Crystal Structure of a New Crystalline Modification of Tetra-arsenic Tetrasulphide (2,4,6,8-Tetrathia-1,3,5,7-tetra-arsatricyclo[3,3,0,$0^{3,7}$]-octane)

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The crystal structure of the title compound was determined from photographic data and solved by direct methods. 598 Unique reflections were refined by least-squares methods to R 0·104. Crystals are monoclinic, space-group $C2/c$, with a = 9·957, b = 9·335, c = 8·889 Å, β = 102·48°, Z = 4. The molecules possess D_{2d} ($\bar{4}2m$) symmetry within experimental error. Mean bond lengths and angles are: As–As 2·593, As–S 2·243 Å; S–As–As 99·1, S–As–S 94·4, and As–S–As 101·2°. The Raman spectra of α- and β-As_4S_4 are presented; the molecules may polymerise on prolonged laser irradiation.

ATTEMPTS to purify tetra-arsenic tetrasulphide by sublimation yield at least two crystalline modifications. α-As_4S_4 appears to be identical with the mineral realgar which by a crystal-structure determination[1] has been shown to consist of discreet As_4S_4 molecules. We report here the crystal structure of the previously unreported β-As_4S_4, and some observations on the Raman spectra of the two forms. This crystal-structure determination yields much more precise dimensions for the As_4S_4 molecule than that for the α modification or the electron diffraction study[2] of the vapour.

EXPERIMENTAL

Crystals of both α- and β-As_4S_4 were obtained by vacuum sublimation of commercial tetra-arsenic tetrasulphide, and were identified by single-crystal X-ray photographs. The β form is probably more stable at higher temperature than the α form. The powder photograph of a sample which had been annealed just below the melting point was consistent with its being the β form. Although the crystals were apparently stable in air, they were sealed in Lindemann glass capillary tubes. No decomposition in the X-ray beam was observed. Intensities were determined visually from equi-inclination Weissenberg photographs (layers $hk0$—7 and $h0$—$4l$) by use of Ni-filtered Cu-K_α radiation. Lorentz, polarisation, and absorption corrections were applied, and the data were placed on a self-consistent scale by a linear least-squares method.[3] The 598 unique, non-zero reflections so obtained were used in the least-squares refinements. Accurate cell-dimensions for both modifications were obtained by least-squares analysis of $\sin^2\theta$ values from powder photographs taken with a Guinier focusing camera and silicon internal calibrant (d = 5·4306 Å). The powder photographs were indexed with the aid of single-crystal intensity data.

RESULTS

Raman Spectra.—These were obtained using a Coderg PH1 spectrometer, with a Spectra Physics helium–neon 6328 Å laser, and were calibrated by use of carbon tetrachloride. Observed frequencies (estimated uncertainty ±2 cm^{-1}) were as follows.

α-As_4S_4: 45m, 53w, 61mw, 71mw, 164w, 166w, 170w, 177s, 191s, 219ms, 220sh, 221sh, 343m, 353s, 354sh.

β-As_4S_4: 56w, 61m, 144m, 165sh, 166m, 187vs, 229vw, 343m, 351mw, 361vs, 382vw (w = weak, m = medium, s = strong, v = very, sh = shoulder).

Crystal Data.—β-As_4S_4, M = 427·5, Monoclinic, a = 9·957(3), b = 9·335(4), c = 8·889(5), β = 102·48(4)°, U = 806·7 $Å^3$, Z = 4, D_c = 3·52,† $F(000)$ = 784. λ(Cu-K_α) = 1·5418 Å, μ(Cu-K_α) = 300 cm^{-1}. Systematic absences: hkl $h + k$ odd, $h0l$ l odd. Consistent space-groups Cc and $C2/c$; the latter centrosymmetric space-group was confirmed by the successful refinement.

The structure was solved immediately by a least-squares application of direct methods,[4] and all the arsenic and sulphur atoms identified. Two of the sulphur atoms lie in special positions $\pm(0, y, 0{\cdot}25) + (0, 0, 0;\ 0{\cdot}5, 0{\cdot}5, 0)$; the remaining atoms lie in general positions $\pm(x, y, z;\ x, -y, z + 0{\cdot}5) + (0, 0, 0;\ 0{\cdot}5, 0{\cdot}5, 0)$. The molecule possesses a crystallographic two-fold axis through the two sulphur atoms in special positions; the asymmetric unit consists of one half of one molecule.

