

Table 7. *Torsion angles*

	$\tau_1$	$\tau_2$	$\tau_3$	$\tau_4$	$E(\text{kcalmole}^{-1})$
Experimental	-57.82	-167.51	176.92	-83.24	7.77
Theoretical	-64.38	-166.98	181.49	-82.01	7.43

### Hydrogen bonding and crystal packing

A system of hydrogen bonds, involving the chlorine ion and the water oxygen atom, links the molecules in the crystal structure. Each chlorine ion is coordinated by three hydrogen atoms, two from water molecules and one from the protonated nitrogen as illustrated in Fig. 3. Two of these hydrogen atoms were located from difference maps and included in the refinement. The hydrogen-bonded distances are  $\text{N-H}\cdots\text{Cl}^- = 3.124$ ,  $\text{O-H}\cdots\text{Cl}^- = 3.151$ ,  $\text{O-H}'\cdots\text{Cl}^- = 3.171$  Å and the angles  $\text{N-H}\cdots\text{Cl}^- = 170.1^\circ$ ,  $\text{O-H}\cdots\text{Cl}^- = 170.1^\circ$ . The system of hydrogen bonds links centrosymmetrically related molecules into columns about the *a* axis with the side chains interpenetrating between the columns.

Interactions between pairs of molecules were calculated by techniques developed by Motherwell & Isaacs (1972). The strongest interaction of  $-8.79$  kcal mole $^{-1}$  is between molecules related by the *a* glide in Fig. 3.

We thank Dr W.D.S. Motherwell for his interest in the packing problems involved in this work, Dr G.M. Sheldrick for his direct-methods programs, the University of Cambridge Computer Laboratory for computing facilities and the S.R.C. for the provision of the diffractometer.

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## The Crystal Structure of 2,2,4,4-Tetramethyl-3-thio-1,3-cyclobutanedione

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The crystal structure of 2,2,4,4-tetramethyl-3-thio-1,3-cyclobutanedione ( $\text{C}_8\text{H}_{12}\text{OS}$ ) has been determined from three-dimensional X-ray diffraction data. The crystals are orthorhombic, space group *Pnma*,  $Z=4$ , with cell dimensions  $a=13.545$  (2),  $b=10.055$  (1), and  $c=6.934$  (3) Å. Data were collected manually on a diffractometer using zirconium-filtered  $\text{Mo K}\alpha$  radiation. 949 independent reflections were observed. The structure was solved by reiterative applications of Sayre's equation and refined by full-matrix least-squares calculation to yield a final *R* value of 0.071. The results indicate a slightly disordered structure with a planar cyclobutane ring.

### Introduction

The simple derivatives of cyclobutane have been studied extensively in the solid state (Table 3, Shirrell &

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Williams, 1973a). These compounds can exist in either planar or puckered conformations. Although the origin of these conformational differences among cyclobutanes is not very well understood, Bohn & Tai (1970)

have suggested that the planar conformations are due to a dominance of crystal packing forces over intramolecular forces.

To gain more information about the nature of these forces that influence the conformation of the cyclobutane ring in the solid state, we have initiated a study of the 1,3-double-bonded derivatives of 2,2,4,4-tetramethylcyclobutane. Previously, the structure of 2,2,4,4-tetramethyl-1,3-cyclobutanedithione has been reported (Shirrell & Williams, 1973*a*).

The substituted thione derivatives of cyclobutane are also of interest in that they contain carbon-sulfur double bonds but show no tendency to dimerize or polymerize at room temperature. We have recently reported the structure of a complex spiro heterocyclic compound which contains these unusual carbon-sulfur double bonds (Shirrell & Williams, 1973*b*).

### Experimental

A sample of this compound was kindly provided by Dr E. U. Elam (Elam & Davis, 1967) of Tennessee Eastman Kodak Company, Kingsport, Tennessee 37662, U.S.A. The crystals used in this study were obtained by allowing a solution, containing the title compound dissolved in a 1:1 mixture of hexane and ethanol, to evaporate very slowly while being maintained at a temperature of  $-16^{\circ}\text{C}$ . Crystallization using many other conditions and solvents was attempted but in each case single crystals could not be obtained.

