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The Structure of Rhombic Sulphur

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From rotation and oscillation photographs with Mo $K\alpha$, rhombic sulphur is found to have the following cell and space group; $a=10.48\text{\AA}$, $b=12.92\text{\AA}$, $c=24.55\text{\AA}$, $Z=128$, space group $V_h^{24}(Fddd)$. The structure contains S_8 molecules which are symmetrical puckered rings with S—S distance 2.12\AA and bond angle $\alpha=105^\circ$. The atomic coordinates are determined by comparison of calculated amplitudes with visual intensity estimates from oscillation photographs. The relation of rhombic sulphur to the high temperature forms is discussed briefly.

INTRODUCTION

SULPHUR is one of the few common elements whose crystalline structure has not hitherto been determined. Below 96°C sulphur is stable in the orthorhombic form. The orthorhombic crystals* are readily obtained, either as natural occurrences or grown from CS_2 solution.

UNIT CELL AND SPACE GROUP

Rotation patterns were made with Mo $K\alpha$ radiation using a small crystal grown from CS_2 solution. The axial lengths obtained were as follows: $a=10.48\text{\AA}$, $b=12.92\text{\AA}$, $c=24.55\text{\AA}$, in good agreement with the results of previous workers.¹ With a value 2.04 for the density, the number of atoms in the unit cell is calculated to be 128. From a set of 15° oscillation photographs, indices were assigned to several hundred reflections. With no exceptions, the systematic vanishings indicated the space group $V_h^{24}(Fddd)$. In this space group the general position is 32-fold, and hence all the atoms may be in the general position. Four atoms in the general position would involve 12 parameters, and as this is too large a number of variables to be determined solely by cut and try, it is necessary to make use of further information in seeking a solution of the structure.

* We are indebted to Professor C. Palache of Harvard University for several large sulphur crystals, and to Dr. H. Berman for selecting and preparing them.

¹ Mark and Wigner, *Zeits. f. physik. Chemie* 111, 398 (1924). $a=10.61\text{\AA}$, $b=12.87\text{\AA}$, $c=24.56\text{\AA}$, $Z=128$, space group V_h^{24} .

THE S_8 MOLECULE

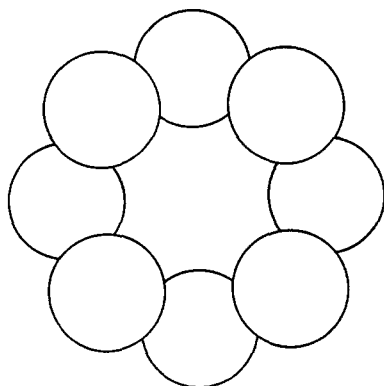
Chemical evidence² suggests strongly the existence of an S_8 molecule in rhombic sulphur. From a Fourier integral analysis of the powder pattern of sulphur,³ it was found that on the average each atom in sulphur has two nearest neighbors at a distance of roughly 2.35\AA . This would require that the structure contain either long chains or closed rings, and since there is nothing about the physical properties of sulphur to indicate long chains, the ring molecule is the more probable. The chemical evidence and the diffraction data, taken together, indicate an S_8 ring molecule.

Although the S—S distance determined from the powder pattern is somewhat approximate, it is nevertheless close enough to the S—S distance found in the trithionate group⁴ to justify the assumption that the bonding in the S_8 molecule is essentially the same as the S—S—S bonding in the trithionate group. Accordingly we assume the interatomic distances and bond angles to be the same as those found by Zachariasen, namely S—S= 2.15\AA and $\alpha=103^\circ$. Assuming a symmetrical puckered ring, the dimensions of the molecule are readily calculated. The ring can be considered as made up of two squares, one turned 45° with respect to the other (see Fig. 1). The planes of the two squares are separated by 1.15\AA , and the side of the square is 3.38\AA .

² Ephraim, *Anorganische Chemie*. Steinkopff, Dresden and Leipzig, 1934.

³ B. Warren and N. Gingrich, *Phys. Rev.* 46, 368 (1934).

⁴ W. H. Zachariasen, *J. Chem. Phys.* 2, 109 (1934).

FIG. 1. S_8 Molecule in rhombic sulphur.

POSSIBLE ARRANGEMENTS

In the space group V_h^{24} there are 8-fold, 16-fold, and 32-fold positions, but since there are only 16 S_8 molecules in the unit cell, only the 8-fold and 16-fold positions come into consideration. With Wyckoff's notation,⁵ the positions (c) and (d) can be immediately excluded as requiring centro-symmetry which the molecule does not possess. In the remaining positions there are nine major possibilities. A number of these can be ruled out immediately by intensity considerations, and others by the fact that atoms in neighboring molecules are brought closer together than is reasonable. The only likely possibility which remains is that involving 16g, with the rings located on the 2-fold axes parallel to c , the plane of the ring containing the c axis. Two parameters are still to be fixed, μ the position of the ring along the c axis, and φ the angle which the plane of the ring makes with the a axis.

The $00l$ spectra will involve only the parameter μ and this was determined by plotting the first six orders of $00l$ as a function of μ , and comparing with quantitative measurements of the integrated intensities obtained by measurements with an ionization spectrometer. The hkl spectra will be independent of μ but will involve the parameter φ . A number of these reflections were

plotted as a function of φ and compared with qualitative estimates of intensity from the oscillation patterns. In this way φ was determined to be about 50° .

From the approximate values of μ and φ determined in this way, the three coordinates of each of the four atoms in the general position were readily calculated. With these approximate coordinates the structure factors were calculated for about 60 planes. Comparing these calculated structure factors with the visual intensity estimates from oscillation photographs, small changes were made in the various coordinates until a generally satisfactory agreement was obtained. A rough but sufficiently good approximation to the Lorentz factor for oscillation photographs is obtained by setting

$$I \propto F^2/\xi,$$

where ξ is the coordinate of the reciprocal lattice⁶ point in the equatorial plane, and F is the structure factor of the unit cell. A comparison of the calculated amplitudes $F/\xi^{1/2}$ with the observed intensity estimates is given in Table I. The general agreement is sufficiently good to verify the proposed structure.

