

The Crystal and Molecular Structure of Tetrameric Arsenic Selenide, As_4Se_4

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From an analysis of three-dimensional X-ray diffraction data, the crystal structure of As_4Se_4 has been shown to be isomorphous with that of realgar, the low-temperature form of As_4S_4 . As_4Se_4 crystallizes in space group $P2_1/n$ with lattice constants $a=9.552$, $b=13.801$, $c=6.719$ Å, $\beta=106.44^\circ$, $U=849.5$ Å³, $Z=4$. Least-squares refinement based on 1466 unique reflections has led to a conventional R of 0.054. The cage-like As_4Se_4 molecule has approximate $\bar{4}2m$ symmetry with the following average bond distances and angles: As–Se = 2.384 ± 0.005 , As–As = 2.566 ± 0.008 Å, As–Se–As = 98.1 ± 0.3 , Se–As–Se = 94.2 ± 0.3 , and As–As–Se = $101.2 \pm 0.6^\circ$. The packing is dominated by short intermolecular separations of the type As...As and As...Se.

Introduction

In their phase studies on the glass-forming As–Se system, Myers & Felty (1967) isolated a crystalline compound at an As/Se atomic ratio of 1. Preliminary crystallographic studies (Myers & Felty, 1967) suggested that the structure of this compound, also reported by Dembovskii (1963), might be isomorphous with that of realgar, the naturally occurring form of As_4S_4 (Ito, Morimoto & Sadanaga, 1952), and hence should consist of As_4Se_4 molecules having the realgar structure. The structure determination of the material was undertaken to verify these deductions and to obtain accurate values for the As–Se bond length and the Se–As–Se and As–Se–As bond angles which could be used in the detailed interpretation of the radial distribution functions of vitreous As–Se alloys (Kaplow, Rowe & Averbach, 1968). The only other source of these parameters was the limited structural study of As_2Se_3 by Vaipolin (1966).

Experimental section

Black rod-shaped crystals of As_4Se_4 prepared by sublimation were obtained from J. Berkes of this laboratory. A crystal of dimensions $0.09 \times 0.10 \times 0.22$ mm with its c axis in the long direction was selected for study. From an analysis of precession photographs, the space group was verified to be $P2_1/n$ and the lattice parameters were found to be similar to those of realgar. Accurate lattice parameters were derived by least-squares refinement of the φ , χ and 2θ settings of 44 carefully centered reflections on a Picker full-circle diffractometer. The values obtained are $a=9.552 \pm 0.002$, $b=13.801 \pm 0.003$, $c=6.719 \pm 0.001$ Å, $\beta=106.44 \pm 0.01^\circ$. Hence U , the volume of the unit cell is 849.5 ± 0.3 Å³ and the calculated X-ray density D_x is 4.811 g cm⁻³ for 4 molecules per unit cell.

Data collection

The intensity data were collected in the θ – 2θ scan mode on a Picker diffractometer controlled by a four-angle programmer and equipped with a modified IBM

card-reader card-punch. Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) monochromated on the incident beam side by the 002 reflection from a graphite monochromator was utilized. The crystal of As_4Se_4 was oriented with its c^* axis parallel to the φ axis of the diffractometer and input settings calculated *via* DIFSET, F. P. Boer's modification of the Case Institute crystal orientation program (Knox, 1966). Scans were carried out at 1° min⁻¹ over a 2θ range of $(\Delta+3)^\circ$ where Δ is the 2θ separation of the α_1 and α_2 components. Background counts were accumulated for 50 s at the ends of each scan range by the stationary-crystal stationary-counter method. Some 5000 reflections comprising a full sphere of data up to 50° in 2θ were recorded. The 004 reflection was monitored after every 20 measurements to check that stability was maintained to $\pm 2\%$ in the total intensity. Although the decomposition of realgar in the presence of light has been reported in the literature (Ito, Morimoto & Sadanaga, 1952; Street & Munir, 1970), this decomposition, if it occurred in As_4Se_4 , would be localized on the surface of the crystal and hence should not have affected our results. The sharpness of the observed reflections and our ability to maintain the intensity of our standard reflection constant during data collection support this contention.

