4	-1	2	16.6	15.1	0	5	-7	0.0	2.9
-4	2	7	12.6	13.2	2	-1	5	9.0	-9.0	4	-1	3	20.9	22.7	0	5	-8	14.4	13.2
-4	3	1	30.3	-30.9	2	-1	6	58.6	-44.2	4	-1	4	0.0	2.5	0	6	-1	0.0	-2.0
-4	3	2	0.0	-4.0	2	-1	7	4.0	-5.6	4	-1	5	38.6	46.6	0	6	-2	32.1	-30.4
-4	3	3	36.5	-35.1	2	-1	8	27.8	-33.7	4	-1	6	0.0	2.9	0	6	-3	6.5	-6.4
-4	3	4	11.9	12.1	2	-1	9	10.1	-9.1	4	-1	7	12.3	-17.2	0	6	-4	19.5	19.0
-4	3	5	9.4	8.3	2	-2	0	33.6	34.1	4	-2	0	7.6	5.4	0	6	-5	11.2	-13.4
-4	3	6	0.0	-3.6	2	-2	1	10.1	7.1	4	-2	1	9.4	12.5	0	6	-6	30.0	29.4
-4	4	1	0.0	1.9	2	-2	2	88.9	92.2	4	-2	2	19.5	-21.4	1	0	-1	55.3	68.6
-4	4	2	32.5	-31.8	2	-2	3	18.1	17.9	4	-2	3	40.8	42.0	1	0	-2	14.8	-17.2
-4	4	3	18.1	-16.6	2	-2	4	34.7	-39.2	4	-2	4	10.8	15.2	1	0	-3	19.1	20.8
-4	4	4	19.1	16.4	2	-2	5	0.0	2.7	4	-2	5	8.7	12.6	1	0	-4	95.4	112.5
-4	4	5	0.0	0.1	2	-2	6	32.1	-31.0	4	-2	6	12.6	14.9	1	0	-5	4.7	-2.3
-5	1	1	23.8	25.1	2	-2	7	26.7	-31.7	4	-2	7	17.7	-22.3	1	0	-6	9.0	3.9
-5	1	2	23.1	-24.4	2	-2	8	0.0	3.4	4	-3	0	24.6	-25.1	1	0	-7	19.5	-17.9
-5	1	3	8.3	-9.4	2	-2	9	7.2	-4.5	4	-3	1	31.4	32.8	1	0	-8	34.0	-36.3
-5	1	4	0.0	-3.1	2	-3	0	55.3	53.5	4	-3	2	11.2	-10.0	1	0	-9	8.3	-2.6
-5	1	5	32.9	-33.3	2	-3	1	33.6	35.2	4	-3	3	10.5	11.6	1	0	-10	18.8	-18.6
-5	1	6	0.0	1.4	2	-3	2	20.2	26.1	4	-3	4	33.6	39.0	1	1	-1	58.9	51.4
-5	2	1	5.4	9.7	2	-3	3	27.5	26.8	4	-3	5	9.0	-9.6	1	1	-2	78.4	74.9
-5	2	2	17.3	-19.0	2	-3	4	42.3	-44.2	4	-3	6	0.0	0.7	1	1	-3	17.0	13.7
-5	2	3	9.0	11.3	2	-3	5	23.1	-23.6	4	-4	0	18.1	-14.3	1	1	-4	72.2	77.2