Approximate cell dimensions, systematic absences ( $hk0:h$  odd;  $0kl:k+l$  odd), and orthorhombic symmetry were obtained from oscillation and Weissenberg photographs taken with nickel-filtered  $\text{Cu } K\alpha$  radiation. The photographic data were taken using two crystals; one was rotated around the  $b$  axis and the other around the  $c$  axis. The possible space groups are  $Pna_2$  and  $Pnma$ . The centrosymmetric space group,  $Pnma$ , was initially chosen on the basis of a statistical analysis of the data and later confirmed by the successful structure determination. This space group requires that

the cyclobutane ring and the sulfur and oxygen atoms lie on a crystallographic mirror plane. There is a possibility of statistical disordering by interchange of the oxygen and sulfur atoms, which are both on the mirror plane. The possibility of further disordering in the form of a nonplanar cyclobutane ring was considered but rejected (see below).

The crystal used for accurate lattice constant and intensity data was a bright-red polyhedron of approximate dimensions  $0.25 \times 0.25 \times 0.30$  mm. It was mounted in a Lindemann capillary tube with the  $0.30$  mm axis ( $c$ ) parallel to the walls of the capillary tube. This compound is extremely volatile. During exposure to the X-ray beam, the crystals would either sublime and reform on the walls of the capillary tube or they would sublime sufficiently to allow them to become misoriented. This problem was overcome by taking the data at slightly below room temperature ( $15^{\circ}\text{C}$ ).

Using vanadium-filtered  $\text{Cr } K\alpha$  radiation ( $\lambda = 2.2916$  Å), 12 reflection angles with high  $2\theta$  values were accurately measured. The lattice constants were determined by a least-squares fit (Williams, 1964) to these data using the extrapolation function of Nelson & Riley (1945). The values obtained are  $a = 13.545(2)$ ,  $b = 10.055(1)$ , and  $c = 6.934(3)$  Å. The volume of the unit cell is  $944.38$  Å<sup>3</sup>, and the calculated density for four molecules of  $\text{C}_8\text{H}_{12}\text{OS}$  (F.W. 156.26) is  $1.10$  g  $\text{cm}^{-3}$ . The observed density, measured by flotation in an aqueous solution of potassium iodide, is  $1.09$  g  $\text{cm}^{-3}$ .

The intensities of 949 independent reflections, up to  $2\theta = 50^{\circ}$ , were measured using zirconium-filtered  $\text{Mo } K\alpha$  radiation ( $\lambda = 0.7107$  Å). Intensities were measured using the  $\theta$ - $2\theta$  scan technique with a scan rate of  $2^{\circ} \text{ min}^{-1}$ . In order to decrease the time of exposure of the crystal to the X-ray beam, the background was determined as a function of crystal setting. The take-off angle was  $3.0^{\circ}$ , and the receiving slit was  $4 \times 4$  mm. A check of the intensities showed them to remain constant within statistical and instrumental fluctuations during the data-collection period. The Lorentz

Table 1. Final atomic positions and anisotropic thermal vibrational parameters ( $\times 10^4$ ) and their estimated standard deviations

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

	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
S(1)	-2550 (1)	2500	-3315 (2)	56 (1)	124 (2)	215 (3)	0	1 (1)	0
O(2)	51 (2)	2500	1567 (4)	54 (2)	89 (4)	192 (8)	0	31 (3)	0
C(3)	-1728 (3)	2500	-1772 (7)	50 (5)	70 (5)	174 (11)	0	13 (5)	0
C(4)	-1734 (3)	2500	458 (7)	42 (3)	71 (5)	183 (12)	0	18 (4)	0
C(5)	-618 (3)	2500	326 (7)	45 (3)	77 (6)	181 (12)	0	22 (5)	0
C(6)	580 (4)	2500	-1865 (8)	59 (3)	69 (5)	217 (13)	0	1 (5)	0
C(7)	-2135 (2)	3804 (4)	1295 (5)	51 (2)	103 (4)	178 (8)	1 (3)	9 (3)	-16 (5)
H(7a)	-2647	3686	2479				Same as C(7)		
H(7b)	-2493	4321	170				Same as C(7)		
H(7c)	-1539	4362	1823				Same as C(7)		
C(8)	-194 (2)	3808 (4)	-2620 (5)	45 (2)	107 (4)	220 (8)	-15 (3)	7 (3)	9 (5)
H(8a)	320	3581	-3707				Same as C(8)		
H(8b)	137	4288	-1434				Same as C(8)		
H(8c)	-806	4330	-3147				Same as C(8)		

and polarization corrections were made in the usual manner. For Mo  $K\alpha$  radiation, the linear absorption coefficient for this compound is  $2.62 \text{ cm}^{-1}$ . No absorption correction was made.