Data processing and reduction

The net intensity I_{net} and its error σ_I were obtained from the scan count P and the background counts B_1 and B_2 by the expressions: $I_{\text{net}}=P-t(B_1+B_2)$ and $\sigma_I=[P+t^2(B_1+B_2)+(0.03 I_{\text{net}})^2]^{1/2}$, where t is the ratio of the scan time to the total background time. The data were corrected for Lorentz and polarization factors by the expression $(Lp)^{-1}=\sin 2\theta(1+q)/(1+q \cos^2 2\theta)$, where $q=\cos^2 2\theta_m$ and θ_m is the Bragg angle at the graphite monochromator. An absorption correction based on a multi-faceted solid (Busing & Levy, 1957) was applied ($\mu=347$ cm⁻¹) *via* the routines ABSRP1 and ABSRP2 obtained from NRC (Ahmed & Singh, 1967). The maximum and minimum values of the absorption correction on a relative scale were 1.571 and 0.691, respectively. The maximum error in the correction is

estimated to be 12% on the basis of the differences between equivalent reflections after its application. Reduction of the data to a unique set of 1466 reflections was accomplished by averaging equivalent reflections according to the method of Hamilton, Rollett & Sparks (1965) with a local version of Sparks's scaling program. The correlation procedure was carried out in two steps. Centrosymmetrically related reflections were averaged first, yielding a value of 0.036 for the discrepancy index

$$G_w = \sum_{hkl} [\sum_i (I_i - \bar{I}_{hkl})^2]^{1/2} / (\sum_i w_i)^{1/2} / \sum_{hkl} (\sum_i w_i)^{1/2} \bar{I}_{hkl}$$

where $w_i = 1/\sigma^2(I_i)$ is the weight and I_i is the intensity of one of a pair of averaged reflections, \bar{I}_{hkl} is the resultant averaged intensity and the external sum is taken over all hkl pairs. The remaining equivalent reflections were averaged following the application of the absorption correction. The value of G_w for this step was 0.076 as opposed to a value of 0.098 had the absorption correction not been applied. The 37 unique reflections which had $I_{net} \leq \sigma_I$ were classified as unobserved.

Structure determination and refinement

Precession photographs had indicated that the structure of As_4Se_4 was isomorphous with that of realgar (Ito, Morimoto & Sadanaga, 1952). Refinement was therefore initiated by full-matrix least-squares techniques with starting values of the atomic fractional coordinates for As and Se taken from those of Ito *et al.* (1952) for As and S, respectively. A Wilson plot calculated as suggested by Rogers (1965) provided the initial values of the scale factor and the overall temperature factor. Atomic scattering factors for neutral As and Se atoms were obtained from Cromer & Waber (1965) and dispersion corrections were applied to all atoms with Cromer's (1965) values of $\Delta f'$ and $\Delta f''$. The function minimized was $\sum w(|F_o| - K|F_c|)^2$ where w , the weight associated with each observational equation, initially had the form

$$w = 1/(1.9)^2 \quad \text{for } |F_o| \leq 4F_{min}$$

and

$$w = 1/(A + B|F_o| + C|F_o|^2) \quad \text{for } |F_o| \geq 4F_{min}$$

F_{min} was 2.5, A , B and C (Cruickshank, 1965) were given the values 1.0, 0.20 and 0.005, respectively, and the sum

was taken over all observed reflections as well as those unobserved reflections for which $|F_o|$ was smaller than $|F_c|$. Three cycles of least-squares refinement with isotropic temperature factors (33 parameters) reduced the conventional agreement index R based on F to 0.081 and the corresponding weighted agreement index R_w to 0.118. Four additional cycles with anisotropic temperature factors on all atoms (73 parameters) yielded $R = 0.063$ and $R_w = 0.097$ for the 1432 reflections included in the refinement. The residual index $S = (\sum w\Delta^2/m-n)^{1/2}$ was 0.60. Three cycles of anisotropic refinement were then carried out (one would have been enough) with $w = 1/\sigma_F^2$ where σ_F is the experimental error in $|F_o|$. R and R_w decreased to 0.052 and 0.037, respectively, and S became 2.7, but little change occurred in the parameters. The maximum shift during the last cycle was 0.06σ and the average shift was 0.02σ . The final value of R for all measured reflections is 0.054. The calculations were carried out on an XDS SIGMA 7 computer. The least-squares program was GROUP 1, a version of ORFLS (Busing, Martin & Levy, 1962) modified by Doedens (1970) for rigid-group refinement.

