

Higher intensities are obtained with an annular surface in the form of a single bent crystal or powder layer acting as monochromator or goniometer (Brentano 1917, 1919). For small angles its resolution is limited.

The use of short wavelengths for small-angle diffraction does not need any special discussion: it only requires sufficiently extended cameras. We found it essential to operate with evacuated instruments in order to avoid disturbance by air scatter.

## References

- BRENTANO, J. C. M. (1917). *Arch. Sci. phys. nat.* **44**, 66.  
 BRENTANO, J. C. M. (1919). *Arch. Sci. phys. nat.* **1**, 550.  
 BRENTANO, J. C. M. (1925). *Proc. Phys. Soc.* **37**, 184.  
 BRENTANO, J. C. M. (1935). *Proc. Phys. Soc.* **47**, 932.  
 BRENTANO, J. C. M. (1946). *J. Appl. Phys.* **17**, 420.  
 BRENTANO, J. C. M. (1949). *J. Appl. Phys.* **20**, 1215.  
 BRENTANO, J. C. M. & LADANY, I. (1953). *Phys. Rev.* **92**, 850.  
 BRENTANO, J. C. M. & LADANY, I. (1954). *Rev. Sci. Instrum.* **25**, 1028.

*Acta Cryst.* (1955). **8**, 661

## The Crystal and Molecular Structure of Orthorhombic Sulfur\*

By S. C. ABRAHAMST†

Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

(Received 7 June 1955)

The lattice constants of orthorhombic sulfur have been determined as  $a = 10.437 \pm 0.010$ ,  $b = 12.845 \pm 0.010$ ,  $c = 24.369 \pm 0.010$  Å. Using Mo  $K\alpha$  radiation, and both Weissenberg and precession cameras, 669 out of a possible 1046 structure factors have been measured. Warren & Burwell's approximation to the structure was refined first by double Fourier series, and then by repeated least-squares analyses, using all the measured structure factors. The coordinates thus obtained, after the least-squares method had completely converged, were used in evaluating a triple Fourier series. The arithmetic mean of the coordinates obtained by the triple-Fourier-series method corrected for series-termination errors, and the final least-squares analysis, correspond to an  $S_8$  molecule in which the mean S-S bond length is  $2.037 \pm 0.005$  Å, the mean S-S-S bond angle is  $107^\circ 48' \pm 25'$  and the mean dihedral angle is  $99^\circ 16' \pm 31'$ . There are no unusual intermolecular contacts. The dimensions in the  $S_8$  molecule are briefly discussed in terms of other recent determinations on sulfur compounds.

### 1. Introduction

The crystal structure of orthorhombic sulfur was first determined by Warren & Burwell (1935) and found to consist of symmetrically puckered  $S_8$  ring molecules. Using an elegantly simple method for reducing the number of positional parameters in the problem from 12 to 2, these parameters were refined by the trial-and-error method until satisfactory agreement was obtained between the 42 observed and calculated intensity amplitudes. The resulting arrangement led to an average S-S bond length of 2.12 Å and a S-S-S bond angle of  $105.4^\circ$ .

A re-examination of Warren & Burwell's structure was made by Ventriglia (1951), who confirmed the original solution to be correct by the use of double Patterson series. He also suggested that the S-S bond distances are about 2.1 Å and the S-S-S bond angles about  $105^\circ$ .

The importance of an accurate knowledge of this S-S bond distance to current discussion concerning the presence of double-bond character in similar bonds, suggested that a new investigation be undertaken. Accordingly, all the reflections observable with molybdenum radiation have been measured, and the resulting 669 structure factors were used in three-dimensional least-squares analyses and triple Fourier series to determine the positional parameters.

### 2. Crystal data

Orthorhombic sulfur,  $S_8$ ; mol. wt. 256.53; transforms at  $95.5^\circ$  C. to monoclinic sulfur and melts at  $118.95^\circ$  C.;  $D_{\text{obs.}} = 2.069$  g.cm.<sup>-3</sup> (Batuecas & Losa, 1951);  $D_{\text{calc.}} = 2.085$  g.cm.<sup>-3</sup>. The lattice constants were redetermined using precession photographs corrected for film shrinkage; the orthorhombic unit cell had

$$a = 10.437 \pm 0.010, \quad b = 12.845 \pm 0.010 \text{ and} \\ c = 24.369 \pm 0.010 \text{ Å}$$

(Warren & Burwell's values were 10.48, 12.92 and 24.55 Å); ( $hkl$ ) present only when  $h+k$ ,  $k+l$ ,  $l+h = 2n$ ;

\* Sponsored by the Office of Naval Research, the Army Signal Corps and the Air Force under ONR Contract N5ori-07801.

† Present address: Chemistry Department; The University, Glasgow W. 2, Scotland.

(*Ok*l) only when  $k+l = 4n$ ; (*h*0l) only when  $h+l = 4n$ ; (*h*k0) only when  $h+k = 4n$ . Space group,  $D_{2h}^{24}$ -*Fddd*. Sixteen molecules per unit cell. Molecular symmetry required,  $C_2$ . Absorption coefficient for Mo  $K\alpha$  X radiation ( $\lambda = 0.7107 \text{ \AA}$ ) =  $20.7 \text{ cm}^{-1}$ . Volume of the unit cell,  $3266.9 \text{ \AA}^3$ . Total number of electrons per unit cell,  $F(000) = 2048$ .