The standard deviation of each intensity measurement was estimated by the formula:

$$\sigma^2(I) + CT + CB + (0.05CT)^2 + (0.05CB)^2$$

where  $CT$  is the total counts and  $CB$  is the background counts. The error in the structure factor,  $\sigma(F_o)$ , was calculated from  $\sigma(I)$  by the finite-difference method (Williams & Rundle, 1964). If  $CT < CB$  then  $F_o$  was set equal to zero. In the least-squares refinement the weight of each reflection was taken as  $1/[\sigma(F_o)]^2$ .

### Structural determination

The structure factors were scaled by Wilson's (1942) method and were converted to normalized structure factors by *FAME* (Dewar, 1970) for use in the phase determination. 133 of these reflections with  $E \geq 1.5$  were used in the computer program of Long (1965). This program iteratively applies the  $\sum_2$  equation to determine sign relationships. The signs of three reflections with large  $E$  were chosen as positive to determine the origin. Four more reflections with large  $E$  of undetermined sign were chosen to complete the starting set, from which the program generates the 16 possible combinations of sets. The choice of the correct set was unambiguous; the correct set had the largest consistency index, 0.937, and converged in the fewest iterations, 5. All 133 signs were determined, giving an  $E$  map for which all of the nonhydrogen atoms appeared as the eight highest peaks.

Isotropic least-squares refinement of these positions using a modification of the full-matrix program of Busing, Martin & Levy (1962) resulted in an  $R$  value of 0.144 for all data. The function minimized in the least-squares calculations was  $\sum(F_o - |F_c|/K)^2/\sigma^2(F_o)$ . The scattering factors of Hanson, Herman, Lea & Skillman (1964) were used for sulfur, oxygen, and carbon.

After several least-squares cycles, using anisotropic temperature factors, the  $R$  value was 0.116. A difference Fourier map then revealed the 6 hydrogen atoms. The anisotropic temperature factors for all hydrogen atoms were set equal to those of the carbons to which they were bonded. No attempt was made to vary their coordinates or temperature factors. The scattering factors of Stewart, Davidson & Simpson (1965) were used for hydrogen. Four cycles of anisotropic full-matrix least-squares refinement were necessary before all parameters shifted less than  $0.05\sigma$  and the final weighted  $R$  value was 0.071. A difference Fourier map was prepared from the final model. The values on this map varied in an apparently random fashion from 0.35 to  $-0.06 \text{ e } \text{Å}^{-3}$ .

The final atomic parameters are listed in Table 1

together with their estimated standard deviations. A list of the calculated and observed structure factors is given in Table 2.

Refinement was also attempted in the noncentrosymmetric space group  $Pna2_1$ . This space group would allow a non planar ring. Anisotropic least-squares refinement for all atoms resulted in a weighted  $R$  value of 0.080. The hydrogen atoms were treated as in the  $Pnma$  refinement. Some of the resulting C-C bond distances were unreasonable; for example C(4)-C(7') was 1.64 Å. Using the Hamilton (1964) statistical test, the  $Pna2_1$  refinement can be rejected as being correct at the 0.995 significance level. We conclude that  $Pnma$  is the correct space group, and that the cyclobutane ring is planar. In the  $Pnma$  refinement, the observed amplitudes of thermal motion perpendicular to the ring are normal; this would not be expected if the structure consisted of a statistical superposition of nonplanar cyclobutane rings.

Table 2. *The observed and calculated structure factors*

The values of  $|kF_o|$  and  $F_c$  are given.

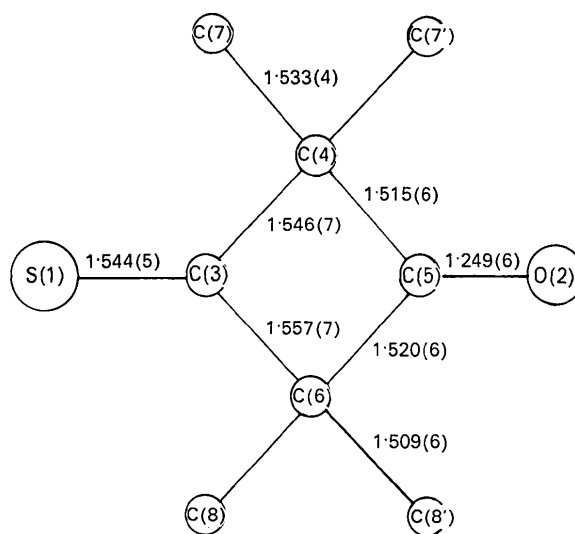


Fig. 1. The uncorrected bond distances (Å) and their estimated standard deviations.