The structure was refined by full-matrix least-squares, with the weighting scheme $w = (12{\cdot}89 + |F_o| + 0{\cdot}006085\ F_o{}^2)^{-1}$. In the final cycles of refinement, anisotropic temperature factors were employed for all the atoms. The Zachariasen secondary extinction coefficient[5] refined to the value $r^* = (41 \pm 6) \times 10^{-4}$. Complex neutral-atom scattering factors[6] were employed for all atoms. The final weighted value R' [$= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}F_o$] was 0·111, with a corresponding unweighted index R of 0·104. An analysis of variance (Table 1) showed little systematic variation of the mean value of $w\Delta^2$ with the magnitude of F_o or $\sin\theta$, and with the parity group. A final difference Fourier synthesis revealed no unexpected features. The results from the final least-squares cycle are given in Tables 2 and 3; these results together with the full covariance matrix and estimated standard deviations in the unit-cell dimensions were used to calculate the bond lengths and angles shown in Table 4. Observed and calculated structure-factors are listed in Supplementary Publication No. SUP 20376 (7 pp., 1 microfiche).‡

We expected that the rigid-body hypothesis might provide a good model for the librational motion of this cage molecule, and so we have attempted to fit the observed temperature factors both by the method of Cruickshank,[7] with the motion centred at the centre of mass, and by the

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† For realgar D_m = 35·6.[1]

‡ For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[1] T. Ito, N. Morimoto, and R. Sadanaga, *Acta Cryst.*, 1952, **5**, 775.

[2] C. S. Lu and J. Donohue, *J. Amer. Chem. Soc.*, 1944, **66**, 818.

[3] A. D. Rae and A. B. Blake, *Acta Cryst.*, 1966, **20**, 586.

[4] G. M. Sheldrick, to be published.

[5] A. C. Larsen, 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 291.

[6] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17; D. T. Cromer and J. T. Waber, *ibid.*, p. 104.

[7] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

method of Schomaker and Trueblood.[8] Both analyses were performed with unit weights and with weights given by the reciprocals of the variances of the parameters from the least-squares refinement of the structure. Taking into account the effect of the crystallographic two-fold axis on the molecular symmetry, the number of independent temperature-factor components is 26, and the numbers of variable parameters are 8 (Cruickshank) and 12 (Schomaker and Trueblood). The resulting values of the generalised R index[9] were 0·126 (unit weights) and 0·146 (weighted) for the Cruickshank treatment, and 0·052 and 0·043 respectively for the Schomaker and Trueblood treatment. The improvement obtained with the latter treatment is significant at the 0·5% level,[9] and the agreement between the observed and calculated temperature factors is excellent.

TABLE 1

Analysis of variance

(*a*) As a function of $\sin\theta$

$100 \sin\theta$	0—42	42—53	53—60	60—67	67—72
N*	60	65	54	62	61
V †	815	854	508	821	644

$100 \sin\theta$	72—78	78—83	83—88	88—93	93—100
N	68	57	60	54	57
V	607	732	676	575	624

(*b*) As a function of $\lvert F_o \rvert$

$100(\lvert F_o\rvert/\lvert F_{max.}\rvert)$	0—24	24—28	28—31	31—33	33—36
N	60	76	64	41	60
V	414	625	619	703	871

$100(\lvert F_o\rvert/\lvert F_{max.}\rvert)$	36—41	41—44	44—49	49—60	60—100
N	70	57	53	62	55
V	642	770	707	829	730

(*c*) As a function of parity group, *etc.*

	ggg	*uug*	*ggu*	*uuu*	0*kl*
N	181	153	131	133	38
V	741	660	649	726	850

	*h*0*l*	*hk*0	All
N	53	57	598
V	767	823	698

* N Is the number of reflections in the group. † V Is the root-mean-square deviation of a reflection of unit weight on an absolute scale of F.

TABLE 2

Atom co-ordinates with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
As(1)	−0·0012(3)	−0·2058(3)	0·0551(3)
As(2)	−0·1599(2)	−0·4012(3)	0·1261(3)
S(1)	0·0000	−0·0531(11)	0·2500
S(2)	0·0000	−0·5522(11)	0·2500
S(3)	−0·2015(6)	−0·3048(9)	0·3406(8)

TABLE 3

Atom anisotropic vibrational amplitudes ($Å^2 \times 10^4$) with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As(1)	495(16)	451(20)	375(17)	91(12)	70(11)	86(14)
As(2)	363(15)	441(21)	459(18)	−70(12)	−38(10)	12(12)
S(1)	565(45)	379(53)	524(53)	0	49(38)	0
S(2)	595(48)	309(52)	663(61)	0	−02(42)	0
S(3)	420(28)	619(50)	591(41)	−113(34)	153(27)	−90(31)

The anisotropic temperature factor takes the form:

$$\exp[-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + \\ + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$$

TABLE 4

(*a*) Bond lengths (Å, corrected for libration) with estimated standard deviations in parentheses