### 3. Intensity measurements and preparation

In order to minimize the introduction of error due to absorption and to a sharp termination of the experimental data, Mo  $K\alpha$  radiation was used for all measurements. Small, regular-shaped crystals were grown from carbon disulfide solution, and found to be quite stable under X irradiation for many weeks. A precession and a modified equi-inclination Weissenberg camera (Abrahams, 1954) were employed to obtain the photographic records. Visual intensity measurements were made using both multiple-exposure and multiple-film methods. In the latter, sheets of 1-mil nickel foil were interleaved between films (Ilford 'Industrial-G' was used almost exclusively), and the resulting intensity reduction in an X-ray beam passing through one thickness of film and foil was determined to be 3.4:1 by Geiger-counter measurement. Five crystals were used, varying in size from  $0.12 \times 0.12 \times 0.25 \text{ mm.}$  to  $0.30 \times 0.15 \times 0.30 \text{ mm.}$  The ratio of the strongest to the weakest intensity in any layer was about 1000:1. The entire reciprocal lattice was explored by recording the intensities of the *hk*0, *hk*1, *hk*2, *hk*3 and *hk*4 layers with a precession camera, and the *h*0l, *h*1l, *h*2l, *h*3l, *h*4l, *h*5l, *h*6l, *h*7l, *Ok*l, *1kl*, *2kl*, *3kl*, *4kl*, *5kl*, *6kl*, *7kl*, *8kl*, *hhl*, *h-1, h+1, l* and *h-2, h+2, l* layers with a Weissenberg camera.

Intensities measured on the precession-camera film were corrected for the Lorentz and polarization factors using the charts of Waser (1951) and of Grenville-Wells & Abrahams (1952), and those on the Weissenberg films by the usual Lorentz and polarization factors, and by the Tunell (1939) rotation factor. Absorption corrections were not made in view of the small crystals and their approximation to a spherical shape. After the intensities in each layer had been reduced to structure factors, they were placed on the same scale by using reflections common to each pair of layers; 269 of these structure factors were observed once only, 307 were observed twice, 80 were observed three times, and 13 were observed four times. In the 400 cases where a given structure factor was measured more than once, the mean value was taken. These observed values for the structure factors are given in Table 9.

The multiple observation of structure factors was used to obtain a measure of the error in the mean value. Whittaker & Robinson (1944) showed that if there are  $n$  observations of  $F_i$ , the standard deviation in any one observation is

$$\sigma(F_i) = \left[ \frac{\sum_i (\bar{F} - F_i)^2}{(n-1)} \right]^{1/2},$$

where

$$\bar{F} = \frac{\sum_i F_i}{n}.$$

This relation clearly holds only for  $n$  large. When  $n = 2, 3, 4$  the significance of  $\sigma(F_i)$  becomes rather ambiguous. Nevertheless,  $\sigma(F_i)$  was evaluated for all  $F(hkl)$ 's observed more than once. The standard deviation in the structure factor was then found to be, approximately, a constant percentage of the structure factor, with  $\sigma(F_i) \approx 0.07|F_i|$ . This relation is violated most for  $|F_i| < 100$ .

### 4. Analysis of the structure

In the space group *Fddd* the general position is 32-fold, and four of the sulfur atoms in this crystal occupy this position. However, by assuming the  $S_8$  molecule to be a symmetrical puckered ring of chosen S-S bond length and S-S-S bond angle, only two parameters remain unknown. The molecule may be regarded as consisting of two squares with one turned through  $45^\circ$  with respect to the other; the chosen bond dimensions then determine the length of the square side and the separation of the two planes of the squares. The center of this molecule lies on a 16-fold position having only the single parameter  $z$ , and the remaining unknown is the angle made by the plane of the rings with the  $a$  axis. Having thus reduced this problem to one of two unknowns only, Warren & Burwell (1935) approximately solved them by a consideration of the *00l* and *hk*0 reflections. Further refinement was then sought by making small adjustments in the atomic coordinates to give better agreement among the 42 observed and calculated intensity amplitudes, which include 14 *hkl* reflections. The resulting atomic coordinates are given in Table 1, which correspond to

Table 1. Warren & Burwell's (1935) atomic coordinates for orthorhombic sulfur

	Origin at 222			Origin at center		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
$S_1$	0.983	0.083	0.072	0.858	0.958	0.947
$S_2$	0.906	0.161	0.200	0.781	0.036	0.075
$S_3$	0.833	0.105	0.125	0.708	0.980	0.000
$S_4$	0.906	0.028	0.250	0.781	0.903	0.125

the bond distances  $S_1-S_1' = 2.18$ ,  $S_4-S_4' = 2.11$ ,  $S_1-S_3 = 2.07$ ,  $S_2-S_3 = 2.11$  and  $S_2-S_4 = 2.12 \text{ \AA}$ . The average S-S-S bond angle was  $105.4^\circ$ .

The  $x$  and  $z$  coordinates from Table 1 were then used to compute (*h*0l) structure factors (see § 5 for the atomic form factors used). The resulting value of  $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$  in this layer, using the observed structure factors in Table 9, was 0.31. After two Fourier-series projections, no further sign changes were observed, and the final series is shown in Fig. 1(a). The coordinates obtained from Fig. 1(a) correspond to

$R_1 = 0.155$ . The  $z$  coordinates from Fig. 1(a) and the  $y$  coordinates from Table 1 were then used in Fourier-series projections along the  $a$  axis to refine the  $y$  coordinates, and two such projections gave Fig. 1(b), with all signs again having ceased to change. Here  $R_1 = 0.217$ . The combined coordinates from Fig. 1(a) and (b) are given in Table 2. The coordinates in Table 2

were then used to calculate the  $hkl$  structure factors, after first transforming to an origin at the center of symmetry. The agreement factor  $R_1$  between the 669 observed  $F(hkl)$ 's and the corresponding set of calculated structure factors, using the second empirical atomic scattering curve (§ 5) at this initial stage in the three-dimensional work, was 0.258.

