

This dissertation has been  
microfilmed exactly as received

69-19,297

HERDKLOTZ, John Key, 1943-  
THE CRYSTAL STRUCTURE OF 4-METHYLTHIO-  
MORPHOLINE-1,1-DIOXIDE.

Rice University, Ph.D., 1969  
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

RICE UNIVERSITY

The Crystal Structure  
of  
4-methylthiomorpholine-1,1-dioxide

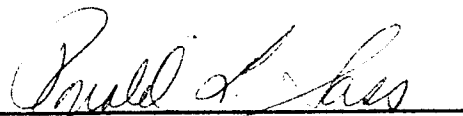
by

John Key Herdklotz

A THESIS SUBMITTED  
IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF

Doctor of Philosophy

Thesis Director's signature:



Paul L. Herd

Houston, Texas

August, 1968

## ACKNOWLEDGEMENTS

The author would like to express his sincere gratitude to Dr. R. L. Sass, whose interest and assistance in this work was invaluable.

The author also wishes to thank:

James W. Edmonds, Maurice Dyke and C. Travis Presley for their assistance with the computer programs;

The Robert A. Welch Foundation for its support of this work;

The Common Research Computer Facility which is supported by United States Public Health Service Grant FR-00254 for the use of its 7094 computer;

The financial support of a National Defense Graduate Fellowship.

Also, the author wishes to thank Kathie Herdklotz for her encouragement.

## TABLE OF CONTENTS

---

INTRODUCTION	1
EXPERIMENTAL	3
STRUCTURE DETERMINATION	7
THREE-DIMENSIONAL REFINEMENT	14
DISCUSSION	18
REFERENCES	20

LIST OF FIGURES

<u>FIGURE No.</u>	<u>TITLE</u>	<u>FOLLOWING PAGE</u>
1	Space Group $P2_1/c$	4
2	Plane Group p2	8
3	$P(u,w)$ Patterson Projection	8
4	[010] Superposition Projection	13
5	[010] Electron Density Projection	13
6	[010] Composite of Three-Dimensional Difference Map	17
7*	Drawing of the Molecule 4-methylthiomorpholine-1,1-dioxide	19
8	Dimensions of the Molecule 4-methylthiomorpholine-1,1-dioxide	19
9	[010] Projection of the Unit Cell	20
10*	Crystal Packing Diagram	20

\*Denotes Stereoscopic Drawings

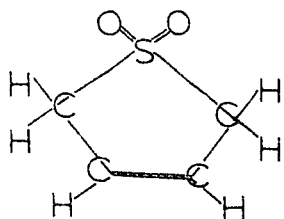
## LIST OF TABLES

<u>TABLE No.</u>		<u>FOLLOWING PAGE</u>
1	Calculated and Observed Structure Factors	17
2	Final Coordinates and Anisotropic Temperature Factors for Non-hydrogen Atoms	17
3	Final Coordinates and Isotropic Temperature Factors for Hydrogen Atoms	17
4	Bond Distances and Angles Involving Non-hydrogen Atoms	19
5	Bond Distances and Angles Involving Hydrogen Atoms	19
6	Description of Thermal Ellipsoids for Non-hydrogen Atoms	19
7	Comparison of Bond Distances and Valency Angles Involving the Sulfur Atom with Related Compounds	19
8	Intermolecular Contacts Less Than 4.0 Å	20

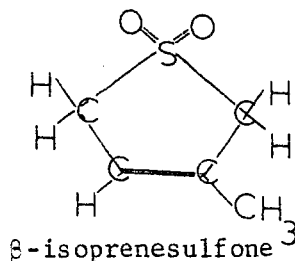
## INTRODUCTION

For the past several years, this laboratory has been investigating the geometry of the sulfone group in small ring systems. This study was initiated after the interesting results obtained by Desiderato and Sass in the determination of the crystal structure of cis-2-butene episulfone.<sup>1</sup> It was found that the ring closing carbon-carbon bond was considerably longer (1.58 Å) than the normally accepted value (1.48 Å).<sup>2</sup> They also observed the sulfur-carbon bond distance to be 1.75 Å, which is somewhat shorter than the value of 1.81 Å reported in the earlier literature.<sup>3</sup> A literature search for similar results revealed that few heterocyclic sulfur systems had been studied.