## Discussion

The bond distances, not corrected for thermal motion, are given in Fig. 1 and the bond angles in Table 3.

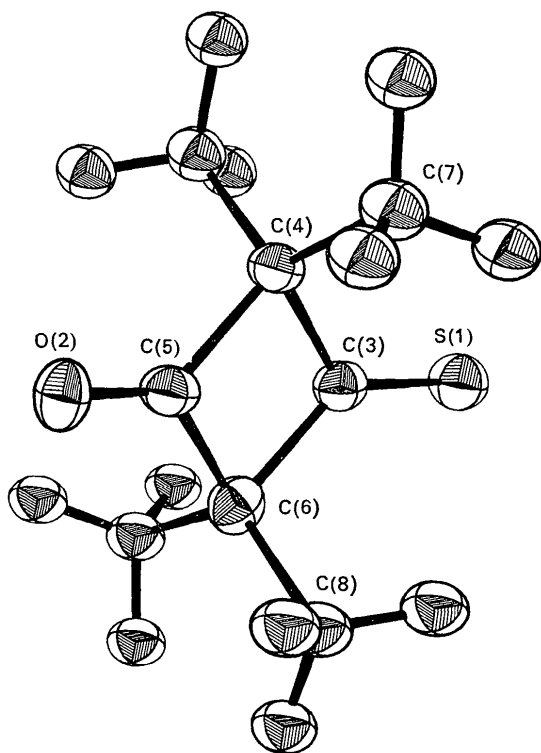


Fig. 2. The molecular structure. The thermal ellipsoids (Johnson, 1965) enclose a probability density of 0.30.

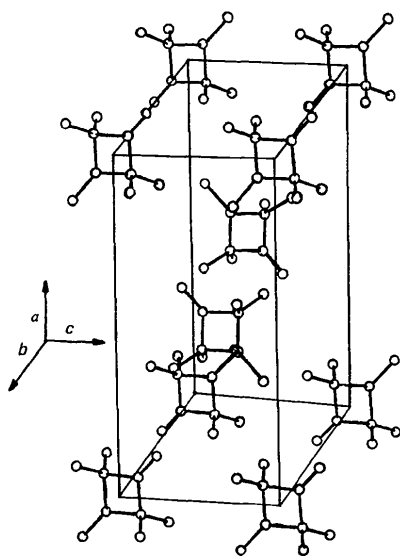


Fig. 3. The packing structure. To aid in the interpretation of the molecular packing, the origin of the unit cell has been shifted to the center of a molecule.

The four-membered ring carbons are coplanar, lying on a crystallographic mirror plane. The bond distances were corrected for the effect of thermal motion according to the rigid-molecule model of Cruickshank (1961). The screw tensor was assumed to be near zero. Table 4 shows the thermally corrected bond distances. The orientation of the thermal ellipsoids, as plotted by the computer program of Johnson (1965), is given by Fig. 2.

Table 3. The bond angles ( $^{\circ}$ ) and their estimated standard deviations

C(1)-C(3)-C(4)	133.6 (4)	C(2)-C(5)-C(4)	133.0 (4)
C(1)-C(3)-C(6)	133.8 (4)	C(2)-C(5)-C(6)	131.6 (4)
C(4)-C(3)-C(6)	92.7 (4)	C(4)-C(5)-C(6)	95.4 (4)
C(3)-C(4)-C(5)	86.3 (4)	C(3)-C(6)-C(5)	85.7 (4)
C(3)-C(4)-C(7)	112.4 (2)	C(3)-C(6)-C(8)	111.1 (3)
C(5)-C(4)-C(7)	112.4 (2)	C(5)-C(6)-C(8)	111.0 (3)
C(7)-C(4)-C(7')	121.3 (2)	C(8)-C(6)-C(8')	117.5 (3)

Table 4. The thermally corrected bond distances ( $\text{\AA}$ )

S(1)-C(3)	1.547 (5)	C(4)-C(5)	1.518 (6)
O(2)-C(5)	1.251 (6)	C(4)-C(7)	1.536 (4)
C(3)-C(4)	1.549 (7)	C(5)-C(6)	1.523 (6)
C(3)-C(6)	1.559 (7)	C(6)-C(8)	1.512 (6)

An analysis of the C=S and the C=O bond lengths would suggest that the structure is partially disordered. The uncorrected thione bond length in 2,2,4,4-tetramethyl-1,3-cyclobutanedithione (Shirrell & Williams, 1973a) is 1.599(7)  $\text{\AA}$ . The thione bond length in this structure is 1.544(5)  $\text{\AA}$ , approximately 11 $\sigma$  smaller than that observed in the corresponding dithione structure. Similarly, the uncorrected dione bond length in 2,2,4,4-tetramethyl-1,3-cyclobutanedione (Shirrell & Williams, 1974) is 1.188(2)  $\text{\AA}$ . The ketone bond length in this structure is 1.249(6)  $\text{\AA}$ , approximately 10 $\sigma$  larger than that observed in the corresponding dione structure.