Table 2. Atomic coordinates from Fourier-series projections along the  $a$  and  $b$  axes

Origin at 222			
	$x$	$y$	$z$
$S_1$	0.9907	0.0810	0.0775
$S_2$	0.9042	0.1549	0.2013
$S_3$	0.8333	0.1122	0.1279
$S_4$	0.9091	0.0326	0.2500

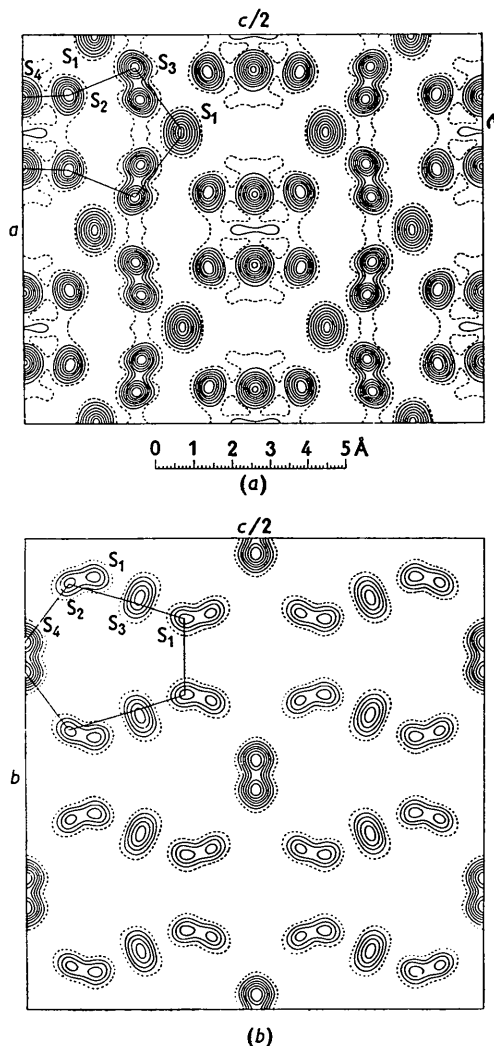


Fig. 1. (a) Projection of one-half unit cell of orthorhombic sulfur along the  $b$  axis. Contours for atoms  $S_2$  and  $S_3$  are at intervals of  $4 \text{ e.}\text{\AA}^{-2}$ ; for atoms  $S_1$  and  $S_4$  the interval is  $8 \text{ e.}\text{\AA}^{-2}$ . The  $4 \text{ e.}\text{\AA}^{-2}$  line is broken. Origin at 222.

(b) Projection of one-half unit cell of orthorhombic sulfur along the  $a$  axis. All contours are at intervals of  $8 \text{ e.}\text{\AA}^{-2}$ , the  $8 \text{ e.}\text{\AA}^{-2}$  line being broken. Origin at 222.

### Three-dimensional least-squares refinement

The means chosen for refining the atomic parameters with all the reflections observable using  $\text{Mo } K\alpha$  radiation was the method of least squares (Whittaker & Robinson, 1944; Hughes, 1941). In this method all weights were initially placed equal. An examination of various weighting schemes shows that this is not the most satisfactory procedure, and in the final use of the method of least squares the most appropriate set of weights available was applied (see § 7). The 669 observational equations were reduced to 12 normal equations in the usual way, and only the coefficients of the diagonal terms were evaluated, hence deriving the corrections ( $\Delta\xi_j$ ) to be made to the atomic coordinates ( $\xi_j$ ), by relations of the form

$$\Delta\xi_j \cdot \sum_{hkl} \left[ (\omega_{hkl})^{\frac{1}{2}} \cdot \frac{\partial F(hkl)}{\partial \xi_j} \right]^2 = \sum_{hkl} \left[ (\omega_{hkl})^{\frac{1}{2}} \cdot \frac{\partial F(hkl)}{\partial \xi_j} \cdot (\omega_{hkl})^{\frac{1}{2}} \cdot \Delta F(hkl) \right],$$

where  $\Delta F(hkl) = F_o(hkl) - F_c(hkl)$ , and  $\omega_{hkl}$  is the weight assigned to each observation.

The first application of this method produced a maximum shift in atomic coordinates of  $0.10 \text{ \AA}$ , and the structure factors calculated on the basis of these corrected coordinates contained 26 with changed sign. The value of  $R_1$  fell to  $0.177$ . A second application produced only 3 changes in the signs of structure factors, with a maximum coordinate correction of  $0.02 \text{ \AA}$ . A total of five applications of this technique was required before the largest value of  $\Delta\xi_j < \sigma(\Delta\xi_j)$ ,

Table 3. Atomic coordinates of orthorhombic sulfur

Origin at center				
	$A$	$B$	$C$	
	(Least squares)	(Fourier series)	(Arithmetic mean)	
$S_1$	$x$	0.8559	0.8549	0.8554
	$y$	0.9528	0.9523	0.9526
	$z$	0.9516	0.9516	0.9516
$S_2$	$x$	0.7844	0.7843	0.7844
	$y$	0.0302	0.0299	0.0301
	$z$	0.0763	0.0762	0.0763
$S_3$	$x$	0.7072	0.7065	0.7069
	$y$	0.9799	0.9791	0.9795
	$z$	0.0039	0.0041	0.0040
$S_4$	$x$	0.7862	0.7861	0.7862
	$y$	0.9077	0.9069	0.9073
	$z$	0.1293	0.1286	0.1290

the standard error in that  $\Delta\xi_j$  (see § 10). The maximum values of  $\Delta\xi_j$  and  $\sigma(\Delta\xi_j)$  after the final least-squares process were respectively 0.001 and 0.006 Å.  $R_1$  then became 0.162. The corresponding set of atomic coordinates is given under *A*, Table 3. As a check on the validity of the diagonal approximation, the 78 different coefficients in the twelfth-order symmetric determinant were evaluated, and the corrections  $\Delta\xi_j$  obtained using all the terms in the normal equations. The maximum change in column *A* was  $\pm 0.0001$ .

