

The Crystal Structure of Monoclinic γ -Sulphur

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(Received 26 July 1973; accepted 30 December 1973)

The crystal structure of γ -sulphur has been determined using yellow needle crystals obtained by evaporation of a pyridine solution of cuprous ethylxanthate, $\text{CuSSCOC}_2\text{H}_5$. The crystals are monoclinic with $a = 8.442$ (30), $b = 13.025$ (10), $c = 9.356$ (50) Å, $\beta = 124.98$ (30)°; the space group is $P2/c$ and $Z = 4$. The molecules of $\text{S}_8(\gamma)$ form a pseudo-hexagonal close-packed structure with the c axis corresponding to the unique axis of the closed-packed hexagonal structure. The molecular packing is the same as that proposed by De Haan [*Physica* (1958), **24**, 855]. Each of the two independent molecules in the unit cell occupies a special position in such a way that the twofold rotation axis of the molecule coincides with that of the space group. The intramolecular configuration of $\text{S}_8(\gamma)$ is similar to that of orthorhombic α -sulphur, $\text{S}_8(\alpha)$. The average bond lengths and angles are: S-S = 2.044 (10) Å and S-S-S = 108.1 (4)° for one of the two independent molecules, and S-S = 2.045 (10) Å and S-S-S = 107.2 (4)° for the other.

Introduction

Monoclinic γ -sulphur $\text{S}_8(\gamma)$ was discovered by Muthmann (1890). Its lattice constants were determined by White (1944), De Haan (1958) and Strunz (1962). Because of the instability and the high absorption of X-rays by the crystals, detailed structural analysis of this material has not been reported. However, De Haan proposed a structure based on rotation photographs and zero-layer Weissenberg photographs around the b and c axes. It shows a pseudo-hexagonal close packing of the molecules in the c axis projection, and vertical 'sheared penny rolls' in the b axis projection. Subsequently, in the course of preparing crystals of cuprous ethylxanthate, $\text{CuSSCOC}_2\text{H}_5$, from pyridine solution, we came across yellow needle crystals. Since the crystals were identified, by X-ray methods, to be monoclinic $\text{S}_8(\gamma)$, it was decided to carry out a structure analysis of the substance in order to establish its detailed crystal structure.

Experimental and crystal data

Aqueous solutions of cupric sulphate and potassium ethylxanthate were mixed slowly in a proportion to precipitate cupric ethylxanthate, $\text{Cu}(\text{SSCOC}_2\text{H}_5)_2$. The precipitate decomposed into cuprous ethylxanthate and diethyldixanthogen. After the dixanthogen was dissolved away by washing with ethyl ether a yellowish powder of cuprous ethylxanthate remained. The powder, when dissolved in pyridine, decomposed instantly to assume a brownish colour. After evaporation of the solvent light-yellow needle crystals were obtained. Preliminary X-ray diffraction work revealed the crystals to be $\text{S}_8(\gamma)$ as studied by De Haan (1958). The crystal was elongated along the c axis and it has a slightly distorted hexagonal cross section of 0.008 mm², so its

shape was approximated by a cylinder with a radius of 0.05 mm. The cell parameters were determined from high-angle reflexions recorded ($\text{Cu } K\alpha_1$, $\lambda = 1.54051$ Å) by a Straumanis-type cassette around the c axis. The space group was assumed to be $P2/c$, which was subsequently confirmed by the solution of the structure.

Crystal data

$a = 8.442$ (30), $b = 13.025$ (10), $c = 9.356$ (50) Å;
 $\beta = 124.98$ (30)°. $V = 843.0$ (5.1) Å³.

Space group: $P2/c$.

$Z = 4$.

$d_o = 2.19$ g cm⁻³ (flotation), $d_c = 2.08$ g cm⁻³.

$\mu = 179.9$ cm⁻¹ ($\text{Cu } K\alpha_1$).