In an attempt to analyze this disorder, a hypothetical model of the disordered structure was calculated based on the following assumptions: (1) the ring carbons which were bonded to the methyl carbons were located correctly; (2) the thione half of the molecule could be determined based on the dithione structure (Shirrell & Williams, 1973a); (3) the dione half of the molecule could be determined based on the dione structure (Shirrell & Williams, 1974). Using the atomic locations based on these and the temperature factors in Table 1 (for each type of atom), least-squares analyses were conducted with different occupancy factors. The scale factor was the only variable. This attempt failed as there was no significant difference in the *R* values up to a 10% disordered structure. In the final difference Fourier map, these disordered atomic positions had slightly positive electron densities which were within the background noise level.

Fig. 2 shows the observed approximately eclipsed conformation of the *gem* methyl hydrogens, corre-

sponding to  $H \cdots H$  nonbonded contacts of 3.2 and 3.4 Å. The shortest transannular  $H \cdots H$  contact is 2.39 Å. The average C–H bond distance, uncorrected for thermal motion, is 1.056 Å; the average H–C–H bond angle is  $110.6^\circ$ .

The internal bond angles and bond lengths are consistent with those previously reported for cyclobutane ring compounds. It is interesting to note that the C–C bonds in the ring on the dione side of the molecule are significantly shorter than those on the thione side. The 1,3-transannular distance,  $C(3)–C(5) = 2.092(7)$  Å, is interesting because of the possibility of  $\pi$ -interaction between the  $p$  orbitals of the 1,3-transannular carbons. The possibility of such an interaction has been discussed by a number of authors (Caserio & Roberts, 1958; Silversmith & Roberts, 1958; Smutny, Caserio & Roberts, 1960; Kosower, 1963; Ferguson & Nnadi, 1965). In the optical absorption spectra of 2,2,4,4-tetramethyl-1,3-cyclobutanedione, the  $n \rightarrow \pi^*$  absorption band appears to be split into two components by the 1,3-transannular  $\pi$  interaction, whereas in the dithione compound there is no such splitting (Ballard & Park, 1970).

With respect to the 1,3-transannular  $\pi$ -interaction, the dithione should not be much different from the dione since the overlapping orbitals are both carbon  $2p$  and since the transannular distances are almost identical. Shirrell & Williams (1973a) have shown that in the dione there is much less steric hindrance toward ring vibrational puckering in solution than in the thione compound. This ring puckering in the dione could result in  $\pi$  interaction between the  $p$  orbitals in the gaseous and liquid states thus leading to the observed spectra. It would be interesting to see if the ring puckering in the mixed thione–ketone compound, the subject of this investigation, would lead to  $\pi$  interaction between the  $p$  orbitals and the corresponding splitting of the spectra. However, a literature search revealed that there exists no detailed published spectral analysis of this compound.

The cyclobutane ring lies on the mirror plane at  $y=0.25$ , implying a planar ring. This is the first simple cyclobutane compound which is known to be planar in the solid state, but does not contain a centrosymmetric arrangement of substituents. However, by analysis of the intramolecular  $CH_3 \cdots O$  and  $CH_3 \cdots S$  interactions one would have supposed the cyclobutane ring to be planar. A simple rule has been postulated (Margulis, 1969; Adman & Margulis, 1969) to aid in predicting the conformation of simple cyclobutane rings without endocyclic or exocyclic double bonds: if the ring is not centrosymmetrically substituted, the ring will be planar.

The packing of the molecule is shown in Fig. 3. The symmetry-related molecules pack in sheets at  $y=0.25$  and  $y=0.75$ . In each sheet the molecules pack in a face-centered configuration. A central molecule is surrounded by eight other molecules, each of which is rotated  $90^\circ$  from the central molecule. The sheet

at  $y=0.25$  is rotated  $180^\circ$  from the adjacent sheets above and below it. The intermolecular distances all appear to be of normal van der Waals type.

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