#### *Triple Fourier-series determination of atomic coordinates*

It was felt desirable to check the final coordinates obtained by the least-squares method, using an independent route. Two common alternatives were considered: the differential synthesis and the triple Fourier-series methods. The former was not used since atomic centers need not necessarily coincide with electron-density maxima if the profile is asymmetric. Since the final least-squares coordinates were, at worst, very close to the true coordinates, the electron density along lines parallel with each axis and passing through these coordinates was computed, i.e.  $\rho(x_j + \Delta x, y_j, z_j)$ , etc., was evaluated for known steps of  $\Delta x$ , as in Fig. 2.

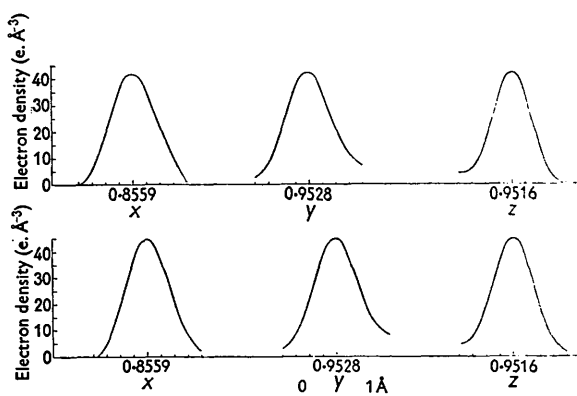


Fig. 2. Electron-density profile of atom  $S_1$  along lines parallel with the *a*, *b* and *c* axes. The upper profiles have been computed with  $F_{\text{meas}}$  as the coefficients in the triple Fourier series, the lower profiles with  $F_{\text{calc}}$ . The coordinates marked are those found by the least-squares method.

The center of gravity of this profile was taken as coincident with the atomic coordinate along the line of profile. Experience suggests that coordinates obtained in this manner are insensitive to small displacements of these lines in directions parallel with the other two axes. Each atomic electron-density profile was evaluated twice, once with the observed structure factors and then with the structure factors calculated on the basis of the final least-squares coordinates as the coefficients in the triple Fourier series. Corrections could thus be made in the usual way [ $\xi_{\text{corr.}} = \xi_{\text{obs.}} + (\xi_{\text{obs.}} - \xi_{\text{calc.}})$ ] for errors introduced into the triple Fourier series using the observed  $F(hkl)$

values, due to series termination. The corrected set of atomic coordinates thus obtained is given under *B*, Table 3.

### 5. Atomic form factors

James & Brindley's (1931) atomic form factor for sulfur was used at first, modified by a temperature factor  $B = 3.25 \text{ \AA}^2$  in the expression  $\exp[-B(\sin\theta/\lambda)^2]$ . This value was obtained by a consideration of the limiting value of  $\sin\theta/\lambda$  at which (*h*0*l*) reflections ceased to be observable. Structure factors, based upon this temperature-factor-modified curve together with the atomic coordinates in Table 1, hence permitted the observed structure factors to be placed upon a scale close to absolute. With this scale a first empirical atomic-scattering-factor curve was derived, using the relation

$$f(h0l) = F_o(h0l) \div 32 \sum_j \cos 2\pi hx_j \cdot \cos 2\pi lz_j.$$

The values of  $f(h0l)$  thus obtained were plotted against  $2 \sin\theta$ , and a mean value of  $f$  was found for each interval of  $2 \sin\theta = 0.1$ . A smooth curve was then drawn through these mean values; this is the form factor used in obtaining  $R_1(h0l) = 0.31$  in § 4.

All the observed structure factors were then placed on the same scale as the final set of observed (*h*0*l*) and (0*kl*) structure factors after completion of the double Fourier-series refinement process. A second empirical atomic form-factor curve was then derived by placing  $f(hkl) = F_o(hkl) \div G(hkl)$ , where  $G(hkl)$ , the geometrical part of the calculated structure factor, was used only if greater than 10 (maximum value is 128), and was based upon the coordinates in Table 2. A smooth curve was drawn, as described previously.

After three least-squares cycles had been completed, a third and final  $f$  curve was derived. The absolute scale was this time determined by Wilson's (1942) method, and the previous scale was found to be 5.1% too high. After adjustment to the Wilson scale, the new  $f$  curve was extracted in the same way as the second empirical curve, the atomic coordinates from the third least-squares process being used to compute

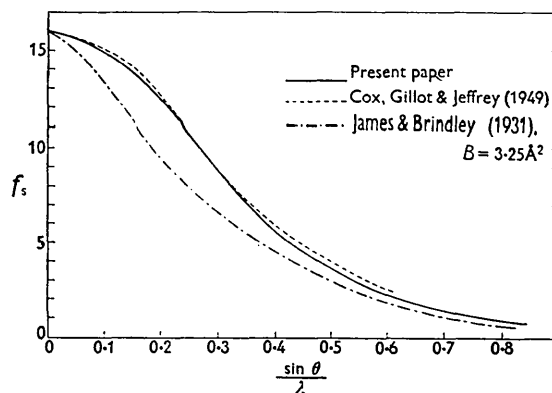


Fig. 3. Atomic-scattering-factor curves for sulfur.