These results prompted Kronfeld and Sass to undertake the study of dibenzothiophine sulfone.<sup>4</sup> The sulfur-carbon bond distances were determined to be 1.74 Å, in agreement with the study of Desiderato and Sass. Another study by Yoo and Sass concerned the structure determination of butadiensulfone.<sup>5</sup> A similar compound,  $\beta$ -isoprenesulfone, had previously been studied by Jeffrey.<sup>6</sup>



Butadiensulfone



$\beta$ -isoprenesulfone

Yoo and Sass found the carbon-carbon double bond distance to be 1.26 Å while Jeffrey found the corresponding bond distance in  $\beta$ -isoprenesulfone to be

1.47 Å. Butadienesulfone, simultaneous with the study of Yoo and Sass, was studied by Sands.<sup>7</sup> They determined the carbon-carbon double bond distance to be 1.29 Å. As yet, the discrepancy in this bond length is unexplained.

The similarity between 4-methylthiomorpholine-1,1-dioxide and the aforementioned molecules is the presence of the sulfone (SO<sub>2</sub>) group in the ring system. However, being a six membered ring, it is a less strained system than those previously studied. Also, unlike the previous studies, the ring system in 4-methylthiomorpholine-1,1-dioxide contains a nitrogen atom. The structure analysis was carried out in order to determine the geometry of the sulfone group in a six membered ring containing an atom other than sulfur and carbon.



## EXPERIMENTAL

A sample of 4-methylthiomorpholine-1,1-dioxide was obtained from the Aldrich Chemical Company. As received, the crystals were unsuitable for study.

Recrystallization from the melt by sublimation onto a cool surface yielded clear, colorless crystals which were flat in shape. Crystals of more uniform dimensions were obtained from slow evaporation of an anhydrous ether solution at a temperature of 40° F. The crystals obtained from the ether solution were clear, colorless, prismatic in habit and averaged 0.15mm in diameter. The crystals obtained from the ether solution were used in the structure analysis.

In the process of aligning a crystal for determination of the cell constants and space group, it was observed that the crystals sublimed at room temperature. It was therefore necessary to seal the crystals in glass capillaries for all diffraction work.

On the basis of equi-inclination Weissenberg photographs, the Laue symmetry was shown to be  $2/m$ . The systematic absences were

$h0\ell$  absent for  $\ell$  odd

$0k0$  absent for  $k$  odd

These systematic absences uniquely determine the space group to be  $P2_1/c$ . Figure 1 contains two views of this space group.

The  $a$  and  $c$  cell constants and the  $\beta$  angle were measured manually