-5	2	4	19.1	-21.0	2	-3	6	0.0	3.2	4	-4	1	12.6	12.5	1	1	-5	24.6	27.1
-5	2	5	19.9	-20.4	2	-3	7	29.3	-33.0	4	-4	2	23.5	23.6	1	1	-6	48.0	-50.3
-5	3	1	0.0	1.6	2	-3	8	9.8	8.5	4	-4	3	7.9	-7.2	1	1	-7	4.7	-3.2
-5	3	2	9.4	8.6	2	-3	9	11.6	14.9	4	-4	4	30.7	34.1	1	1	-8	26.4	-25.9
-5	3	3	0.0	-0.3	2	-4	0	11.6	8.4	4	-4	5	0.0	0.2	1	1	-9	14.1	-14.4
-6	1	1	0.0	2.1	2	-4	1	51.3	52.8	4	-5	0	14.8	16.3	1	1	-10	0.0	6.2
					2	-4	2	8.3	-6.3	4	-5	1	0.0	-4.4	1	2	-1	13.7	10.2
1	-1	0	18.8	-15.8	2	-4	3	9.4	-9.8	4	-5	2	28.5	28.9	1	2	-2	48.0	48.7
1	-1	1	113.4	-134.3	2	-4	4	20.9	-21.3	5	-1	0	19.5	19.0	1	2	-3	39.0	37.7
1	-1	2	15.2	10.8	2	-4	5	30.7	-31.3	5	-1	1	11.9	14.0	1	2	-4	10.5	10.5
1	-1	3	7.9	-2.2	2	-4	6	6.1	2.0	5	-1	2	25.3	26.5	1	2	-5	24.2	23.2
1	-1	4	8.7	-9.5	2	-4	7	11.6	-13.5	5	-1	3	10.8	-13.1	1	2	-6	61.8	-60.9
1	-1	5	47.7	51.8	2	-4	8	0.0	-3.4	5	-1	4	0.0	4.0	1	2	-7	18.4	-18.1
1	-1	6	12.6	13.1	2	-5	0	6.9	-5.9	5	-1	5	0.0	-5.0	1	2	-8	0.0	0.2
1	-1	7	14.8	18.8	2	-5	1	24.9	26.2	5	-2	0	35.0	38.4	1	2	-9	26.4	-27.8
1	-1	8	17.0	20.2	2	-5	2	6.9	3.8	5	-2	1	0.0	-0.8	1	2	-10	7.9	8.2
1	-1	9	34.7	-41.2	2	-5	3	29.3	-31.9	5	-2	2	5.4	6.3	1	3	-1	19.1	17.1
1	-1	10	7.9	-6.9	2	-5	4	8.7	-11.3	5	-2	3	6.5	3.6	1	3	-2	10.1	10.2
1	-2	0	6.5	-6.2	2	-5	5	19.9	-18.7	5	-2	4	17.0	-17.7	1	3	-3	43.0	42.1
1	-2	1	86.7	-89.2	2	-5	6	10.5	-11.8	5	-3	0	26.0	29.9	1	3	-4	12.3	-10.5
1	-2	2	34.0	-32.4	2	-5	7	9.8	7.1	5	-3	1	10.8	10.4	1	3	-5	9.4	-9.1
1	-2	3	64.3	67.0	2	-6	0	9.4	7.9	5	-3	2							