Intensity measurement

Multiple-film equi-inclination Weissenberg photographs were taken by the use of an integration cassette around the c axis (0 to 8 layers) with Ni-filtered $\text{Cu } K\alpha$ radiation. The interlayer scale factors were determined by the double-screen method. In all, 1107 reflexions (61.8% of the total number of independent reflexions observable with $\text{Cu } K\alpha$ radiation) were recorded. The intensities were corrected for Lorentz and polarization effects and reflexion spot extension by the method of Phillips (1956). Because of high absorption of $\text{Cu } K\alpha$ radiation by the crystal the transmission factor for a cylindrical shape ($\mu r = 0.90$) was applied.

Determination of the structure

The structure analysis was carried out on the basis of the atomic coordinates expected from the molecular configuration in the unit cell proposed by De Haan. Isotropic diagonal least-squares refinement reduced the

R value to 0.178. A further three cycles of full-matrix least-squares refinement with anisotropic temperature factors, in which anomalous dispersion corrections for sulphur atoms, namely $\Delta f' = 0.30$ and $\Delta f'' = 0.60$, were applied, reduced the R value to 0.075. The atomic scattering factors was taken from *International Tables for X-ray Crystallography* (1962). The quantity $\sum w(kF_o - F_c)^2$ was minimized, where k is a scale factor. The weight w was chosen so as to make the average values of $\Delta F^2 = (kF_o - F_c)^2$ constant when plotted against $|F_o|$ for every proper range of $|F_o|$. As a result w was chosen as 1 for $0 < |F_o| < 50$ and $(50/F_o)^2$ for $|F_o| \geq 50$.

The final atomic coordinates and thermal parameters are given in Table 1. The structure is shown in Figs. 1 and 2 with thermal ellipsoids. The observed and calculated structure factors are listed in Table 2.

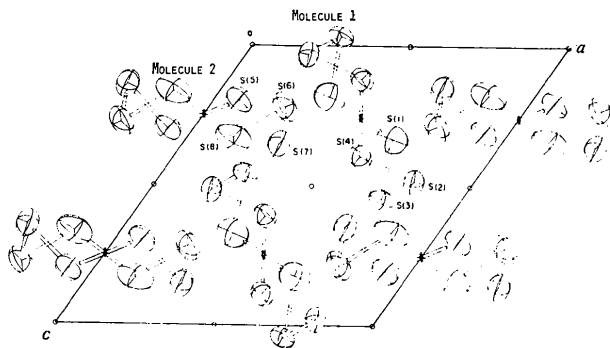


Fig. 1. The b -axis projection of the structure of $S_8(\gamma)$, showing the configurations of the S_8 molecules, with thermal ellipsoids.

Discussion of the structure

Intramolecular configuration

Each independent molecule of $S_8(\gamma)$ has a twofold rotation axis, like the molecule of $S_8(\alpha)$, as shown in Fig. 1. The intramolecular bond distances and angles are given in Table 3 and shown in Fig. 3.

The average S-S bond length is 2.044 (10) Å for the molecule 1 and 2.045 (10) Å for the molecule 2. These values agree well with the average S-S bond distance of 2.047 (3) Å for $S_8(\alpha)$. The differences between the longest bond length and the shortest, Δl_1 and Δl_2 , amount to 0.028 (12) and 0.034 (11) Å for molecules 1 and 2 respectively. These differences are on the basis of Cruickshank's (1958) criterion, 'possibly significant' or 'significant', *i.e.* $0.028 (2.33\sigma_1)$ Å $\leq \Delta l_1 < 0.037 (3.09\sigma_1)$ Å and $0.027 (2.33\sigma_2)$ Å $< \Delta l_2 < 0.035 (3.09\sigma_2)$ Å for the molecules 1 and 2 respectively. To confirm their significance due consideration should, however, be paid to possible effects of systematic errors in the intensity data. Since the systematic errors are thought to be mainly due to absorption, in order to estimate its effect on bond lengths the refinement of the structure based on intensities uncorrected for transmission factors was attempted. We then compared the S-S bond lengths obtained with those based on corrected intensities. The result is shown in Table 4. The maximum differences between corresponding bond lengths were 0.009 Å for S(1)-S(3) in molecule 1, and 0.008 Å for S(7)-S(6) in molecule 2. In both cases the shortening effects of the longest bond were much larger than those of the shortest one, resulting in a decrease of the distortion of the molecules by the correction.