As(1)–As(2)	2·593(6)	
As(1)–S(1)	2·252(9)	2·243 *
As(1)–S(3)	2·241(9)	
As(2)–S(2)	2·241(9)	
As(2)–S(3′)	2·238(9)	

(*b*) Bond angles (°) with estimated standard deviations in parentheses

S(1)–As(1)–As(2)	99·3(3)	99·1 *
S(3)–As(1)–As(2)	98·7(3)	
S(3′)–As(2)–As(1)	99·4(3)	
S(2)–As(2)–As(1)	99·1(3)	
S(3)–As(1)–S(1)	94·7(4)	94·4 *
S(2)–As(2)–S(3′)	94·1(4)	
As(1)–S(1)–As(1′)	101·0(5)	101·2 *
As(2)–S(2)–As(2′)	101·6(5)	
As(1)–S(3)–As(2′)	101·1(5)	

* Weighted mean.

(*c*) Non-bonded distances (Å) within the molecule

As(1) · · · As(1′)	3·46	As(1) · · · S(2)	3·70
As(1) · · · As(2′)	3·46	As(1) · · · S(3′)	3·67
S(1) · · · S(3)	3·30	As(2) · · · S(1)	3·68
S(2) · · · S(3)	3·27	As(2) · · · S(3)	3·66

(*d*) Non-bonded distances (<4·0 Å)

(i) Between molecules related by a C face centre

S(1) · · · S(3)	3·72	S(2) · · · S(3)	3·74

(ii) Between molecules related by a centre of symmetry

As(1) · · · As(1)	3·97	As(1) · · · S(2)	3·53
As(1) · · · S(1)	3·64	S(2) · · · S(3)	3·99

(iii) Between molecules related by a c glide

As(1) · · · S(1)	3·64	As(2) · · · S(3)	3·70
As(1) · · · S(2)	3·53	S(2) · · · S(3)	3·99

TABLE 5

Rigid-body libration analysis

Centre of mass (crystallographic co-ordinates): 0·0000, −0·3036, 0·2500

Tensors * with respect to orthogonal axes and origin at centre of mass, with estimated standard deviations in parentheses:

L	12·8(1·3)	0·0	4·4(0·8)
		14·2(1·0)	0·0
			16·0(1·2)
T	34·3(0·8)	0·0	−4·7(0·4)
		33·1(1·2)	0·0
			34·6(0·9)
S	0·116(0·012)	0·0	0·005(0·018)
	0·0	−0·205(0·014)	0·0
	−0·003(0·014)	0·0	0·039(0·014)

Origin (crystallographic co-ordinates) which gives symmetric **S** tensor: 0·0000, −0·3054, 0·2500

Distance (Å) of this origin from the centre of mass: 0·017

* The libration tensor **L**, translation tensor **T**, and translation–rotation correlation tensor **S** are defined as in ref. 8; the units are: **L** $(°)^2$, **T** 10^{-3} $Å^2$, and **S**, (°) Å.

The results of the weighted Schomaker and Trueblood treatment are presented in Table 5, and have been used to apply the librational corrections to the bond lengths given in Table 4. These librational corrections were in the range 0·009—0·012 Å; very similar values were obtained by use of the Cruickshank treatment. The thermal motion of the molecule is illustrated in Figure 1.

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[8] V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, **B24**, 63.

[9] W. C. Hamilton, 'Statistics in Physical Science,' Ronald Press, New York, 1964.

DISCUSSION

The unit-cell constants obtained for α-As$_4$S$_4$ [$P2_1/n$, $a = 9{\cdot}320(6)$, $b = 13{\cdot}551(6)$, $c = 6{\cdot}585(4)$ Å, $\beta = 106{\cdot}52°(4)$] are more precise than the literature values,[1] and give a better fit to the reported density [$D_c = 3{\cdot}56$, $D_m = 3{\cdot}56$]. The two modifications both have $Z = 4$ and the cell volumes are fairly close (α 797·4, β 806·7 Å^3).

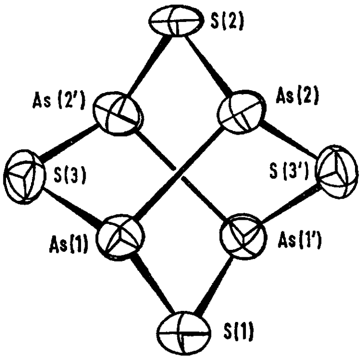

FIGURE 1 The As$_4$S$_4$ molecule projected perpendicular to [$\bar{1}$ 0 $\bar{2}$] (close to the inverse tetrad axis) showing the 50% probability ellipsoids of thermal motion and their principal axes

The β modification consists of discrete As$_4$S$_4$ molecules which possess D_{2d} symmetry within experimental error. The larger deviations from D_{2d} symmetry for α-As$_4$S$_4$ probably reflect experimental errors; the determination[1] was based on limited data and Fourier calculations only. The As–As bond length [2·49(4) Å] obtained in the electron diffraction study[2] is shorter than the values from the two crystallographic studies [2·59,[1] and 2·593(6)]; the other mean bond lengths and angles are consistent in all three determinations. Somewhat shorter bond lengths (mean As–As 2·45, mean As–S 2·21 Å) were reported[10] for As$_4$S$_3$.