TABLE 1. (Continued.)

<i>h</i>	<i>k</i>	<i>l</i>	F_o	F_c	<i>h</i>	<i>k</i>	<i>l</i>	F_o	F_c	<i>h</i>	<i>k</i>	<i>l</i>	F_o	F_c	<i>h</i>	<i>k</i>	<i>l</i>	F_o	F_c
1	4	-7	27.1	-24.2	2	3	-5	10.5	7.6	3	2	-5	58.2	-58.6	4	2	-7	0.0	-6.9
1	4	-8	7.6	-8.0	2	3	-6	47.7	47.2	3	2	-6	0.0	-1.2	4	2	-8	16.6	-14.6
1	4	-9	13.7	12.5	2	3	-7	11.2	-10.7	3	2	-7	0.0	6.7	4	3	-1	11.9	-9.2
1	5	-1	44.1	41.9	2	3	-8	6.1	-5.9	3	2	-8	14.4	-14.9	4	3	-2	26.7	26.7
1	5	-2	8.7	7.8	2	3	-9	7.9	11.2	3	2	-9	39.7	41.6	4	3	-3	47.0	45.3
1	5	-3	0.0	-3.8	2	3	-10	31.4	-33.6	3	3	-1	20.2	18.7	4	3	-4	12.6	-9.7
1	5	-4	15.2	14.9	2	4	-1	17.7	12.1	3	3	-2	33.2	37.2	4	3	-5	18.1	18.1
1	5	-5	41.5	-39.4	2	4	-2	21.3	-18.7	3	3	-3	74.0	-69.7	4	3	-6	0.0	2.0
1	5	-6	25.6	-25.0	2	4	-3	20.6	-18.4	3	3	-4	17.7	-16.3	4	3	-7	27.8	-26.9
1	5	-7	7.9	7.8	2	4	-4	64.3	61.4	3	3	-5	0.0	-2.7	4	3	-8	7.6	-8.4
1	5	-8	0.0	-5.5	2	4	-5	9.8	5.8	3	3	-6	28.9	-29.7	4	4	-1	23.1	22.9
1	6	-1	5.4	5.4	2	4	-6	0.0	1.3	3	3	-7	25.3	26.9	4	4	-2	14.1	11.2
1	6	-2	15.9	15.0	2	4	-7	20.6	20.4	3	3	-8	6.5	7.7	4	4	-3	31.1	30.1
1	6	-3	14.4	-12.5	2	4	-8	22.4	-22.8	3	3	-9	14.1	11.5	4	4	-4	0.0	-0.4
1	6	-4	11.6	-12.6	2	4	-9	10.5	-8.1	3	4	-1	26.4	-23.1	4	4	-5	10.8	-9.3
1	6	-5	14.4	-14.9	2	5	-1	14.8	-15.1	3	4	-2	11.6	5.5	4	4	-6	0.0	4.5
1	6	-6	27.5	-25.2	2	5	-2	23.5	22.3	3	4	-3	34.0	-31.2	4	5	-1	26.7	25.5
2	0	-1	19.1	15.0	2	5	-3	11.9	-8.3	3	4	-4	53.5	-50.2	4	5	-2	19.1	15.5
2	0	-2	22.0	-22.1	2	5	-4	30.3	28.0	3	4	-5	30.7	27.0	4	5	-3	0.0	0.9
2	0	-3	83.4	-103.5	2	5	-5	42.6	40.8	3	4	-6	16.3	-16.4	4	5	-4	0.0	6.1
2	0	-4	6.5	-2.8	2	5	-6	24.2	-22.8	3	4	-7	0.0	-0.4	5	0	-1	0.0	1.9
2	0	-5	17.0	15.5	2	5	-7	9.4	9.2	3	4	-8	35.0	34.8	5	0	-2	12.3	-9.5
2	0	-6	0.0	-4.1	2	5	-8	0.0	-2.1	3	5	-1	5.4	-6.7	5	0	-3	27.8	-31.9
2	0	-7	40.8	42.9	2	6	-1	22.0	-19.7	3	5	-2	34.3	-31.5	5	0	-4	6.1	3.0