If the present approximation of a cylindrical crystal shape were still insufficient, the real differences could

Table 1. Atomic parameters with *e.s.d.'s* in parentheses

Atomic coordinates ($\times 10^4$)			
	x/a	y/b	z/c
S(1)	6472 (5)	3453 (2)	3236 (4)
S(2)	8097 (3)	5794 (2)	4696 (3)
S(3)	7457 (4)	4430 (2)	5316 (3)
S(4)	5839 (4)	6766 (2)	3839 (3)
S(5)	812 (4)	7979 (2)	1999 (4)
S(6)	2423 (4)	10313 (3)	2205 (4)
S(7)	3067 (4)	8938 (3)	3499 (4)
S(8)	1482 (5)	11275 (2)	3293 (4)

Thermal parameters

The U_{ij} values as given here are defined by: $T = \exp \{-10^{-4} 2\pi^2 (U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)\}$. The B_{eq} values are the equivalent isotropic temperature factors of Hamilton (1959).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
S(1)	878 (21)	633 (16)	675 (18)	299 (15)	449 (17)	109 (14)	5.7
S(2)	385 (11)	767 (16)	552 (15)	-34 (11)	260 (11)	63 (12)	4.5
S(3)	570 (14)	757 (16)	402 (14)	71 (12)	299 (12)	131 (12)	4.5
S(4)	546 (13)	550 (13)	510 (14)	-68 (10)	340 (12)	-86 (10)	4.1
S(5)	717 (17)	562 (14)	637 (17)	26 (12)	446 (15)	-85 (12)	4.8
S(6)	769 (19)	932 (21)	735 (19)	-349 (16)	565 (17)	-290 (16)	5.8
S(7)	429 (13)	998 (22)	647 (18)	35 (14)	269 (13)	-125 (16)	5.6
S(8)	1143 (26)	568 (15)	700 (20)	-303 (16)	569 (19)	-219 (14)	6.2