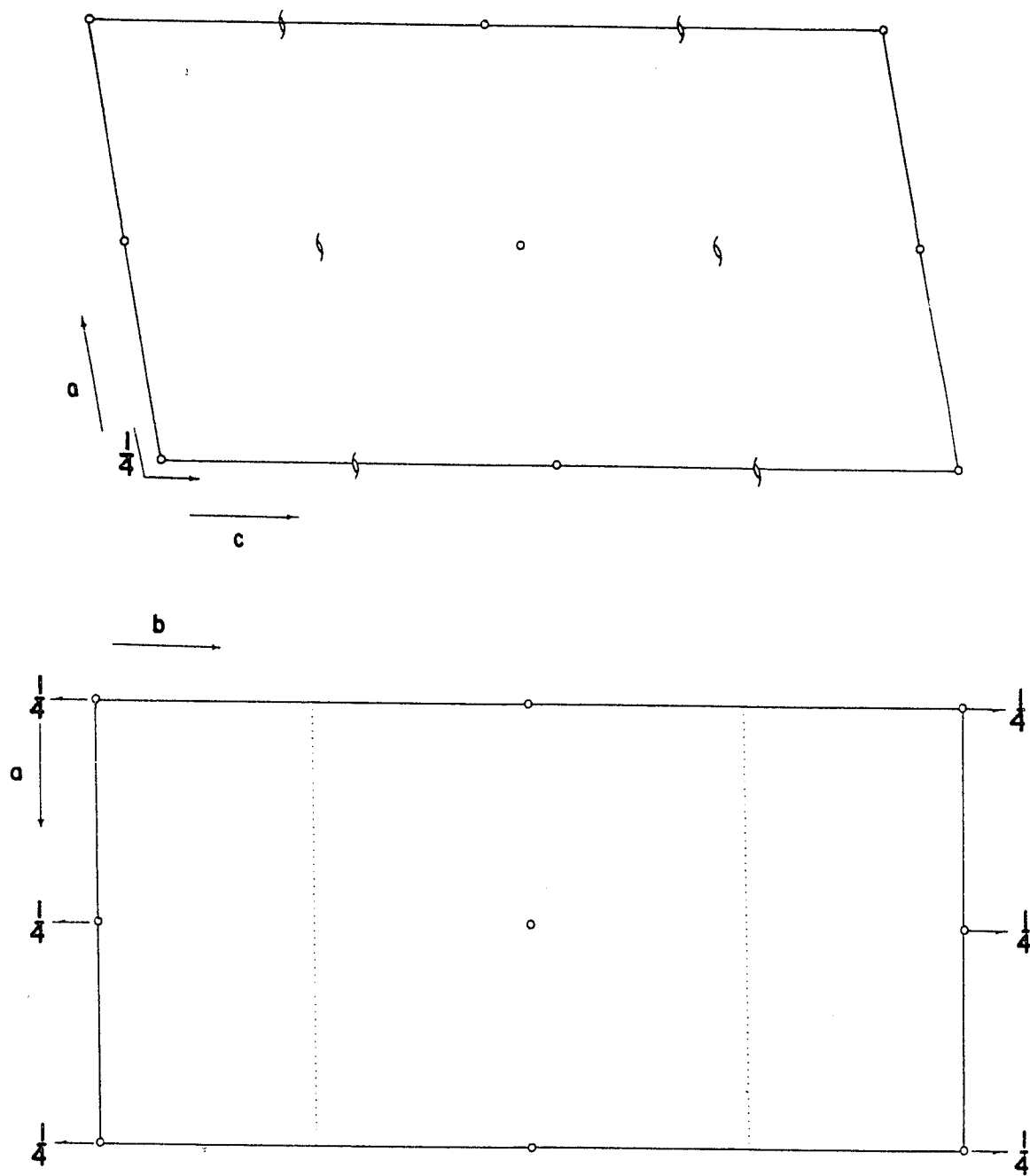


Figure 1. Space Group  $P2_1/c$

on a Phillips PAILRED diffractometer. The b cell constant was determined from sodium chloride calibrated rotation photographs.

The method employed in measuring the a and c cell constants was that of omega differences.<sup>8</sup> The omega angular displacements about the rotation axis which are necessary to record the diffraction maxima along a row of the reciprocal lattice were measured. Monochromatized Molybdenum K<sub>α</sub> radiation (α<sub>1</sub>, λ = 0.70926 Å; α<sub>2</sub>, λ = 0.71354 Å) was used in taking measurements.

The set of omega angular displacements were then substituted into the expression

$$\frac{\lambda n}{2d} = \sin(\omega + \alpha),$$

where

α = phase angle

n = diffraction order

λ = radiation wavelength

1/d = reciprocal lattice spacing

By minimizing the sum of the squares of the residuals in the phase angles, the best values of 1/d were chosen, from which a and c were calculated.