2	0	-8	12.3	9.4	2	6	-2	9.8	8.1	3	5	-3	0.0	0.6	5	0	-5	21.7	-21.1
2	0	-9	7.6	8.6	2	6	-3	28.9	28.7	3	5	-4	35.0	-33.4	5	0	-6	4.7	-3.6
2	0	-10	7.6	7.0	2	6	-4	0.0	2.8	3	5	-5	0.0	3.4	5	0	-7	31.4	30.6
2	1	-1	56.7	-57.3	2	6	-5	26.0	26.0	3	5	-6	23.1	20.8	5	1	-1	30.3	-31.4
2	1	-2	0.0	-2.9	3	0	-1	18.4	-15.0	3	5	-7	14.8	-14.3	5	1	-2	0.0	-5.2
2	1	-3	54.9	-57.0	3	0	-2	48.0	53.2	4	0	-1	7.9	-7.9	5	1	-3	26.0	-26.4
2	1	-4	32.5	-31.5	3	0	-3	33.2	34.3	4	0	-2	18.1	-19.5	5	1	-4	13.0	-14.8
2	1	-5	71.9	74.9	3	0	-4	69.0	-78.8	4	0	-3	26.4	31.3	5	1	-5	6.5	7.5
2	1	-6	8.3	7.4	3	0	-5	15.5	16.3	4	0	-4	30.7	32.9	5	1	-6	9.4	-7.9
2	1	-7	22.0	24.0	3	0	-6	20.9	-21.9	4	0	-5	10.1	-7.5	5	1	-7	26.0	23.5
2	1	-8	32.9	31.6	3	0	-7	45.2	-47.5	4	0	-6	34.0	36.4	5	2	-1	40.8	-37.9
2	1	-9	9.8	-11.5	3	0	-8	11.2	15.1	4	0	-7	0.0	3.2	5	2	-2	18.8	-21.2
2	1	-10	5.8	-4.0	3	0	-9	0.0	-4.1	4	0	-8	26.4	-26.6	5	2	-3	9.4	7.0
2	2	-1	48.4	-50.5	3	1	-1	49.1	47.5	4	1	-1	12.3	-9.6	5	2	-4	31.4	-29.6
2	2	-2	50.6	-49.3	3	1	-2	17.7	-16.2	4	1	-2	24.9	22.3	5	2	-5	9.8	8.9
2	2	-3	0.0	5.2	3	1	-3	43.3	42.4	4	1	-3	0.0	-0.4	5	2	-6	15.2	15.5
2	2	-4	12.3	-8.0	3	1	-4	44.1	-45.1	4	1	-4	40.1	41.8	5	3	-1	12.6	-10.1
2	2	-5	56.7	58.7	3	1	-5	48.0	-51.9	4	1	-5	0.0	0.3	5	3	-2	35.4	-33.6
2	2	-6	41.9	41.3	3	1	-6	21.7	20.7	4	1	-6	0.0	2.4	5	3	-3	17.0	11.6
2	2	-7	11.2	-10.9	3	1	-7	44.4	-45.0	4	1	-7	14.4	14.7	5	3	-4	0.0	-3.0
2	2	-8	27.8	31.4	3	1	-8	4.3	-5.0	4	1	-8	29.6	-33.0	5	3	-5	11.9	-8.1
2	2	-9	0.0	-5.0	3	1	-9	37.2	35.9	4	2	-1	29.3	-24.7	6	0	-1	11.9	-8.6
2	2	-10	30.7	-29.9	3	1	-10	0.0	-2.6	4	2	-2	50.6	49.0	6	0	-2	18.8	21.3
2	3	-1	4.7	-2.8	3	2	-1	89.9	86.8	4	2	-3	17.0	12.7	6	0	-3	15.9	18.7
2	3	-2	59.2	-57.4	3	2	-2	5.4	4.7	4	2	-4	6.5	7.2	6	1	-1	16.3	17.3
2	3	-3	9.0	8.6	3	2	-3	42.3	-40.4	4	2	-5	31.4	30.8	6	1	-2	12.3	-6.0
2	3	-4	38.6	36.6	3	2	-4	9.4	10.4	4	2	-6	10.1	-10.4					