Table 2. Observed and calculated structure factors

h	k	l	F_o	F_c	F_o/F_c	$F_o - F_c$	$F_o + F_c$
0	0	0	100	100	1.00	0	200
0	0	1	100	100	1.00	0	200
0	0	2	100	100	1.00	0	200
0	0	3	100	100	1.00	0	200
0	0	4	100	100	1.00	0	200
0	0	5	100	100	1.00	0	200
0	0	6	100	100	1.00	0	200
0	0	7	100	100	1.00	0	200
0	0	8	100	100	1.00	0	200
0	0	9	100	100	1.00	0	200
0	0	10	100	100	1.00	0	200
0	0	11	100	100	1.00	0	200
0	0	12	100	100	1.00	0	200
0	0	13	100	100	1.00	0	200
0	0	14	100	100	1.00	0	200
0	0	15	100	100	1.00	0	200
0	0	16	100	100	1.00	0	200
0	0	17	100	100	1.00	0	200
0	0	18	100	100	1.00	0	200
0	0	19	100	100	1.00	0	200
0	0	20	100	100	1.00	0	200
0	0	21	100	100	1.00	0	200
0	0	22	100	100	1.00	0	200
0	0	23	100	100	1.00	0	200
0	0	24	100	100	1.00	0	200
0	0	25	100	100	1.00	0	200
0	0	26	100	100	1.00	0	200
0	0	27	100	100	1.00	0	200
0	0	28	100	100	1.00	0	200
0	0	29	100	100	1.00	0	200
0	0	30	100	100	1.00	0	200
0	0	31	100	100	1.00	0	200
0	0	32	100	100	1.00	0	200
0	0	33	100	100	1.00	0	200
0	0	34	100	100	1.00	0	200
0	0	35	100	100	1.00	0	200
0	0	36	100	100	1.00	0	200
0	0	37	100	100	1.00	0	200
0	0	38	100	100	1.00	0	200
0	0	39	100	100	1.00	0	200
0	0	40	100	100	1.00	0	200
0	0	41	100	100	1.00	0	200
0	0	42	100	100	1.00	0	200
0	0	43	100	100	1.00	0	200
0	0	44	100	100	1.00	0	200
0	0	45	100	100	1.00	0	200
0	0	46	100	100	1.00	0	200
0	0	47	100	100	1.00	0	200
0	0	48	100	100	1.00	0	200
0	0	49	100	100	1.00	0	200
0	0	50	100	100	1.00	0	200
0	0	51	100	100	1.00	0	200
0	0	52	100	100	1.00	0	200
0	0	53	100	100	1.00	0	200
0	0	54	100	100	1.00	0	200
0	0	55	100	100	1.00	0	200
0	0	56	100	100	1.00	0	200
0	0	57	100	100	1.00	0	200
0	0	58	100	100	1.00	0	200
0	0	59	100	100	1.00	0	200
0	0	60	100	100	1.00	0	200
0	0	61	100	100	1.00	0	200
0	0	62	100	100	1.00	0	200
0	0	63	100	100	1.00	0	200
0	0	64	100	100	1.00	0	200
0	0	65	100	100	1.00	0	200
0	0	66	100	100	1.00	0	200
0	0	67	100	100	1.00	0	200
0	0	68	100	100	1.00	0	200
0	0	69	100	100	1.00	0	200
0	0	70	100	100	1.00	0	200
0	0	71	100	100	1.00	0	200
0	0	72	100	100	1.00	0	200
0	0	73	100	100	1.00	0	200
0	0	74	100	100	1.00	0	200
0	0	75	100	100	1.00	0	200
0	0	76	100	100	1.00	0	200
0	0	77	100	100	1.00	0	200
0	0	78	100	100	1.00	0	200
0	0	79	100	100	1.00	0	200
0	0	80	100	100	1.00	0	200
0	0	81	100	100	1.00	0	200
0	0	82	100	100	1.00	0	200
0	0	83	100	100	1.00	0	200
0	0	84	100	100	1.00	0	200
0	0	85	100	100	1.00	0	200
0	0	86	100	100	1.00	0	200
0	0	87	100	100	1.00	0	200
0	0	88	100	100	1.00	0	200
0	0	89	100	100	1.00	0	200
0	0	90	100	100	1.00	0	200
0	0	91	100	100	1.00	0	200
0	0	92	100	100	1.00	0	200
0	0	93	100	100	1.00	0	200
0	0	94	100	100	1.00	0	200
0	0	95	100	100	1.00	0	200
0	0	96	100	100	1.00	0	200
0	0	97	100	100	1.00	0	200
0	0	98	100	100	1.00	0	200
0	0	99	100	100	1.00	0	200
0	0	100	100	100	1.00	0	200

Table 4. A comparison of S-S distances uncorrected for transmission factors, with those corrected in the two molecules

Molecule 1	Uncorrected, L_{uncor}	Corrected, L_{cor}	$L_{cor} - L_{uncor}$
S(1)-S(1')	2.036 (12) Å	2.038 (11) Å	0.002 Å
S(1)-S(3)	2.069 (11)	2.060 (10)	-0.009
S(3)-S(2)	2.036 (7)	2.036 (5)	0.000
S(2)-S(4)	2.030 (8)	2.032 (7)	0.002
S(4)-S(4')	2.059 (15)	2.053 (15)	-0.006
Molecule 2			
S(5)-S(5')	2.058 (12)	2.057 (9)	-0.001
S(5)-S(7)	2.024 (9)	2.023 (7)	-0.001
S(7)-S(6)	2.061 (8)	2.053 (6)	-0.008
S(6)-S(8)	2.043 (11)	2.040 (8)	-0.003
S(8)-S(8')	2.047 (12)	2.051 (11)	0.004

be smaller and fall on the 'possibly significant' or 'insignificant' level. Under such circumstances it may be premature to conclude that the molecules of $S_8(\gamma)$ are distorted on a significant level.