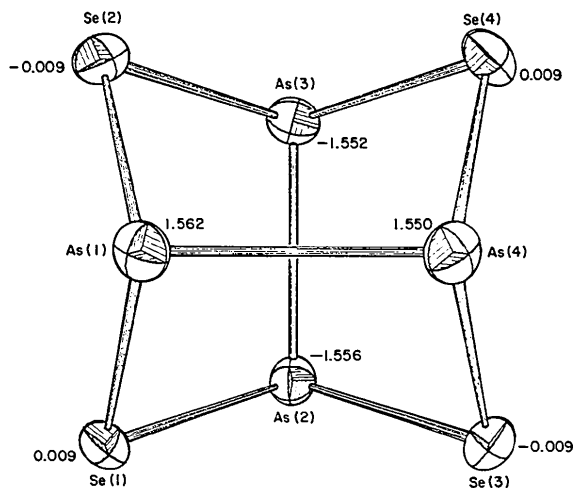


Fig. 1. ORTEP drawing of the As_4Se_4 molecule along a direction perpendicular to both the As(1)–As(4) and As(2)–As(3) bonds. Contours for the thermal vibrational ellipsoids are shown at the 50% probability level. The distances of the atoms from the best least-squares plane through the four Se atoms are indicated.

Table 1. Final fractional coordinates and anisotropic thermal parameters

The standard deviations are given in parentheses. All values have been multiplied by 10^5 . The temperature factor is of the form

$$\exp [- (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$$

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As(1)	11545 (11)	1809 (7)	-24346 (16)	601 (13)	240 (6)	1172 (27)	64 (7)	187 (15)	70 (10)
As(2)	42758 (11)	-14054 (7)	-13653 (17)	461 (12)	253 (6)	1408 (28)	11 (6)	322 (15)	-42 (10)
As(3)	32513 (11)	-13104 (8)	17546 (16)	509 (12)	302 (6)	1009 (26)	11 (7)	157 (14)	65 (10)
As(4)	3746 (11)	-16022 (8)	-29701 (17)	488 (12)	296 (6)	1264 (27)	-64 (7)	119 (15)	-69 (10)
Se(1)	34925 (11)	958 (7)	-30587 (16)	676 (13)	257 (6)	1277 (27)	-62 (7)	408 (15)	36 (9)
Se(2)	21289 (11)	2465 (7)	12330 (16)	583 (13)	278 (6)	1226 (26)	18 (7)	276 (15)	-102 (10)
Se(3)	24200 (12)	-23215 (7)	-37278 (17)	738 (14)	256 (6)	1423 (28)	-45 (7)	364 (16)	-150 (10)
Se(4)	10211 (12)	-21803 (8)	4990 (17)	654 (14)	330 (6)	1469 (29)	-106 (7)	393 (16)	102 (10)

Results and discussion

Values of the positional coordinates and anisotropic thermal parameters at the end of the least-squares refinement are given in Table 1. Intramolecular distances and angles associated with bonded and non-bonded atoms are presented in Table 2. The e.s.d.'s derived from the inverse least-squares matrix range from 0.0013 to 0.0018 Å in the distances and from 0.03 to 0.06° in the angles. The errors in the librational correction increase these e.s.d.'s by approximately 0.001 Å and 0.05°, respectively.†

Table 2. *Intramolecular distances (Å) and angles (°) in As₄Se₄*

The average estimated standard deviations are 0.003 Å in the distances and 0.1° in the angles.

Values in parentheses are before correction for librational motion.