In determining the b cell constant, CuK<sub>α</sub> radiation (λ = 1.54051 Å) was employed. The camera radius was calibrated by superimposing NaCl (a<sub>0</sub> = 5.637 Å) powder patterns onto the rotation photographs from which

measurements were made.

The results of these measurements and their estimated standard deviations are:

$$a = 11.439 (4) \text{ \AA},$$

$$b = 5.88 (1) \text{ \AA},$$

$$c = 11.090 (3) \text{ \AA},$$

$$\beta = 98.566^\circ (6).$$

The density of 4-methylthiomorpholine-1,1-dioxide was measured by flotation in a mixture of ortho- and para-dichlorobenzene. The measured density was 1.340g/cc. This value agrees with the calculated value of 1.341g/cc assuming four molecules per unit cell. Since the space group  $P2_1/c$  has fourfold general positions, it was apparent that the asymmetric unit consisted of one molecule of 4-methylthiomorpholine-1,1-dioxide.

Two methods of recording intensities were employed. A set of  $h0\ell$  data was collected using multiple film techniques and a set of three-dimensional data ( $h, k = 0-4, \ell$ ) using a Phillips PAILRED diffractometer.

The  $h0\ell$  intensity record was collected on Kodak No-Screen Medical X-ray film using  $\text{CuK}_\alpha$  radiation. The intensities were estimated visually by comparison with a standard intensity strip. This set of intensities was corrected for Lorentz, polarization and Tunell factors.<sup>9</sup>

Three-dimensional data were collected using the Phillips PAILRED diffractometer employing equi-inclination geometry. One crystal,

mounted along the b crystallographic axis, was used throughout the experiment. All data were collected using quartz monochromatized (from the [111] face) Molybdenum  $K_{\alpha}$  radiation. During the measurement of a diffraction maxima, the counter remained fixed while the crystal was rotated through a small range in omega (ie., about the rotation axis, which in this case was the b axis). A  $1.5^{\circ}$  scan range in omega and a  $1^{\circ}$  per minute scan rate were used in the data collection. Background measurements of 0.4 minutes were made at the beginning and end of each scan. All intensities for which the relative counting statistical error,  $\Delta I/I$ , exceeded 40% of the measured intensity were rejected.

$$\frac{\Delta I}{I} = \frac{(T + t^2 B)^{\frac{1}{2}}}{T - tB}$$

where

T = total number of counts recorded in a scan,

t = ratio of scan time to time spent counting background,

B = total number of background counts.

All intensities measured on the PAILRED were corrected for Lorentz, polarization and Tunell factors.<sup>10</sup>

The maximum value of the absorption coefficient multiplied by the radius of the crystal was 0.36 and no absorption corrections were made. Other corrections, such as extinction, were not attempted.

## STRUCTURE DETERMINATION

Before discussing in detail the structure determination, it seems appropriate to give a brief account as to the nature of the Patterson function, since solution of the [010] projection of this function was of major importance. The Patterson function is a map of all interatomic distances in an electron density function translated to a common origin. The magnitude of the peaks in a Patterson map will be proportional to the product of the atomic numbers of the atoms involved. When a molecule is studied which contains one atom which has an atomic number considerably larger than the other atoms, it can be expected that vectors between this atom and its symmetry equivalent atoms will be prominent in the Patterson map. In projection, the prominence of such peaks depends on there being a minimum of overlap. It is usually possible to solve a Patterson projection if the projection axis is of the order of 6 Å or less. The b axis in 4-methylthiomorpholine-1,1-dioxide meets this requirement.

From the first available data, the  $h0l$  data collected by film methods, the Patterson projection  $P(u,w)$  was synthesized. The plane group for the [010] projection of the Patterson space group  $P2/m$  is  $p2$ , and is shown in Figure 2.