$G(hkl)$ . Since the absolute scale was not directly measured by an absolute experimental method, it is possible that the final scale of the  $f$  curve reproduced in Fig. 3 might be in error. Such an error is thought to be not more than about 5%. The true temperature factor to be applied to the James & Brindley atomic-scattering-factor curve was derived simultaneously with the absolute scale by Wilson's (1942) method and was found to be  $3.46 \text{ \AA}^2$ . For comparison, the James & Brindley  $f_s$  curve (with  $B = 3.25 \text{ \AA}^2$ ) and also the empirical  $f_s$  curve found by Cox, Gillot & Jeffrey (1949) for thiophthene are given in Fig. 3.

## 6. Anisotropy in the thermal vibrations

The empirical scattering curve (Fig. 3) used in the final determination of the atomic coordinates gives a measure of the amplitude of X-ray scattering by the sulfur atoms undergoing certain thermal vibrations. The absolute value of the amplitude of this vibration has not been determined, but has been assumed equal in all directions. The validity of assuming isotropic thermal motion may be tested by replacing  $f(hkl)$  for each  $j$ th atom by  $f(hkl) \exp -[\alpha_j h^2 + \beta_j k^2 + \gamma_j l^2]$  (James, 1948). In this expression,  $\alpha_j$ ,  $\beta_j$  and  $\gamma_j$  are corrections to the overall temperature factor implicit in the curve of Fig. 3 for each  $j$ th atom in directions parallel with the  $a$ ,  $b$  and  $c$  axes, respectively. The structure-factor expression thus becomes

$$F(hkl) = f(hkl) \sum_j G_j(hkl) \exp -[\alpha_j h^2 + \beta_j k^2 + \gamma_j l^2].$$

Evaluation of these corrections was made by the method of least squares, using the coordinates under  $A$ , Table 3. It was assumed that, to a close approximation, the values of  $\alpha_j$ ,  $\beta_j$ ,  $\gamma_j$  are independent of further changes in the  $\Delta\xi_j$ 's. Diagonal terms only of the form

$$\Sigma \left[ \frac{\partial F(hkl)}{\partial \alpha_j} \right]^2 \Delta \alpha_j = \Sigma \left[ \frac{\partial F(hkl)}{\partial \alpha_j} \cdot \Delta F(hkl) \right]$$

were computed, and resulted in the values given in Table 4. The standard deviations in these corrections

Table 4. Values of the corrections to the empirical isotropic temperature factor

	$\alpha$	$\beta$	$\gamma$
$S_1$	-0.00010	-0.00069	-0.00013
$S_2$	-0.00025	-0.00022	-0.00003
$S_3$	-0.00027	-0.00008	-0.00008
$S_4$	-0.00030	+0.00009	-0.00005

had the following average values:

$$\overline{\sigma(\alpha_j)} = 0.0005, \quad \overline{\sigma(\beta_j)} = 0.0003 \quad \text{and} \quad \overline{\sigma(\gamma_j)} = 0.0003,$$

which are very similar to the actual values observed in Table 4. Nevertheless, these values were used in computing a new set of structure factors. This set

changed  $R_1$  from 0.162, corresponding to the coordinates under  $A$ , Table 3, to 0.161. The scarcely significant reduction in  $R_1$ , together with the magnitude of the standard deviation in  $\alpha_j$ ,  $\beta_j$ ,  $\gamma_j$ , suggest that indeed there is an isotropic and equal thermal motion for each atom. A simple experimental observation supporting this suggestion is that in each Weissenberg photograph, for each layer recorded, there is a very uniform value of  $\sin \theta$  at which reflections cease to be observable.

## 7. The weighting factor

In the correct use of the method of least squares, each observation should be properly weighted so that each equation of condition possesses unit weight. Each weight is proportional to the square of the modulus of precision of the observation,  $h(F)$  (Whittaker & Robinson, 1944, p. 223). Further,  $\sigma(F) = 1/[1/2 \cdot h(F)]$ , and hence by computing the standard error in each structure factor, the correct weight should readily be assignable. However, in most crystal-structure determinations  $\sigma(F)$  cannot properly be obtained, owing to the small experimental sampling of the value of each structure factor. Various alternative weighting schemes are possible, and several are examined here. In all the following schemes the coordinates under  $A$ , Table 3, were used in evaluating  $F_c$ , and hence the  $\Delta F(hkl)$  terms required in the equations of condition:

- All weights were taken equal to unity.
- Each weight was taken as  $\{1/\sqrt{2}\sigma[F(hkl)]\}^2$ , where  $\sigma[F(hkl)]$  is the average value of the standard error for each structure factor and was obtained from a smooth curve  $\overline{\sigma[F(hkl)]} \simeq 0.07|F(hkl)|$ , drawn through the 400 experimentally estimated  $\sigma[F(hkl)]$  values.
- Since the variation of  $\sigma[F(hkl)]$  with  $|F(hkl)|$  given in (b) is most violated for  $|F(hkl)| < 100$ , the weights in (b) were retained only for  $|F(hkl)| > 100$ , and, for  $|F(hkl)| \leq 100$ ,  $(\omega_{hkl})^{\frac{1}{2}}$  was kept constant at 0.100. This is the value of  $(\omega_{hkl})^{\frac{1}{2}}$  obtained from (b) for  $|F(hkl)| = 100$ .
- The weights of (b) were again used for  $|F(hkl)| > 100$ , and, for the remaining observations,  $(\omega_{hkl})^{\frac{1}{2}}$  was made *directly* proportional to  $|F(hkl)|$ , so that  $(\omega_{hkl})^{\frac{1}{2}} = |F(hkl)| \div 1000$ .

The results of these four weighting procedures are summarized in Table 5.