As(1)—As(4)	2.571 (2.567)	As(1)—Se(1)—As(2)	98.2
As(2)—As(3)	2.560 (2.556)	As(2)—Se(3)—As(4)	97.9
As(1)—Se(1)	2.393 (2.389)	As(4)—Se(4)—As(3)	97.8
As(2)—Se(1)	2.385 (2.380)	As(3)—Se(2)—As(1)	98.4
As(2)—Se(3)	2.384 (2.381)	Se(1)—As(2)—Se(3)	94.0
As(4)—Se(3)	2.376 (2.372)	Se(3)—As(4)—Se(4)	93.9
As(4)—Se(4)	2.378 (2.374)	Se(4)—As(3)—Se(2)	94.7
As(3)—Se(4)	2.386 (2.382)	Se(2)—As(1)—Se(1)	94.2
As(3)—Se(2)	2.387 (2.383)	As(4)—As(1)—Se(2)	101.2
As(1)—Se(2)	2.381 (2.377)	As(4)—As(1)—Se(1)	100.2
Se(1)···Se(3)	3.487 (3.481)	As(3)—As(2)—Se(1)	101.9
Se(3)···Se(4)	3.475 (3.470)	As(3)—As(2)—Se(3)	100.9
Se(4)···Se(2)	3.511 (3.505)	As(1)—As(4)—Se(3)	102.0
Se(2)···Se(1)	3.496 (3.490)	As(1)—As(4)—Se(4)	101.6
As(1)···As(2)	3.610 (3.603)	As(2)—As(3)—Se(4)	101.3
As(2)···As(4)	3.591 (3.584)	As(2)—As(3)—Se(2)	100.7
As(4)···As(3)	3.591 (3.585)	Se(1)···Se(3)···Se(4)	90.5
As(3)···As(1)	3.610 (3.603)	Se(3)···Se(4)···Se(2)	89.9
		Se(4)···Se(2)···Se(1)	89.7
		Se(2)···Se(1)···Se(3)	89.9

Molecular geometry

The crystal structure of As₄Se₄ is isomorphous with that of realgar (Ito, Morimoto & Sadanaga, 1952). The As₄Se₄ molecule, like that of realgar (As₄S₄), has a cage-like structure (Fig. 1) in which a square of Se atoms bisects a distorted tetrahedron of As atoms. The distances of the As and Se atoms from the best least-

squares plane through the four Se atoms are shown in Fig. 1. The equation of this plane is $0.7474X + 0.2841Y - 0.6006Z + 1.716 = 0$, where X , Y , Z are orthogonal coordinates in Å along the crystallographic axes a , b and c^* , respectively. Table 3 presents some of the torsion angles. The deviations from ideal $\bar{4}2m$ symmetry are small but significant and presumably stem from the non-uniform crystallographic environment of the As₄Se₄ molecules.

Bond distances and angles

The average values of the intramolecular distances and angles in the structures of As₄Se₄ and As₄S₄ are compared in Table 4. The average As—As bond length in As₄Se₄, 2.566 Å, is intermediate between 2.59 Å, the value reported by Ito *et al.* (1952) in realgar, and 2.49 Å, the value reported by Lu & Donohue (1944) in gaseous As₄S₄. These values are considerably longer than 2.42 Å, the covalent diameter of the As atom (Schomaker & Stevenson, 1941). By comparison, the As—As bond length is 2.44 Å in gaseous As₄ (Maxwell, Hendricks & Moseley, 1935), 2.477 ± 0.003 Å in As₄S₃ (Whitfield, 1970), 2.428 ± 0.008 Å in (MeAs)₃ (Burns & Waser, 1957) and 2.456 ± 0.005 Å in (PhAs)₆ (Hedberg, Hughes & Waser, 1961). In rhombohedral As, where the distance between an As atom and its three nearest neighbors is 2.517 Å (Schiferl & Barrett, 1969), each As atom also has three other neighbors 3.12 Å, away and the lengthening of the As—As bond can be ascribed to partial metallic bonding (Mooser & Pearson, 1958). In As₄Se₄ and As₄S₄, however, the elongation of the As—As bond must arise from the preference of the molecules for a bonding configuration having $\bar{4}2m$ symmetry concomitant with a minimization of the intramolecular repulsions between non-bonded atoms. Evidence of these repulsions is seen in the short average intramolecular Se···Se separations (3.49 ± 0.01 Å) in As₄Se₄. By contrast, the shortest intra-ring and intra-chain non-bonded Se···Se separations are, respectively, 3.72 ± 0.04 Å in α -Se (Cherin & Unger, 1972) and 3.716 Å in trigonal Se (Cherin & Unger, 1967).

The importance of atomic contact diameters in stabilizing the geometry of the As₄X₄ molecule is brought out further if one compares the average values of the shortest non-bonded intramolecular separations between atoms at the tetrahedral positions (As) to those between atoms at the square positions (S or Se). One finds that the differences have the same sign and

Table 3. *Values of the smaller torsion angles in the As₄Se₄ molecule*

The torsion angle $A-B-C-D$ is defined as the dihedral angle between planes ABC and BCD . It is taken as positive if the projection of bond CD onto the plane perpendicular to bond BC lies clockwise to the projection of bond BA when seen along bond BC .