The ends of vectors between centrosymmetrically related atoms will lie at the positions  $(2x,2z)$  in the projection  $P(u,w)$ . Such a sulfur-sulfur vector was located. Figure 3 shows the Patterson projection  $P(u,w)$  for 4-methylthiomorpholine-1,1-dioxide with the location of the sulfur-

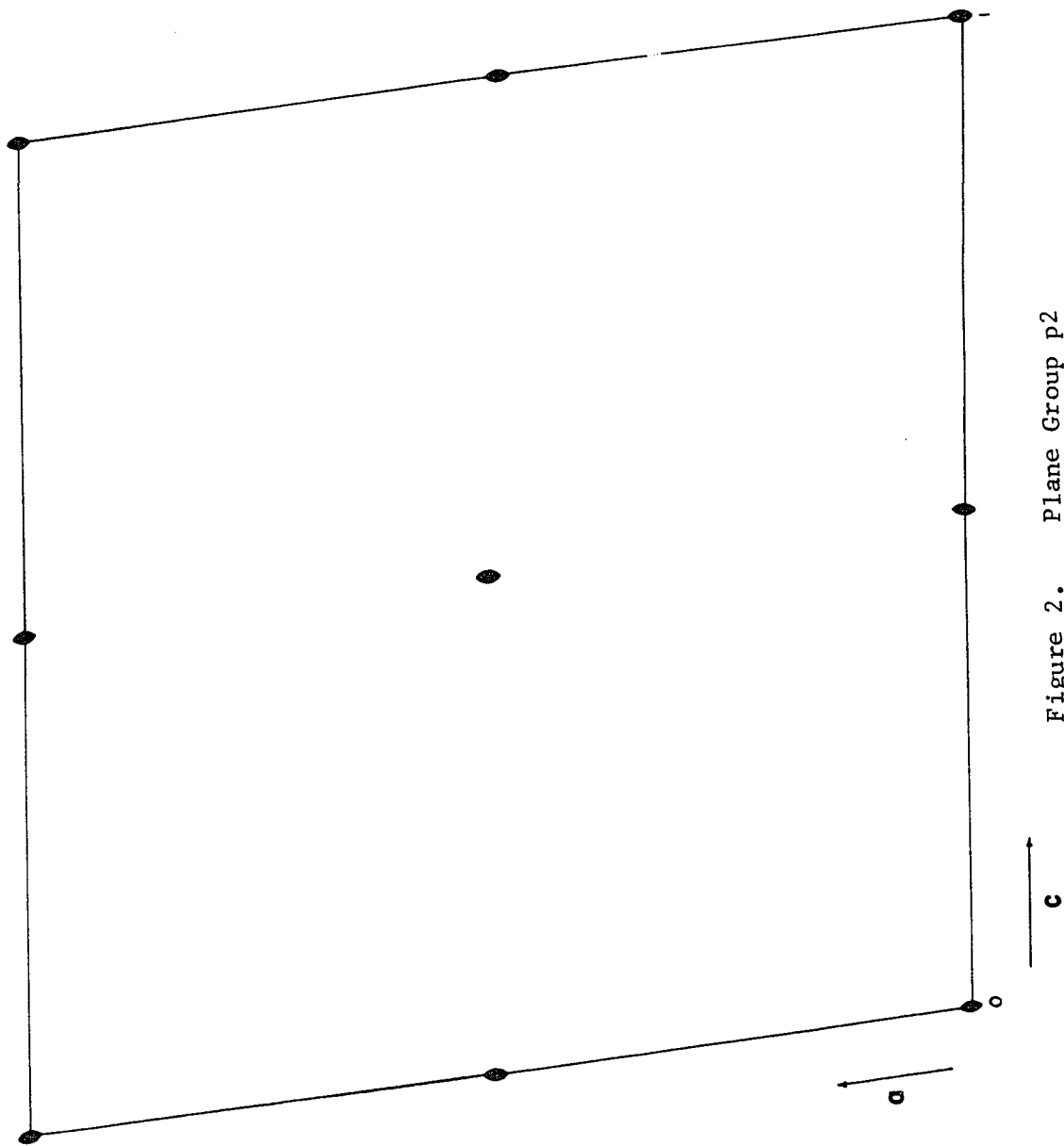


Figure 2. Plane Group p2