TABLE 2.

Final positional parameters (fractional) with standard deviations (\AA), and temperature factors and standard deviations (\AA^2).

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$B(\text{\AA}^2)$	$\sigma(B)$
As ₁	0.3161	0.2240	0.3668	0.0024	0.0024	0.0025	3.22	0.05
As ₂	0.3700	-0.0619	0.1033	0.0025	0.0025	0.0026	3.76	0.05
S ₃	0.6419	0.2461	0.3645	0.0074	0.0073	0.0074	5.09	0.16
S ₄	0.1789	-0.0498	0.2641	0.0069	0.0065	0.0068	4.18	0.14
C ₅	0.2180	0.2229	0.5238	0.025	0.026	0.025	4.63	0.56
C ₆	0.1664	0.4265	0.2969	0.026	0.025	0.023	4.29	0.54
C ₇	0.5950	-0.2441	0.1467	0.027	0.027	0.027	5.37	0.63
C ₈	0.1786	-0.2432	-0.0100	0.026	0.026	0.027	5.09	0.60

TABLE 3.

Bond distances (\AA) and valency angles, and standard deviations.

As ₁ -S ₃	2.075 ± 0.007	As ₁ -C ₅	1.947 ± 0.025	S ₄ -As ₁ -S ₃	113.3 ± 0.3°	As ₁ -S ₄ -As ₂	96.5 ± 0.3
As ₁ -S ₄	2.214 ± 0.007	As ₁ -C ₆	1.963 ± 0.025	S ₄ -As ₁ -C ₅	101.0 ± 0.7		
As ₂ -S ₄	2.279 ± 0.007	As ₂ -C ₇	2.009 ± 0.027	S ₄ -As ₁ -C ₆	106.2 ± 0.7	S ₄ -As ₂ -C ₇	99.1 ± 0.7
		As ₂ -C ₈	1.972 ± 0.026	S ₃ -As ₁ -C ₅	115.7 ± 0.7	S ₄ -As ₂ -C ₈	96.2 ± 0.7
				S ₃ -As ₁ -C ₆	111.9 ± 0.7	C ₇ -As ₂ -C ₈	99.2 ± 1.1
				C ₅ -As ₁ -C ₆	107.9 ± 1.1		

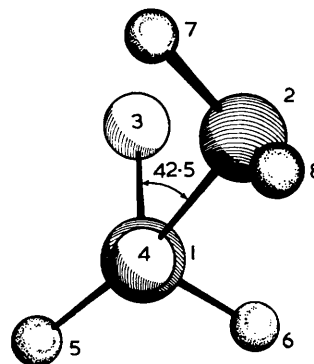
TABLE 4.

Shorter intermolecular distances.

(All distances $\leq 5 \text{ \AA}$ between molecule 1, at x, y, z , and neighbouring molecules were calculated; only the crystallographically independent distances $\leq 4 \text{ \AA}$ are listed.)

Atom (in molecule 1)	to Atom	in Molecule	d (\AA)	Atom (in molecule 1)	to Atom	in Molecule	d (\AA)
As ₂	As ₂	4	3.24	S ₄	C ₅	5	3.99
As ₂	C ₇	4	3.89	C ₅	C ₆	9	3.93
As ₂	C ₈	4	3.93	C ₅	C ₇	6	3.79
S ₃	C ₅	2	3.93	C ₆	S ₄	7	3.81
S ₃	C ₆	2	3.76	C ₆	C ₈	3	3.76
S ₃	C ₅	6	3.85	C ₇	S ₄	2	3.97
S ₃	C ₅	10	3.84				
Molecule 1 at	$x,$	$y,$	z	Molecule 6 at	$1-x,$	$-y,$	$1-z$
2 at	$1+x,$	$y,$	z	7 at	$x,$	$1+y,$	z
3 at	$-x,$	$-y,$	$-z$	8 at	$1+x,$	$1+y,$	z
4 at	$1-x,$	$-y,$	$-z$	9 at	$-x,$	$1-y,$	$1-z$
5 at	$-x,$	$-y,$	$1-z$	10 at	$1-x,$	$1-y,$	$1-z$

tervalent and one quinevalent arsenic atom. Other compounds are known with two arsenic atoms in the same molecule in different valency states, and in fact once one of the arsenic atoms in compounds of the type $R_2As \cdot X \cdot AsR_2$ has been oxidized (say, by forming a methiodide), it is often quite difficult to oxidize the other.⁹ Formulation (III) is in accord with the preparation of the compound from cacodyl sulphide and sulphur³ and with the formation of salts of dimethyldithioarsinic acid by reaction with metal halides.²

FIG. 3. View of the molecule along the S₄-As₁ bond.