The bond angles S-S-S and torsion angles S-S-S-S for each molecule are listed in Table 3. The average bond angles S-S-S are 108.1 (4) and 107.2 (4)° for the molecules 1 and 2 respectively, showing good agreement with that for $S_8(\alpha)$ 108.1 (5)° (Abrahams, 1955). The average torsion angles for the molecules 1 and 2 are 98.6 (5) and 99.6 (5)° respectively; they agree with the value for $S_8(\alpha)$ of 99.3 (4)°. The differences between maximum and minimum values of S-S-S bond

Table 3. Bond distances and angles with e.s.d.'s and torsion angles

Intramolecular distances and angles			
Molecule 1		Molecule 2	
S(1)-S(1')	2.038 (11) Å	S(5)-S(5')	2.057 (9) Å
S(1)-S(3)	2.060 (10)	S(5)-S(7)	2.023 (7)
S(3)-S(2)	2.036 (5)	S(7)-S(6)	2.053 (6)
S(2)-S(4)	2.032 (7)	S(6)-S(8)	2.040 (8)
S(4)-S(4')	2.053 (15)	S(8)-S(8')	2.051 (11)
S(1')-S(1)-S(3)	108.3 (4)°	S(5')-S(5)-S(7)	107.0 (4)°
S(1)-S(3)-S(2)	107.4 (4)	S(5)-S(7)-S(6)	107.7 (3)
S(3)-S(2)-S(4)	108.3 (3)	S(7)-S(6)-S(8)	106.8 (4)
S(2)-S(4)-S(4')	108.5 (3)	S(6)-S(8)-S(8')	107.5 (4)
Intramolecular distances			
Notation: unprimed: x, y, z ; single primed: $-x, y, -z$; double primed: $-x, -y, -z$			
S(2)-S(5'')	$a, c/2$	3.62 (1) Å	
S(2)-S(2'')	$2a, b, c$	3.58 (1)	
S(3)-S(4'')	a, b, c	3.65 (1)	
S(4)-S(7)		3.57 (1)	
S(4)-S(8'')	a, b, c	3.45 (1)	
S(4)-S(5')	$a, c/2$	3.69 (1)	
Torsion angles			
Molecule 1		Molecule 2	
S(3')-S(1')-S(1)-S(3)	98.8°	S(7')-S(5')-S(5)-S(7)	99.5°
S(1')-S(1)-S(3)-S(2)	98.5	S(5')-S(5)-S(7)-S(6)	100.1
S(1)-S(3)-S(2)-S(4)	98.8	S(5)-S(7)-S(6)-S(8)	99.9
S(3)-S(2)-S(4)-S(4')	98.8	S(7)-S(6)-S(8)-S(8')	98.9
S(2)-S(4)-S(4')-S(2')	97.9	S(6)-S(8)-S(8')-S(6')	99.8

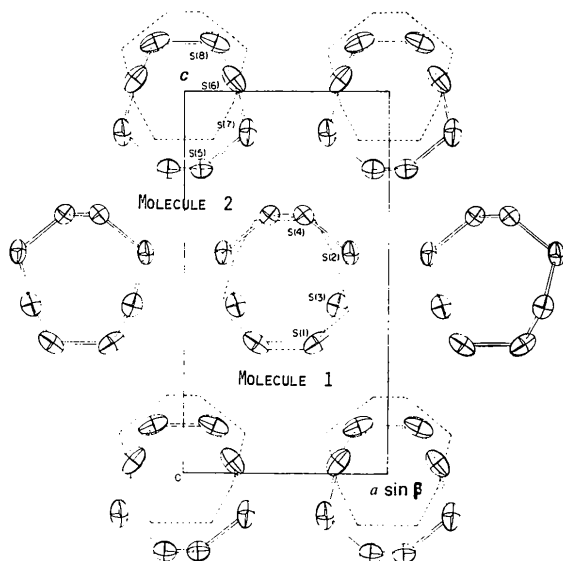


Fig. 2. Molecular configurations viewed along the c axis. Molecules shown by broken lines are related to the molecules shown by solid lines by glide planes.