Se(1)—As(2)—As(3)—Se(2)	−1.2°	As(3)—As(2)—Se(3)—As(4)	39.2°
Se(3)—As(2)—As(3)—Se(4)	−0.5	As(1)—As(4)—Se(3)—As(2)	38.1
Se(1)—As(1)—As(4)—Se(3)	0.8	As(1)—As(4)—Se(4)—As(3)	−38.9
Se(2)—As(1)—As(4)—Se(4)	1.0	As(2)—As(3)—Se(4)—As(4)	−38.4
As(4)—As(1)—Se(1)—As(2)	−39.4	As(2)—As(3)—Se(2)—As(1)	39.4
As(3)—As(2)—Se(1)—As(1)	−37.4	As(4)—As(1)—Se(2)—As(3)	37.3

† A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30308 (27 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

possess magnitudes which range from 0.11 Å in As_4Se_4 to 0.18 Å in As_4S_4 . The same relationship between the non-bonded separations of atoms at the two different sites occurs in the molecules of N_4S_4 (Sharma & Donohue, 1963) and N_4Se_4 (Bärnighausen, von Volkmann & Jander, 1966), which also crystallize with approximate $\bar{4}2m$ symmetry except that now the N atoms lie at the corners of a square and the S or Se atoms occupy the distorted tetrahedral positions. The average values in the intramolecular non-bonded separations of the type $\text{N}\cdots\text{N}$ and $\text{X}\cdots\text{X}$, where $\text{X}=\text{S}$ or Se , are 2.55 and 2.69 Å respectively in N_4S_4 , and 2.78 and 2.97 Å in N_4Se_4 . The atoms at the tetrahedral positions (S or Se) are therefore again further from one another than the atoms at the square positions (N) this time by 0.14 Å in N_4S_4 and 0.19 Å in N_4Se_4 .

Table 4. Average values of the intramolecular distances and angles in As_4X_4 ($\text{X}=\text{Se}, \text{S}$) and the root mean square deviations in these values

The values for As_4S_4 were obtained directly from the atomic coordinates published by Ito, Morimoto & Sadanaga (1952) with the use of their reported lattice parameters. The starred values (*) differ both from the average values quoted by these authors in their paper and from the values derived from their Table 4.

	X=Se	X=S
As-X	$2.384 \pm 0.005 \text{ \AA}$	$2.24 \pm 0.04 \text{ \AA}$
As-As	2.566 ± 0.008	$2.595 \pm 0.007^*$
As-X-As	$98.1 \pm 0.3^\circ$	$101.8 \pm 0.7^*$
X-As-X	94.2 ± 0.3	$94.6 \pm 3.5^*$
As-As-X	101.2 ± 0.6	$99.0 \pm 1.3^*$
X \cdots X	3.492 ± 0.015	$3.30 \pm 0.04^*$
As \cdots As	3.601 ± 0.011	3.48 ± 0.04
As \cdots X	3.827 ± 0.014	3.68 ± 0.05
X \cdots X \cdots X	$90.0 \pm 0.3^\circ$	$90.0 \pm 1.2^\circ$

The average As-Se bond length found in As_4Se_4 , $2.384 \pm 0.005 \text{ \AA}$, is equal to the sum of the covalent radii of As and Se and slightly shorter than the average As-Se bond length ($2.41 \pm 0.05 \text{ \AA}$) reported in crystalline As_2Se_3 (Vaipolin, 1966). No other accurate crystal structures containing As-Se bond lengths are available for comparison. However, the As-Se bond length in As_4Se_4 is consistent with the As-S bond length in realgar, $2.24 \pm 0.04 \text{ \AA}$, if the effect of substituting Se

for S is taken to correspond to the difference between 1.17 and 1.04 Å, the covalent radii of Se and S, respectively (Schomaker & Stevenson, 1941). A comparison of the average bond angles in As_4Se_4 and As_4S_4 (Table 4) shows that corresponding X-As-X angles ($\text{X}=\text{S}, \text{Se}$) are the same but corresponding As-As-X and As-X-As angles differ somewhat. The observed difference in the As-X-As angles is consistent with the effect on the Y-X-Y angle of substituting $\text{X}=\text{Se}$ for $\text{X}=\text{S}$. This effect is illustrated in Table 5 by examples taken from the literature. The average value of the bond angle at the Se atom reported by Vaipolin (1966) in As_2Se_3 seems to be rather low according to this analysis. However, a recent refinement of the structure of As_2Se_3 by least-squares methods using Vaipolin's observed structure factors (Goldstein, 1973) has yielded structural parameters more in line with those of As_2S_3 (Morimoto, 1954), namely $2.40 \pm 0.04 \text{ \AA}$ for the average As-Se bond length and 95.4 ± 8.0 and $98.9 \pm 6.4^\circ$ for the average As-Se-As and Se-As-Se bond angles, respectively.