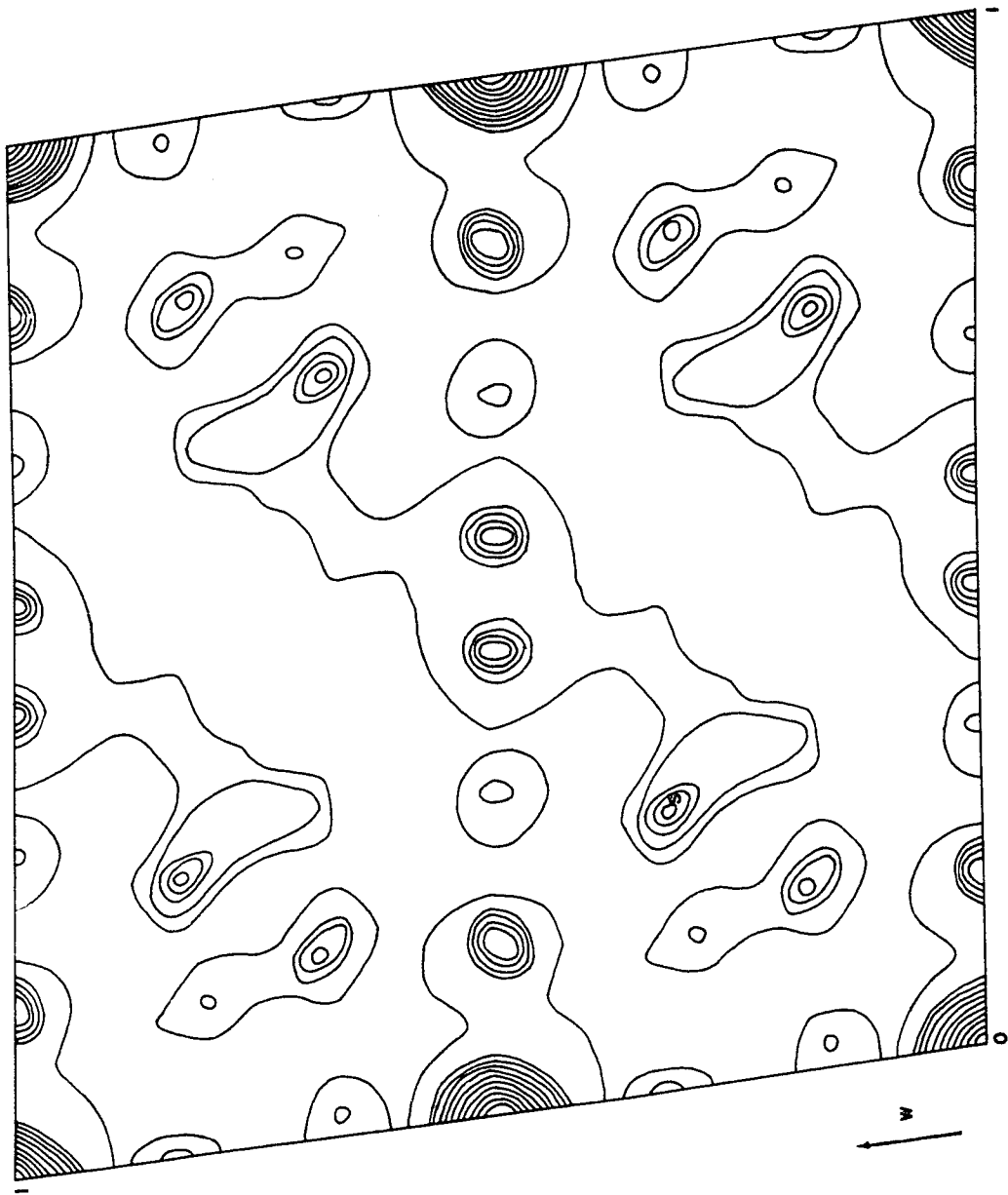


Figure 3. Patterson Projection,  $P(u,w)$



sulfur peak indicated. Although there are other peaks of similar magnitude in the Patterson map, they were eliminated as possible sulfur-sulfur interactions as they lie too close to centers of symmetry to give reasonable sulfur-sulfur interatomic distances as calculated from van der Waals radii.<sup>11</sup>