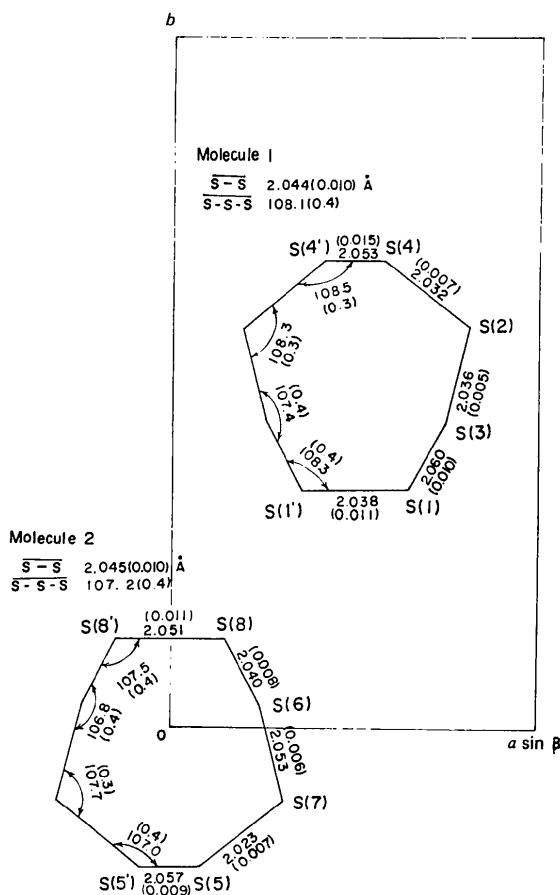


Fig. 3. Intramolecular distances and angles of molecules 1 and 2.

angles and S-S-S-S torsion angles both amount to about 1.0° for the two molecules of $S_8(\gamma)$.

Molecular packing

The molecular packing as viewed along the b and c axes is shown in Figs. 4 and 5 respectively. Each of the two planes of the independent $S_8(\gamma)$ ring makes an angle of 27.5° with the plane normal to the c axis, as shown in Fig. 4. The centre of the $S_8(\gamma)$ is 0.14 and 0.49 Å from the glide plane for molecules 1 and 2 respectively. In Fig. 5 double each of these distances, 0.28 and 0.97 Å, is drawn in with respect to the two $S_8(\gamma)$ rings related by the glide plane.

Intermolecular distances shorter than 3.70 Å, and the van der Waals distances between two sulphur atoms (Pauling, 1960), are given in Table 3. The shortest van der Waals contact is observed between S(4) and S(8'), amounting to 3.45 Å. This value is comparable with 3.49 Å observed in $S_8(\alpha)$ (Caron & Donohue, 1965) or 3.44 Å for monoclinic disordered β -sulphur, $S_8(\beta)$ (Sands, 1965). This short van der Waals contact distance is observed not only in the structure of allotropes of solid sulphur, but also in $S_6(NH)_2$, which is isostructural with $S_8(\gamma)$. In this case the shortest intermolecular S-S distance is 3.48 Å (Grampel & Vos, 1969). The angle S(2)-S(4)-S(4')-S(2') is smaller by about 0.9° than any other torsion angle in molecule 1. For the torsion angle S(7)-S(6)-S(8)-S(8') the situation is the same as in molecule 1. The thermal parameters of the S(4) and S(4') atoms of molecule 1 suggest that these atoms exhibit the smallest thermal vibrations among sulphur atoms. We assume this to be, as suggested, due to the comparatively strong intermolecular bindings between these atoms and the sulphur atoms of the surrounding molecules.