Thermal motion

The analysis of rigid-body motion by the method of Schomaker & Trueblood (1968) gave extremely good agreement between the observed and calculated thermal parameters, as indicated by the value of 0.027 \AA^2 for the agreement factor $(\sum d^2/\sum U_{ij})^{1/2}$ and 0.0005 \AA^2 for the r.m.s. ΔU_{ij} . The fit to the thermal parameters in the present case is considerably better than that obtained by Forder (1971) in his analysis of rigid-body motion in phosphorus chalcogenides having cage-like structures and seems to preclude the presence of gross systematic errors associated with improper absorption corrections. The principal values, namely 2.80, 2.64 and 2.33° for the librational tensor and 0.143, 0.131 and 0.141 Å for the translational tensor, are similar to, albeit more nearly isotropic than, those reported by Forder. The librational correction consequently increases the bond distances by 0.003 to 0.005 Å without altering the bond angles. The orientations and shapes of the individual vibrational ellipsoids are shown in Fig. 1, which was drawn with the ORTEP program (Johnson, 1965).

Table 5. Mean values and root mean square deviations from the mean of the bond angles at the S and Se atoms in a number of pairs of homologous compounds containing these elements

	X=S	X=Se	Compound	Reference
As-X-As	$101.8 \pm 0.7^\circ$	$98.1 \pm 0.3^\circ$	As_4X_4	(a)
N-X-N	104.5 ± 0.8	102.2 ± 0.1	N_4X_4	(b)
P-X-P	103.0 ± 0.4	100.1 ± 0.6	P_4X_3	(c)
C-X-C	91.5	86.7	$\text{C}_{10}\text{H}_8\text{X}$	(d)
X-X-X	107.9 ± 0.6	105.6 ± 1.8	X_8	(e)
As-X-As	99 ± 4	89 ± 3	As_2X_3	(f)

(a) As_4S_4 (from Table 4); As_4Se_4 (present work).

(b) N_4S_4 (Sharma & Donohue, 1963); N_4Se_4 (Bärnighausen *et al.*, 1966).

(c) P_4S_3 (Leung *et al.*, 1957); P_4Se_3 (Keulen & Vos, 1959).

(d) Dibenzothiophene, $\text{C}_{10}\text{H}_8\text{S}$ (Schaffrin & Trotter, 1970); dibenzoselenophene, $\text{C}_{10}\text{H}_8\text{Se}$ (Hope, Knobler & McCullough, 1970).

(e) Orthorhombic S (Abrahams, 1955; Caron & Donohue, 1961); monoclinic α -Se (Cherin & Unger, 1970).

(f) As_2S_3 (Morimoto, 1954); As_2Se_3 (Vaipolin, 1966).

Molecular packing

The packing arrangement is the same as the one found in realgar (Ito *et al.*, 1952). The intermolecular distances less than 3.70 Å are shown in Figs. 2 and 3 which present ORTEP-derived views of the structure projected along directions parallel to the *a* and *c* axes, respectively. A close correspondence exists between these intermolecular separations, which are considerably shorter than the predicted van der Waals distance of 4.0 Å (Pauling, 1960), and those occurring in realgar. Analogously short intermolecular separations have also been reported in the structure of α -Se (Cherin & Unger, 1972), where they have been taken to imply the presence of relatively strong intermolecular interactions. However, they also suggest that Pauling's values for the van der Waals radii of the As and Se atoms may be too large. More appropriate values based on the intramolecular separations in α -Se and arsenobenzene (Hedberg, Hughes & Waser, 1961) would be 1.85 Å for Se and 1.8 Å for As. With these values for the contact radii, only separations of the type As...Se and As...As would be shorter than the van der Waals contact distances in crystalline As₄Se₄ and hence could be associated with strong intermolecular interactions. A similar situation exists in realgar where all the intermolecular distances less than 3.72 Å are either of the type As...S or As...As.

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