It is evident from Table 5 that the procedure in which all weights are placed equal to unity gives the largest errors in the individual bond lengths, assuming that all the S-S bonds are equal. The best of these weighting methods is (c), and this is the method used to obtain the coordinates in Table 3, column  $A$ .

Table 5. Variation of bond lengths with weighting procedure

	(a)	(b)	(c)	(d)
$S_1-S_3$	2.044 Å	2.033 Å	2.038 Å	2.049 Å
$S_2-S_3$	2.047	2.040	2.044	2.047
$S_2-S_4$	2.029	2.046	2.036	2.037
$S_1-S_3'$	2.027	2.024	2.037	2.043
$S_2-S_3'$	2.056	2.026	2.036	2.036
Mean S-S	2.040	2.036	2.038	2.042
Max. diff.	0.029	0.022	0.008	0.013
$\sigma(S-S)^*$	0.008	0.007	0.007	0.007

\* This is the standard deviation in the bond length of  $S_1-S_3$ ,  $S_2-S_3$  and  $S_2-S_4$ . The corresponding standard deviation in  $S_1-S_1'$  and  $S_4-S_4'$  is  $1/2$  greater.

## 8. Final coordinates

The coordinates obtained from the final least-squares treatment of § 7 are under *A*, Table 3; those from the triple Fourier-series method, corrected for finite termination of the series by Booth's (1947) method, under *B*. These corrections were small with a maximum value of 0.007 Å and a root-mean-square value of 0.003 Å. The arithmetic mean (column *C*) of these two sets of coordinates is taken as the final set. Structure factors, based on the arithmetic mean of the coordinates obtained by the method of least squares with weights of unity, and the triple Fourier-series method corrected for series termination, using the empirical atomic scattering curve in Fig. 3 and assuming no anisotropy in the thermal vibrations, are given in Table 9 under *F<sub>c</sub>*. The final value of  $R_1$  for all the reflections given in Table 9 is 0.172.

## 9. Molecular dimensions

The coordinates under *C*, Table 3, correspond to the bond distances and angles in Table 6.

Since the distances  $S_1-S_1'$  and  $S_4-S_4'$  lie across a twofold axis, they have only half the weight of the other three distances. Similarly, the angles  $S_1'-S_1-S_3$  and  $S_4'-S_4-S_2$  have half the weight of the other two

Table 6. Bond distances and angles

$S_1-S_1' = 2.036$ Å	$S_1'-S_1-S_3 = 108^\circ 33'$
$S_4-S_4' = 2.031$	$S_3-S_2-S_4 = 107^\circ 33'$
$S_1-S_3 = 2.037$	$S_1-S_3-S_2 = 107^\circ 4'$
$S_2-S_4 = 2.034$	$S_4-S_4-S_2 = 108^\circ 59'$
$S_2-S_3 = 2.043$	
Mean S-S = 2.037 Å	Mean S-S-S = $107^\circ 48'$

angles. With these weights, the mean S-S distance is 2.037 Å and the mean S-S-S angle is  $107^\circ 48'$ .

The  $S_8$  molecule in this crystal may be described as consisting of two 'squares' formed by atoms  $S_1S_2S_3S_4'$  and  $S_1'S_2'S_3S_4$ , with a distance of 0.99 Å between their mean planes. One 'square' is turned through  $45^\circ$  with respect to the other, and their two planes are identically parallel. The average length of the side of the 'square' is 3.297 Å and the average angle is  $89^\circ 59'$ ; the individual lengths and angles are shown in Fig. 4. The atoms in the 'square' have a r.m.s. deviation of 0.030 Å from their mean plane.

There are three different dihedral angles in this molecule, as given in Table 7.

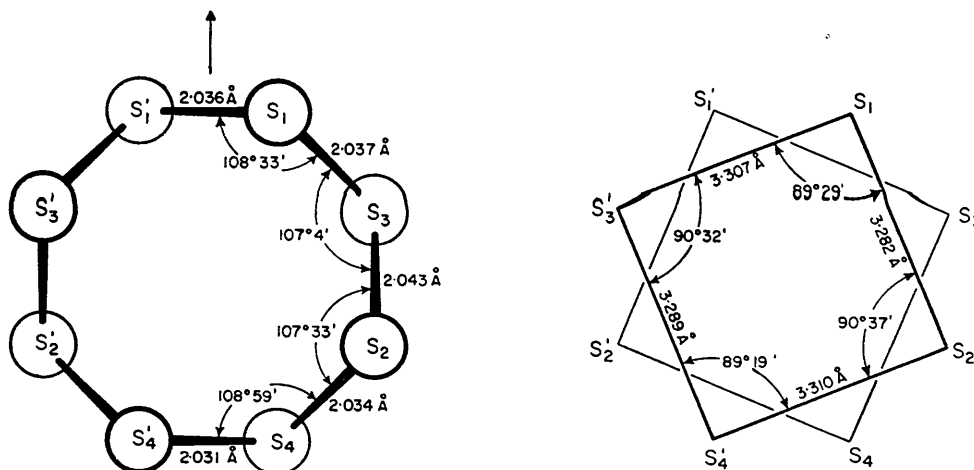
Table 7. Dihedral angles in  $S_8$ 

$S_1S_2S_3/S_3S_3S_4 = 100^\circ 37'$
$S_1S_2S_3/S_1'S_1S_3 = 98^\circ 45'$
$S_3S_2S_4/S_2S_4S_4' = 98^\circ 25'$

The angles obtained using the primed atoms have only half the weight of the first angle. Hence the mean dihedral angle is  $99^\circ 16'$ . It may be observed that if this angle were  $90^\circ$ , the distance between every fourth sulfur atom, keeping the average S-S distance and S-S-S angle in Table 6, would be 4.276 Å, whereas  $S_3-S_3'$ , for example, is 4.417 Å.