Rigid-body vibration

By transforming the anisotropic temperature parameters of each atom into translational and librational tensors (T and Ω) of the molecules (Cruickshank, 1956), the rigid-body vibrations of the molecules were calculated. In order to compare the results for $S_8(\gamma)$ with those of $S_8(\alpha)$ the principal axes of the moment of inertia of the molecule were defined as shown in Fig. 6. The tensors referred to these molecular axes are shown in Table 5. Translational and librational parameters are listed in Table 6.

Table 5. Tensors of rigid-body vibration of the molecule

	Translation (10^{-2} Å ²)	Libration (deg ²)
Molecule 1	$\begin{pmatrix} 4.2 & 0.0 & 0.2 \\ 0.0 & 5.2 & 0.0 \\ 0.2 & 0.0 & 0.3 \end{pmatrix}$	$\begin{pmatrix} 37 & 0 & 7 \\ 0 & 24 & 0 \\ 7 & 0 & 16 \end{pmatrix}$
Molecule 2	$\begin{pmatrix} 4.1 & 0.0 & -0.3 \\ 0.0 & 4.8 & 0.0 \\ -0.3 & 0.0 & 1.9 \end{pmatrix}$	$\begin{pmatrix} 26 & 0 & 6 \\ 0 & 31 & 0 \\ 6 & 0 & 32 \end{pmatrix}$

Since each S_8 molecule has a twofold rotation axis passing through it, one of the principal axes of T and

Table 6. Principal axes \mathbf{t}_i and ω_i of translational and librational tensors \mathbf{T} and $\mathbf{\Omega}$

a_{ij} and b_{ij} are defined by $\mathbf{t}_i = \sum a_{ij} \mathbf{p}_j$ and $\mathbf{w}_i = \sum b_{ij} \mathbf{p}_j$; \mathbf{p}_j : principal axis of the moment of inertia of the molecule (see Fig. 6)

	Translational (a_{ij})	R.m.s. displacement (\AA)
$S_8(\gamma)$ Molecule 1	$\begin{pmatrix} 0.9986 & 0 & 0.0528 \\ 0 & 1 & 0 \\ -0.0528 & 0 & 0.9986 \end{pmatrix}$	0.206 0.227 0.054
$S_8(\gamma)$ Molecule 2	$\begin{pmatrix} 0.9877 & 0 & 0.1561 \\ 0 & 1 & 0 \\ -0.1561 & 0 & 0.9877 \end{pmatrix}$	0.205 0.219 0.137
$S_8(\alpha)$	$\begin{pmatrix} 0.9987 & 0 & 0.0500 \\ 0 & 1 & 0 \\ -0.0500 & 0 & 0.9987 \end{pmatrix}$	0.213 0.189 0.105
	Librational (b_{ij})	R.m.s. displacement ($^\circ$)
$S_8(\gamma)$ Molecule 1	$\begin{pmatrix} 0.9564 & 0 & 0.2921 \\ 0 & 1 & 0 \\ -0.2921 & 0 & 0.9564 \end{pmatrix}$	6.2 4.9 3.7
$S_8(\gamma)$ Molecule 2	$\begin{pmatrix} 0.8616 & 0 & 0.5076 \\ 0 & 1 & 0 \\ -0.5076 & 0 & 0.8616 \end{pmatrix}$	4.7 5.5 6.0
$S_8(\alpha)$	$\begin{pmatrix} 0.9878 & 0 & 0.1553 \\ 0 & 1 & 0 \\ -0.1553 & 0 & 0.9878 \end{pmatrix}$	5.2 5.6 2.5

$\mathbf{\Omega}$ is restricted to this direction. The other components of \mathbf{T} and $\mathbf{\Omega}$ were found to deviate from the molecular axes by about 2.9° and 16.9° respectively for molecule 1, and by 9.0 and 30.5° respectively for molecule 2. These deviations are larger than the corresponding values for $S_8(\alpha)$, which amount to 2.7 and 8.9° . Such deviations are probably caused by the difference of environments of $S_8(\gamma)$ and $S_8(\alpha)$. The root-mean-square displacements along each principal axis of \mathbf{T} and $\mathbf{\Omega}$ have values comparable to those of $S_8(\alpha)$, as shown in Table 6. Both $S_8(\gamma)$ and $S_8(\alpha)$ show a similar vibration, the translational component T_{33} being normal to the S_8 ring and smaller than T_{11} and T_{22} , components parallel to the ring.