In dimethylarsino dimethyldithioarsinate the configuration around the trivalent arsenic (As₂) is trigonal pyramidal, and that around the quinevalent arsenic (As₁) is tetrahedral. The angles at the quinevalent arsenic atom differ significantly from the regular tetrahedral value; those angles involving the doubly bonded sulphur, S₃, ($S=As^V-S_4$, $S=As^V-C_5$, $S=As^V-C_6$) are all larger than $109^\circ 28'$ (Table 3), while the angles not involving S₃ are smaller than the regular tetrahedral angle and have values which are not too much larger than the angles at the trigonal As^{III} atom. There are, in addition, deviations from the symmetry which might pertain in the two parts of the molecule separately: $S_4-As^{III}-C_7$ (99.1°) \neq $S_4-As^{III}-C_8$ (96.2°); $S_4-As^V-C_5$ (101.0°) \neq $S_4-As^V-C_6$ (106.2°); $S_3=As^V-C_5$ (115.7°) \neq $S_3=As^V-C_6$ (111.9°). These differences are probably a result of minor steric interferences in the molecule; Figs. 1 and 3 show that C₆ is much closer to As^{III} than is C₅, and C₇ is much closer to S₃ than is C₈. Slight repulsions due to these closer approaches would tend to increase $S_4-As^V-C_6$ and $S_4-As^{III}-C_7$.

The angle $As^{III}-S-As^V$ is 96.5° , only a little larger than the angle in H_2S (93°).¹⁰ The corresponding angles in arsenic trisulphide and arsenic sulphide (realgar) are $100^\circ \pm 2^\circ$

⁹ See, e.g., Mann, in "Progress in Organic Chemistry," ed. J. W. Cook, Butterworths, London, 1958, Vol. IV, p. 237.

and about 102° , respectively,¹⁰ and the S-As^{III}-S angle in arsenic trisulphide is $114^\circ \pm 2^\circ$, very similar to the S-As^V=S angle in dimethylarsino dimethyldithioarsinate ($113.5^\circ \pm 0.3^\circ$). However, this agreement is probably fortuitous since the molecules are so different. There appear to be no results available with which the other angles can be strictly compared, data for quinevalent arsenic in particular being very sparse. For trivalent arsenic in compounds of the types R₂AsX (R = alkyl or aryl, X = halogen) and R₃As (R = alkyl or aryl) some measurements are available. The C-As-X and C-As-C angles are each about $96\text{--}98^\circ$ (within rather wide limits of error) in the halogenodimethylarsines;¹⁰ $95\text{--}96^\circ \pm 1^\circ$ and $105^\circ \pm 2^\circ$, respectively, in the halogenodiphenylarsines;¹¹ and $91^\circ \pm 1\frac{1}{2}^\circ$ and $105^\circ \pm 2^\circ$, respectively, in cyanodimethylarsine (cacodyl cyanide).¹² The C-As-C angles are $96^\circ \pm 5^\circ$ in trimethylarsine,¹⁰ $100^\circ \pm 3.5^\circ$ in perfluorotrimethylarsine,¹⁰ and $102^\circ \pm 2^\circ$ in both tri-*p*-tolylarsine¹³ and tri-*p*-xylylarsine.¹ The angles at As₂^{III} in the present analysis (96.2° , 99.1° , and 99.2°) are in the same range as the corresponding angles in these other molecules; no stricter comparison is useful in any case since the bond angles are so readily distorted by slight steric strains in the various molecules.