## 10. Uncertainties in the atomic coordinates, bond lengths and angles

The standard deviation in the corrections to the atomic coordinates is readily computed after the normal

Fig. 4. Dimensions in the  $S_8$  molecule in orthorhombic sulfur.

equations have been evaluated in the least-squares process, using the relation (Whittaker & Robinson, 1944)

$$\sigma(\Delta\xi_j) = \left\{ \frac{\sum v^2}{m-s} \cdot \frac{A_{11}}{D} \right\}^{\frac{1}{2}}, \quad (1)$$

where  $v$  is the residual,  $D$  the determinant formed by the coefficients of the normal equations,  $A_{11}$  the minor determinant of the coefficient of the correction  $\Delta\xi_j$ ,  $m$  the number of observational equations, and  $s$  the number of parameters. Equation (1) may be closely approximated by

$$\sigma(\Delta\xi_j) = \left\{ \frac{\sum \omega_{hkl} [\Delta F(hkl)]^2}{(m-s) \sum \omega_{hkl} [\partial F(hkl) / \partial \xi_j]^2} \right\}^{\frac{1}{2}}, \quad (2)$$

and (2) was used in this work since it has already been demonstrated in § 4 that the diagonal assumption introduces no appreciable error. The standard deviation of each coordinate in Ångström units was very nearly equal throughout. The standard deviation in the corrections produced by the first three-dimensional least-squares application was about 0.009 Å per coordinate. The final corrections leading to Table 3, column  $A$ , had a standard deviation of about 0.0051 Å per coordinate. Hence the standard deviation in the position of each atom is 0.005 Å.

Cruickshank's (1949) method was used to determine the estimated standard deviation in the atomic coordinates obtained by the triple Fourier-series method ( $B$ , Table 3). Retaining his nomenclature,

$p_x$  and  $p_y$  are 4.21,  $p_z$  is 6.00;  
 $A_{hh} = A_{kk}$  is 209.2,  $A_{ll}$  is 507.5 e.Å<sup>-5</sup>;  
 $\sigma(A_h)$  is 1.609,  $\sigma(A_k)$  is 1.511, and  $\sigma(A_l)$  is 1.796 e.Å<sup>-4</sup>.

Thus

$$\sigma(x) = 0.008, \quad \sigma(y) = 0.007, \quad \text{and} \quad \sigma(z) = 0.004 \text{ Å},$$

so that the estimated standard deviation in the position of each atom by Cruickshank's method is 0.007 Å.

The mean value of the standard deviation in the coordinate of each atom is thus taken to be 0.007 Å since the relative weights of the two sets of standard deviations are not known. The standard deviation in any one S-S bond is hence 0.010 Å. However, this bond length is measured independently four times, in the  $S_8$  molecule. The arithmetic mean of the four S-S bond distances hence has a standard deviation of  $\sigma(S-S)/\sqrt{4} = 0.005$  Å (Whittaker & Robinson, 1944). The limit of error in this arithmetic-mean distance

can be taken as double the standard deviation, i.e. 0.010 Å. It may be noticed in Table 6 that all the individual values of the S-S bond length lie well within their limit of error of the mean distance.

The standard deviation in each S-S-S bond angle is readily computed from the data above to be 44'. This angle is independently measured three times, and hence the standard deviation in the mean of these values is 25'. Each of these bond angles lies within its limit of error, i.e. 1° 28', of the mean S-S-S bond angle (Table 6). The standard deviation in the dihedral angle is the same as in the bond angle, namely 44'. This angle is independently measured only twice, since two of the observations have half the weight of the other, and hence the standard error in the mean dihedral angle is 44'/√2 = 31'.

## 11. Intermolecular contacts

In this crystal, there are four contacts only between atoms of neighboring molecules that are less than 4 Å. The shortest of these is of 3.692 Å between  $S'_3$  and  $S_2$  of the molecule related by a center. The primed atom is related to the unprimed in Table 3 by the twofold axis passing through the molecule.

## 12. Discussion

In any scheme of representing bond lengths in terms of corresponding bond orders, the lengths of the pure single and double bonds are of particular importance. For the case of sulfur, a scheme has been proposed in which the length of the bond of order zero is taken as 2.08 Å and that of order unity as 1.88 Å, with intermediate points derived from the alternating S-S bond lengths found in the hexasulfide and tetrasulfide ions (Abrahams, 1954). The S-S bond distance in the  $S_8$  molecule was examined in case it could be taken as an example of a pure single bond. However, the measured distance of 2.037 Å in orthorhombic sulfur appears to correspond not to a pure single bond, but to one with order 0.3 according to the scheme above.

The possibility of substantial double-bond character occurring in the  $S_8$  molecule was suggested previously by Powell & Eyring (1943). These authors discussed the reaction  $(x/8)S_8 \text{ ring} \rightarrow S_x \text{ chain}$ , for which the heat of reaction is 27.5 ± 5 kcal., in terms of the S-S bond strength, recently determined in several alkyl disulfides by Franklin & Lumpkin (1952) to be between 70 and 73.2 kcal. The large energy difference

Table 8. S-S-S bond angles

Compound	Value	Reference
Cesium hexasulfide	108.8 ± 2°	Abrahams & Grison, 1953
Barium tetrasulfide monohydrate	104.5 ± 2°	Abrahams, 1954
Di- <i>p</i> -tolyl sulfide (C-S-C)	109.0 ± 2°	Blackmore & Abrahams, 1955
Dimethanesulfonyl disulfide	104.0 ± 3°	Sörum, 1953
Barium tetrathionate dihydrate	103.0 ± 2°	Foss, Furberg & Zachariasen, 1954
Barium pentathionate dihydrate	104.5 ± 2°	Foss & Zachariasen, 1954









measured by Lu & Donohue (1944), using the method of electron diffraction. They obtained  $2.07 \pm 0.02$  Å for the S-S bond length and  $104^\circ 50' \pm 2^\circ$  for the S-S-S bond angle. The disagreement between these results and the present values is probably not significant (Donohue, 1955), in view of the standard errors in the two determinations, and the limiting scattering angle at which the electron-diffraction data could be observed ( $q = 100^\circ$ ).