Since the molecules of $S_8(\gamma)$ do not possess a centre of symmetry, the estimation of \mathbf{T} and $\mathbf{\Omega}$ was repeated by taking account of the correlated translation-libration tensors of Schomaker & Trueblood (1968). The results were not significantly different from those obtained by Cruickshank's method. However, the correlation be-

tween the translational component T_{33} and librational components Ω_{11} and Ω_{22} , as well as that between Ω_{33} and T_{11} or T_{22} was found to be not negligible.

Recently Pawley & Rinaldi (1972) have pointed out that the molecules of $S_8(\alpha)$ appear distorted in the crystal structure as the result of a constrained refinement of $S_8(\alpha)$. Exact treatment of this kind for the molecular motion of $S_8(\gamma)$, namely the effect of internal mode upon rigid-body motion, the correlation between translational and librational parameters, *etc.*, will be discussed elsewhere.

The results for the thermal motion of $S_8(\gamma)$ are summarized as follows. First, T_{33} of molecule 1 is smaller than that of molecule 2. Secondly, the deviation of the vibration axes from the molecular axes is larger for molecule 2 than molecule 1. This is expected from the fact that the S(4) or S(4') atom in molecule 1 is rigidly fixed by strong intermolecular interaction with the surrounding molecules as shown in Figs. 4 and 5.

The corrections for bond lengths and angles by the librational motion of the molecules were applied to atomic positional parameters. The shortening effect of the bond lengths has also been recognized for $S_8(\gamma)$. The corrected bond distances and angles are listed in Table 7.

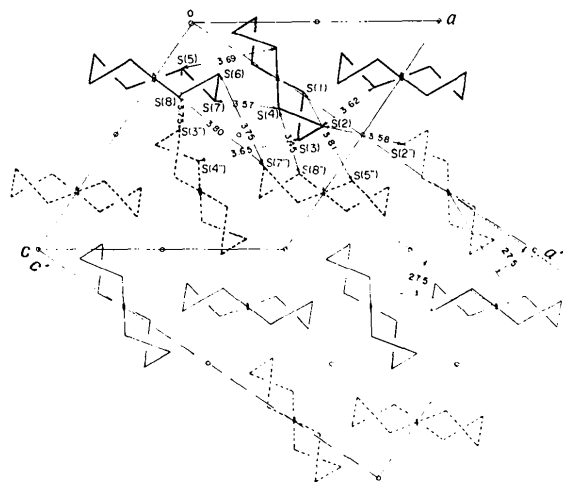


Fig. 4. Molecular packing viewed along the b axis. Molecules drawn with broken lines are related by glide planes. The pseudo-orthorhombic cell is shown with chained lines.

Table 7. Bond distances and angles corrected by librational motion of the molecule

Molecule 1		Molecule 2	
S(1)–S(1')	2.053 (6) \AA	S(5)–S(5')	2.074 (5) \AA
S(1)–S(3)	2.073 (5)	S(5)–S(7)	2.041 (5)
S(3)–S(2)	2.052 (5)	S(7)–S(6)	2.070 (5)
S(2)–S(4)	2.047 (4)	S(6)–S(8)	2.056 (6)
S(4)–S(4')	2.064 (4)	S(8)–S(8')	2.071 (5)
S(1')–S(1)–S(3)	108.1 (2) $^\circ$	S(5')–S(5)–S(7)	107.0 (2) $^\circ$
S(1)–S(3)–S(2)	107.4 (2)	S(5)–S(7)–S(6)	107.7 (2)
S(3)–S(2)–S(4)	108.2 (2)	S(7)–S(6)–S(8)	106.8 (2)
S(2)–S(4)–S(4')	108.4 (2)	S(6)–S(8)–S(8')	107.6 (3)