All Patterson maps necessarily contain an image of the molecule around the origin. It was not possible to resolve the image of the 4-methylthiomorpholine-1,1-dioxide molecule in the projection P(u,w). As a result the orientation of the molecule in the unit cell, at this point in the analysis, remained undetermined.

From the projection P(u,w) it was not possible to determine the x and z coordinates of any other atoms. To locate the other atoms, an image of the molecule was sought using the "Vector Convergence Method" of Beevers and Robertson.<sup>12</sup> The method involved the superposition of four Patterson maps by placing the origin of the Patterson map, P(u,w), on the four sulfur atom positions. The Patterson function translated in this manner will yield coincidences at the atomic positions.

To accomplish the desired translations of the Patterson function, use was made of function convolution theory.<sup>13</sup> To derive the desired superposition function, let  $p(\underline{r})$  and  $q(\underline{r})$  be functions in real space, and their transforms in reciprocal space be  $G_p(\underline{S})$  and  $G_q(\underline{S})$  respectively. The Fourier transform of the product of  $G_p(\underline{S})$  and  $G_q(\underline{S})$  is given by

$$\int G_p(\underline{S}) \cdot G_q(\underline{S}) \exp[2\pi i \underline{r} \cdot \underline{S}] dV_{\underline{S}} \quad (1)$$

From the definition of the Fourier transform of  $p(\underline{r})$ ,

$$G_p(\underline{S}) = \int p(\underline{r}') \exp[-2\pi i \underline{r}' \cdot \underline{S}] dV_{\underline{r}'},$$

If substitution of this expression for  $G_p(\underline{S})$  is made in (I),

$$\begin{aligned} \int G_q(\underline{S}) \left[ \int p(\underline{r}') \exp\{-2\pi i \underline{r}' \cdot \underline{S}\} dV_{\underline{r}'} \right] \exp[2\pi i \underline{r} \cdot \underline{S}] dV_{\underline{S}}, \\ = \int p(\underline{r}') \left[ \int G_q(\underline{S}) \exp\{2\pi i (\underline{r} - \underline{r}') \cdot \underline{S}\} dV_{\underline{S}} \right] dV_{\underline{r}'}, \\ = \int p(\underline{r}') \cdot q(\underline{r} - \underline{r}') dV_{\underline{r}'}, \\ = \widehat{pq}(\underline{r}). \end{aligned}$$

This operation is known as convolution and the symbol  $\widehat{pq}(\underline{r})$  designates the convolution of the function  $p(\underline{r})$  with the function  $q(\underline{r})$ .

To make use of this operation in constructing the superposition function, the function  $p(\underline{r})$  is designated to be a peak function. A peak function has the property of its value being zero everywhere except at specified points, and at these points its value is infinite, but with a finite integrated volume under the peak. The peak function can be identified with the electron density arising from the placement of the sulfur atoms at the four known sulfur atom locations. For this electron density to approximate a peak function, the sulfur atoms must be treated as point scatterers. Therefore, the electron density is computed using scattering factors for the sulfur atoms which do not vary with  $\sin \theta/\lambda$ .

$$\begin{aligned} p(\underline{r}) &= \text{infinity, if } \underline{r} = \underline{r}_s, \\ p(\underline{r}) &= 0, \text{ if } \underline{r} \neq \underline{r}_s, \end{aligned}$$

$$\int p(\underline{r}_s) dV_{\underline{r}} = z_s,$$

where

$\underline{r}_s$  = positions of sulfur atoms,

$z_s$  = atomic number of sulfur.