The As-S single bond distances are $2.28 \pm 0.007 \text{ \AA}$ for As^{III}-S and $2.21 \pm 0.007 \text{ \AA}$ for As^V-S. The difference between these values is highly significant, and suggests a slightly smaller covalent radius (by 0.07 \AA) for As^V. The As₁^V-S₃ distance (2.07 \AA) indicates that this is a double bond, the difference between As^V-S₄ and As^V=S₃ being 0.14 \AA , about the same as the difference between single- and double-bond covalent radii for sulphur (0.10 \AA).^{14a} The only As-S distances given in the literature are those in realgar ($2.21\text{--}2.23 \pm 0.02 \text{ \AA}$) and in arsenic trisulphide ($2.25 \pm 0.02 \text{ \AA}$).¹⁰

The arsenic-carbon distances average $1.990 \pm 0.019 \text{ \AA}$ for As^{III}-C and $1.955 \pm 0.018 \text{ \AA}$ for As^V-C; as with the arsenic-sulphur distances, the bonds involving quinevalent arsenic are slightly shorter (0.035 \AA), but on the basis of the estimated standard deviations the difference cannot be claimed to be significant in this case. The As-C distances are very similar to the lengths of corresponding bonds in other arsenic derivatives (mean value about 1.98 \AA).^{1, 10-13}

The thermal parameters of the atoms vary in a manner (Table 2) which might be expected from the molecular structure. As₂, which is bonded to only three other atoms, is able to execute slightly larger vibrations ($B = 3.76 \text{ \AA}^2$) than As₁ ($B = 3.22 \text{ \AA}^2$) which is bonded to four atoms. Similarly S₃ vibrates more than S₄, and C₇ and C₈, which are bonded to As₂, vibrate more than C₅ and C₆ (we might, however, have expected that S₃ would vibrate less than C₅ and C₆).

The shortest intermolecular contact is an As^{III}...As^{III} separation of 3.24 \AA (Table 5). This is considerably less than the sum of the van der Waals radii (4.0 \AA)^{14b} and suggests charge-transfer bonding involving donation of lone-pair electrons (probably in *sp*³-hybrid orbitals) on each As^{III} to vacant *4d*-orbitals on the other arsenic atom. The direction of the short intermolecular contact is shown in Fig. 2, which indicates that the molecules are associated in pairs and that the lone pairs (assumed to make approximately equal angles with the bonds at each arsenic atom) are so directed that there is little steric interference between them, and each can therefore overlap with a *4d*-orbital of the other atom. Similar interactions have been observed in other structures, but usually with the arsenic acting only as an electron-acceptor, the donor atom being nitrogen. In cyanodimethylarsine¹² an intermolecular As...N separation of 3.18 \AA is observed (sum of van der Waals radii^{14b} 3.5 \AA), and in arsenic tricyanide¹⁵ a similar but even shorter contact

¹⁰ Sutton *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc., Special Publ.* No. 11, 1958.

¹¹ Trotter, *J.*, 1962, 2567; *Canad. J. Chem.*, 1962, **40**, 1590.

¹² Camerman and Trotter, *Canad. J. Chem.*, 1963, **41**, 460.

¹³ Trotter, *Canad. J. Chem.*, 1963, **41**, 14.

¹⁴ Pauling, "The Nature of the Chemical Bond," 3rd Edn., Cornell University Press, Ithaca, 1960, pp. (a) 224, (b) 260.

¹⁵ Emerson and Britton, *Acta Cryst.*, 1963, **16**, 113.

(2.85 Å). Both these compounds have relatively high melting points and low volatilities in comparison with the corresponding halides, and these facts suggest that the short intermolecular distances represent charge-transfer bonds with energies of 1–2 kcal. mole⁻¹ in excess of the usual van der Waals forces. The situation in the present case is somewhat similar, except that each tervalent arsenic atom acts as both an electron-donor and an electron-acceptor.

All the other intermolecular distances (Table 4) correspond to normal van der Waals interactions.

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