The atomic coordinates are given in Table II. The origin of coordinates is at the intersection of three 2-fold axes, and the coordinates are given (a) in degrees, with 360° representing the

TABLE I. Comparison of calculated amplitudes with observed intensity estimates.

hkl	F	$F/\xi^{1/2}$	I	hkl	F	$F/\xi^{1/2}$	I	hkl	F	$F/\xi^{1/2}$	I
004	0	0	Nil	606	31	49	Nil	311	314	690	M.S.
008	93	193	W.M.	800	61	83	V.W.	313	356	782	M.S.
0012	0	0	Nil	804	97	132	V.W.	315	51	112	Nil
0016	655	961	S	808	295	403	W.M.	317	376	825	M.S.
0020	0	0	Nil	220	229	546	M	171	59	94	V.W.
0024	520	623	M	222	602	1440	V.S.	173	143	228	W
022	125	376	W	224	122	291	W	175	403	645	M.S.
026	602	1815	V.S.	242	141	276	W				
040	472	1010	S	244	298	583	M.S.				
044	577	1230	S	246	29	57	Nil				
048	268	570	M	260	22	37	Nil				
062	610	1060	S	262	230	383	W.M.				
066	216	375	W.M.	264	60	100	V.W.				
0610	188	327	W.M.	440	56	95	V.W.				
080	3	5	Nil	442	147	258	W				
084	95	143	Nil	444	225	381	W.M.				
088	368	555	W.M.	2100	90	119	W				
202	34	93	V.W.	480	170	236	W				
206	440	1200	V.S.	620	55	85	Nil				
400	338	652	M.S.	660	740	1020	S				
404	242	467	M	6100	493	597	M				
408	427	824	M.S.	840	52	68	Nil				
602	633	1000	S								

⁵ R. W. G. Wyckoff, *The analytical expression of the results of the theory of space groups*.

⁶ J. D. Bernal, *Proc. Roy. Soc. (London)* **A113**, 117 (1926).

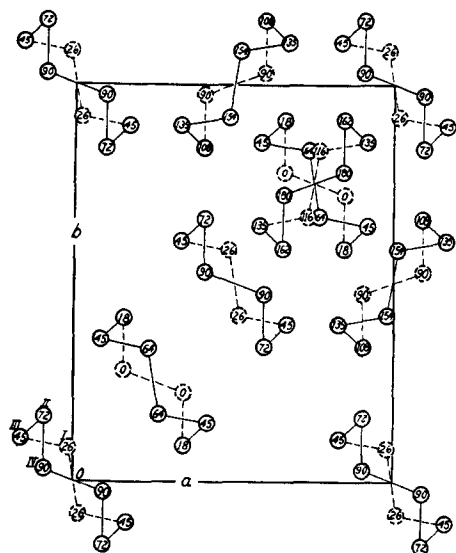


FIG. 2. Structure of rhombic sulphur. Only part of the molecules in the cell are shown, the "c" coordinates are given in degrees.

axial length, (b) as a fractional part of the axial length.

The complete structure is shown in Fig. 2. The c coordinates of the atoms are given in degrees, so that for example 90° means one-fourth of the c axis up from the plane of the paper. To avoid confusion, only part of the molecules in the cell are shown, in the lower left hand portion from $0-90^\circ$, and in the upper right hand portion from $0-180^\circ$.

The final values of the atomic coordinates were obtained by making small adjustments until a generally satisfactory agreement between calculated amplitudes and observed intensities was found. From these coordinates we can now calculate the S-S distances in the molecule and the bond angle. The results are given in Table III. As the coordinates were only fixed to the nearest degree they are uncertain by about 0.04\AA and hence the differences in the S-S distances in Table III probably have no significance.

TABLE II. Atomic coordinates in rhombic sulphur.

	θ_1	θ_2	θ_3	x	y	z
I	-6	30	26	-0.017	0.083	0.072
II	-34	58	72	-.094	.161	.200
III	-60	38	45	-.167	.105	.125
IV	-34	10	90	-.094	.028	.250

TABLE III. Interatomic distances and bond angles in S_8 molecule.

S-S	Distance	Bond angles	
IV-IV	2.11A	I	105.0°
I-I	2.18	II	103.0°
IV-II	2.12	III	108.0°
II-III	2.11	IV	105.6°
III-I	2.07		
Aver.	2.12A	Aver.	105.4°

DISCUSSION

The structure of rhombic sulphur is definitely molecular. The S_8 molecule is a puckered 8 atom ring, with an S-S distance of 2.12\AA and bond angle of 105° . The closest distance of approach of atoms in neighboring molecules is about 3.3\AA . It is interesting to note that the molecules are arranged approximately in layers perpendicular to the c axis, with 4 molecules in each quarter of c . From the orientation of the molecules, the number of close neighbors which an atom in one layer has with atoms in the next layer is small, and hence the forces holding the layers together should be relatively weak. This is undoubtedly the reason for the very good c face cleavage.

Above 96°C rhombic sulphur changes over to a monoclinic form, and at 119°C the latter melts. Chemical evidence suggests that the molecule is still S_8 in both the monoclinic form and in the melt at temperatures not too far above the melting point. At about 200°C the limpid melt changes to a red highly viscous form. This is probably due to the S_8 rings breaking open, and forming irregular chains which tangle with one another and give rise to the marked increase in viscosity. Further study of the high temperature forms of sulphur is in progress.