Crystal Structure of the β-Form of Tetra-arsenic Trisulphide

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The crystal structure of synthetic β-dimorphite, As_4S_3, has been determined by a three-dimensional single-crystal *X*-ray study from photographic data. Crystals are orthorhombic, space group *Pnma*, with $Z = 4$ in a unit cell of dimensions $a = 11{\cdot}21 \pm 0{\cdot}02$, $b = 9{\cdot}90 \pm 0{\cdot}02$, and $c = 6{\cdot}58 \pm 0{\cdot}01$ Å. The structure is built of As_4S_3 molecules similar to those observed for α-dimorphite. The structure was solved by Patterson and Fourier methods and refined by least squares to R 0·09 for 438 observed reflections.

Scacchi [1] in 1849 found that naturally occurring As_4S_3 exists in two forms which he named α- and β-dimorphite. Dimorphite may be synthesized by direct combination of arsenic and sulphur mixed in stoicheiometric proportions, and single crystals of the two forms grown by sublimation in an evacuated ampoule. The β-form is stable at room temperature but is transformed into the α-form on heating above 130 °C. The structure of β-dimorphite, determined by a single-crystal *X*-ray study, is presented here, that of α-dimorphite having been reported earlier.[2]

[1] 'Dana's System of Mineralogy,' vol. 1, Wiley, New York, 1944, 7th edn., p. 197.
[2] H. J. Whitfield, *J. Chem. Soc.* (*A*), 1970, 1800.

TABLE 1

Positional (Å) and thermal parameters (Å²),* with standard deviations in parentheses

	As(1)	As(2)	As(3)	S(1)	S(2)
x	0·6850(6)	0·4145(6)	0·5705(4)	0·7020(9)	0·4868(13)
y	0·2500	0·2500	0·1247(3)	0·0796(8)	0·2500
z	0·1741(6)	−0·1045(7)	−0·2880(4)	−0·0456(11)	0·2097(16)
β_{xx}	0·0036(8)	0·0023(7)	0·0061(5)	0·0042(12)	0·0010(18)
β_{yy}	0·0085(5)	0·0070(5)	0·0038(3)	0·0043(6)	0·0078(11)
β_{zz}	0·0065(9)	0·0117(10)	0·0094(6)	0·0127(16)	0·0067(20)
β_{xy}	0·0000	0·0000	0·0001(3)	−0·0031(7)	0·0000
β_{yz}	0·0000	0·0000	−0·0021(5)	−0·0006(9)	0·0000
β_{xz}	−0·0007(6)	−0·0016(6)	−0·0008(3)	−0·0001(10)	−0·0006(14)

* The temperature factor is given by: $\exp -(\beta_{xx}h^2 + \beta_{yy}k^2 + \beta_{zz}l^2 + 2\beta_{xy}hk + 2\beta_{xz}hl + 2\beta_{yz}kl)$.

RESULTS AND DISCUSSION

The positional and thermal parameters of the asymmetric unit are given in Table 1, interatomic distances and bond angles in Table 2, and observed and calculated

TABLE 2

Bond distances and angles with standard deviations in parentheses

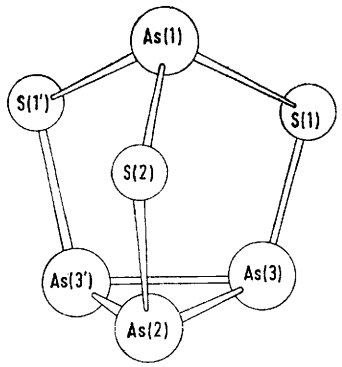
(*a*) Distances (Å)

As(1)–S(1)	2·230(8)	As(2)–S(2)	2·221(12)
As(1)–S(2)	2·234(16)	As(2)–As(3)	2·460(7)
As(3)–S(1)	2·218(10)	As(3)–As(3′)	2·480(7)

(*b*) Angles (°)

S(1)–As(1)–S(2)	98·8(0·4)	As(2)–As(3)–As(3′)	59·7(0·1)
S(1)–As(1)–S(1′)	98·3(0·5)	As(3)–As(2)–As(3′)	60·5(0·2)
S(1)–As(3)–As(2)	102·8(0·3)	As(1)–S(1)–As(3)	105·0(0·4)
S(1)–As(3)–As(3′)	101·6(0·2)	As(1)–S(2)–As(2)	105·4(0·5)
S(2)–As(2)–As(3)	101·4(0·4)		

structure factors are listed in Supplementary Publication No. SUP 20718 (3 pp.).†



A perspective view of the molecule

The crystals consist of As_4S_3 molecules (Figure), of molecular symmetry C_{3v}, as previously found for the α-form of dimorphite. The bond distances and angles in the two forms are not significantly different. The asymmetric unit consists of one half of an As_4S_3 molecule, one of the mirror planes of the molecule being a mirror plane of the crystal. Atoms As(1), As(2), and S(2) lie on the mirror plane in a special four-fold set of positions (*c*) of the space group *Pnma*, while atoms As(3) and S(1) are in general eight-fold positions (*d*).[3]

The shortest intermolecular As · · · As and As · · · S distances in β-As_4S_3 are 3·83 and 3·47 Å compared with values of 3·60 and 3·47 Å for the α-form. None of these indicates strongly directional intermolecular bonding as the van der Waals radii for arsenic and sulphur atoms are 2·0 and 1·85 Å. Indeed this conclusion is supported by the small differences observed[4] between the far-i.r. and n.q.r. spectra of the two forms.

EXPERIMENTAL

Crystal Data.—As_4S_3, M = 395·85, Orthorhombic, a = 11·21 ± 0·02, b = 9·90 ± 0·02, c = 6·58 ± 0·01 Å, U = 730·2 Å³, D_m = 3·55 ± 0·05, Z = 4, D_c = 3·57, $F(000)$ = 720. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 306 cm⁻¹. Space group *Pnma* from systematic absences: $0kl$ for $k + l$ odd, $hk0$ for h odd.‡

From a crystal of dimensions 0·1 × 0·1 × 0·1 mm multiple-film equi-inclination Weissenberg data were obtained with Ni-filtered Cu-K_α radiation for layers 0—7*kl* and *h*0—3*l*. Intensities estimated visually by comparison with a calibrated series of spots were corrected for Lorentz, polarization, and spot extension and scaled by use of reflections common to different layers.

The approximate positions of the arsenic atoms in the unit cell were inferred from a three-dimensional Patterson function. The positions of the sulphur atoms were obtained by a Fourier synthesis using the phases calculated for the trial structure of arsenic atoms. Least-squares refinement of the complete structure using isotropic temperature factors gave R 0·13. Two further cycles of refinement with anisotropic temperature factors gave R 0·09 for the 438 observed 0—7*kl* reflections.

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-sized copies.)

‡ These absences are compatible with space group *Pnma* or $Pn2_1a$, but a statistical test [5] indicated that the crystal is centrosymmetric and thus space group *Pnma* is indicated; this was confirmed by the subsequent satisfactory refinement of the structure.

[3] 'International Tables for *X*-Ray Crystallography,' vol. II, Kynoch Press, Birmingham, 1959.

[4] T. J. Bastow, D. C. Campbell, and H. J. Whitfield, *Austral. J. Chem.*, 1972, **25**, 2291.

[5] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, 1950, **3**, 210.