It has been suggested\* that the S-S bond length measured in the present investigation might suffer from the same effect as operates on the C-C bond length in benzene (Cox, Cruickshank & Smith, 1955). Here, the bond length had been found to be 1.378 Å, as compared with the spectroscopic value of 1.397 Å (Stoicheff, 1954). This shortening effect appears to be produced primarily by oscillations of the benzene molecule about its senary axis, in agreement with the highly anisotropic temperature factors in the benzene crystal at  $-3^\circ$  C. If a similar effect were present in orthorhombic sulfur, the S-S bond could appear to be reduced in length by a maximum of 0.008 Å.

The S-S-S bond angle of  $107^\circ 48' \pm 25'$  is close to other recently measured values for this angle (Table 8). This angle hence appears to be rather insensitive to changes in the electronic structure of the bonds which form it. This bond angle may also be compared with the corresponding angle in the  $\text{Se}_8$  molecule. In  $\alpha$ -selenium (Burbank, 1951) it is  $105.3 \pm 2.3^\circ$  and in  $\beta$ -selenium (Marsh, Pauling & McCullough, 1953) it is  $105.7 \pm 0.8^\circ$ .

### 13. Computing methods

All structure factors (Table 9), least-squares analyses and triple Fourier series were computed on the International Business Machines 604 calculator and associated reproducer, tabulator, etc. In the methods used, developed in conjunction with the Office of Statistical Services, Massachusetts Institute of Technology, trigonometric and exponential functions were evaluated by power expansions, and four-figure accuracy was maintained throughout. The double Fourier series were summed using Beevers-Lipson strips, subdividing the  $a$ ,  $b$ , and  $c$  axes into 60, 60, and 120 parts, respectively. The positions of the contour lines in Fig. 1 were obtained from the summation totals by graphical interpolation.

\* I am indebted to Dr W. N. Lipscomb (private communication) for this suggestion.

It is a pleasure to thank Mr J. R. Steinberg of the Office of Statistical Services, Massachusetts Institute of Technology, for carrying out all the calculations on IBM equipment, Dr L. R. Lavine for helpful discussions on weighting factors, Mr J. Kalnajs for preparing the crystals, and Prof. A. R. von Hippel for his constant interest and support throughout this work.

### References

- ABRAHAMS, S. C. (1954). *Acta Cryst.* **7**, 423.  
 ABRAHAMS, S. C. & GRISON, E. (1953). *Acta Cryst.* **6**, 206.  
 BATUECAS, T. & LOSA, C. G. (1951). *An. Soc. esp. Fis. Quim. B*, **47**, 5.  
 BLACKMORE, W. R. & ABRAHAMS, S. C. (1955). *Acta Cryst.* **8**, 317, 323, 329.  
 BOOTH, A. D. (1947). *Proc. Roy. Soc. A*, **188**, 77.  
 BURBANK, R. D. (1951). *Acta Cryst.* **4**, 140.  
 COX, E. G., CRUICKSHANK, D. W. J. & SMITH, J. A. S. (1955). *Nature, Lond.* **175**, 766.  
 COX, E. G., GILLOT, R. J. J. H. & JEFFREY, G. A. (1949). *Acta Cryst.* **2**, 356.  
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.  
 DONOHUE, J. (1955). Private communication.  
 FOSS, O., FURBERG, S. & ZACHARIASEN, H. (1954). *Acta chem. scand.* **8**, 459.  
 FOSS, O. & ZACHARIASEN, H. (1954). *Acta chem. scand.* **8**, 473.  
 FRANKLIN, J. L. & LUMPKIN, H. E. (1952). *J. Amer. Chem. Soc.* **74**, 1023.  
 GRENVILLE-WELLS, H. J. & ABRAHAMS, S. C. (1952). *Rev. Sci. Instrum.* **23**, 328.  
 HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.  
 JAMES, R. W. (1948). *The Optical Principles of the Diffraction of X-rays*. London: Bell.  
 JAMES, R. W. & BRENDLEY, G. W. (1931). *Z. Kristallogr.* **78**, 470.  
 LU, C.-S. & DONOHUE, J. (1944). *J. Amer. Chem. Soc.* **66**, 818.  
 MARSH, R. E., PAULING, L. & MCCULLOUGH, J. D. (1953). *Acta Cryst.* **6**, 71.  
 POWELL, R. E. & EYRING, H. (1943). *J. Amer. Chem. Soc.* **65**, 648.  
 SÖRUM, H. (1953). *Acta chem. scand.* **7**, 1.  
 STOICHEFF, E. P. (1954). *Canad. J. Phys.* **32**, 339.  
 TUNELL, G. (1939). *Amer. Min.* **24**, 448.  
 VENTRIGLIA, U. (1951). *Period. Miner.* **20**, 237.  
 WARREN, B. E. & BURWELL, J. T. (1935). *J. Chem. Phys.* **3**, 6.  
 WASER, J. (1951). *Rev. Sci. Instrum.* **22**, 567.  
 WHITTAKER, E. T. & ROBINSON, G. (1944). *The Calculus of Observations*, 4th ed. Glasgow: Blackie.  
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.