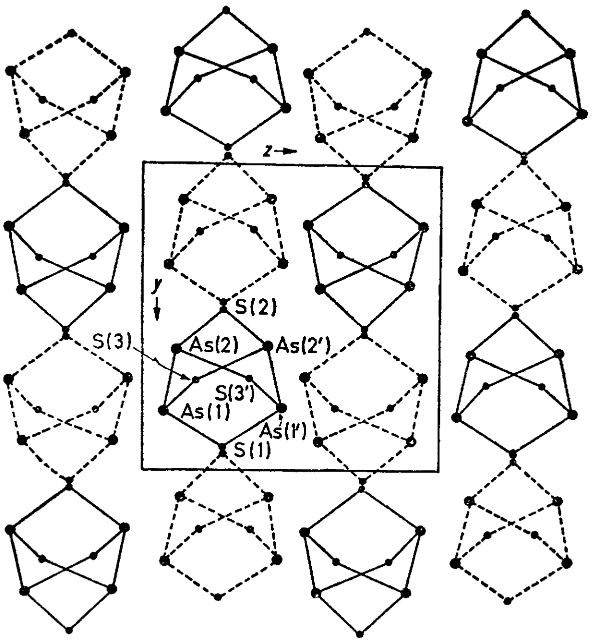

FIGURE 2 The structure in projection down the x axis

The packing of the molecules of β-As$_4$S$_4$ is illustrated in Figure 2. The molecules are in an approximately cubic close-packed array, with no particularly short intermolecular distances (Table 4). In particular, the shortest intermolecular As · · · As contacts are appreciably longer than in α-As$_4$S$_4$, where there are several of *ca.* 3·50 Å.

The Raman spectra of α- and β-As$_4$S$_4$ are presented in Figure 3. The spectrum of α-As$_4$S$_4$ agrees with that published for realgar.[11] The α- and β-spectra are fairly similar, the main difference being that the two strong lines in the α form at 177 and 191 cm^{-1} (assigned to A_1 and B_1 modes respectively[11]) are replaced by a single intense line at 187 cm^{-1}. After irradiation for *ca.* 1 h with a helium–neon laser, changes were observed in the spectra; the spectra obtained after prolonged irradiation are also presented in Figure 3. A sample sealed under vacuum showed the same effect. The complexity of the resulting spectra, and the disappearance of the lattice modes, suggests that the product is polymeric; the α and β forms give very similar spectra after prolonged irradiation, but the β form was converted more slowly. An X-ray powder photograph of the α form taken after prolonged laser irradiation did not exhibit any extra lines.

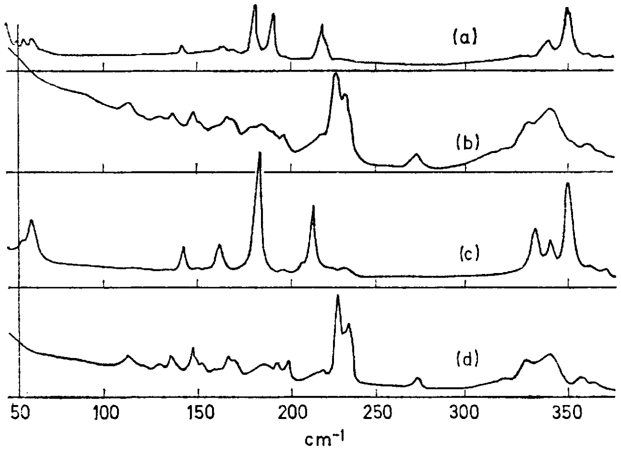

FIGURE 3 Raman spectra: a, α-As$_4$S$_4$ (realgar); b, α-As$_4$S$_4$ after prolonged laser irradiation; c, β-As$_4$S$_4$; and d, β-As$_4$S$_4$ after prolonged laser irradiation

The calculations were performed on the Cambridge University ' Titan ' computer; the rigid-body analysis and plotting of thermal ellipsoids were performed by use of programs written by Dr. R. A. Forder,[12] and the remaining calculations using programs written by G. M. S. We thank the S.R.C. for a maintenance grant (to E. J. P.), and Dr. P. J. Wheatley and the S.R.C. for experimental facilities.

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