The Fourier transform of the sulfur atom electron density is given by

$$G_p(\underline{S}) = \int p(\underline{r}') \exp[-2\pi i \underline{r}' \cdot \underline{S}] dV_{\underline{r}'},$$

This integral will only be non-zero when  $\underline{r} = \underline{r}_s$ , the positions of the sulfur atoms. Since we are summing over four sulfur atom positions we may write

$$\begin{aligned} G_p(\underline{S}) &= \int p(\underline{r}_s) \exp[-2\pi i \underline{r}_s \cdot \underline{S}] dV_{\underline{r}_s} \\ &= \sum_{n=1}^4 z_s \exp[-2\pi i (\underline{r}_s)_n \cdot \underline{S}] \end{aligned}$$

If the function  $q(\underline{r})$  is identified with the Patterson function we may write

$$\overline{pq}(\underline{r}) = \int p(\underline{r}') q(\underline{r}-\underline{r}') dV_{\underline{r}'},$$

This represents the convolution of the sulfur electron density with the Patterson function. Since  $p(\underline{r}')$  is only non-zero for  $\underline{r}' = \underline{r}_s$ , the above integrand will be non-zero only if the same condition is met. Therefore,

$$\overline{pq}(\underline{r}) = \int p(\underline{r}_s) q(\underline{r}-\underline{r}_s) dV_{\underline{r}_s}$$

The function  $q(\underline{r}-\underline{r}_s)$  will have four definite values corresponding to the

four sulfur atom positions for any particular value of  $\underline{r}$ . Therefore, the convolution may be expressed as follows:

$$\begin{aligned} \overline{pq}(\underline{r}) &= \sum_{n=1}^4 q[\underline{r} - (\underline{r}_s)_n] \int p(\underline{r}_s) dV_{\underline{r}_s} \\ &= \sum_{n=1}^4 z_s q[\underline{r} - (\underline{r}_s)_n]. \end{aligned} \quad (I')$$

The function  $q[\underline{r} - (\underline{r}_s)_n]$  is just the function  $q(\underline{r})$  with its origin translated to  $\underline{r} = (\underline{r}_s)_n$ . We have, therefore, through the process of convolution, accomplished the desired translation of the origin of the Patterson function to the four sulfur atom positions.

To cast these expressions into crystallographic notation, the following identifications must be made:

- 1)  $\underline{r} = \underline{ax} + \underline{by} + \underline{cz}$   
 where  $\underline{a}$ ,  $\underline{b}$ ,  $\underline{c}$  are vectors defining the unit cell
- 2)  $\underline{a} \cdot \underline{S} = h$       ( $h, k, l$ , are Miller indices)  
 $\underline{b} \cdot \underline{S} = k$   
 $\underline{c} \cdot \underline{S} = l$   
 $\underline{r} \cdot \underline{S} = hx + ky + lz$
- 3)  $p(\underline{r}_s) = \rho_s =$  sulfur electron density  
 $G_p(\underline{S}) =$  Fourier coefficients for sulfur electron density  
 $= (F_{hkl})_s$   
 $q(\underline{r}) = P(xyz) =$  Patterson function  
 $G_p(\underline{S}) =$  Fourier coefficients for Patterson function  
 $= |F_{hkl}|^2$

Substituting these values in (I)

$$\widehat{\rho}_s P(xyz) = \int (F_{hk\ell})_s |F_{hk\ell}|^2 \exp 2\pi i(hx + ky + \ell z) dV_r.$$

It is seen that the desired superposition function can be constructed by convoluting the sulfur electron density peak function with the Patterson function.

A superposition function was calculated using only the  $h0\ell$  data and is shown in Figure 4. As can be seen, the positions of most atoms were clearly indicated. It was not possible, however, to resolve the C(3) and N peaks or the C(1) and O(2) peaks. As a result, only very approximate x and z coordinates were obtained for these atoms from the superposition map.

The x and z coordinates were refined by the method of least squares to an R index of 20%. The reliability index, R, is defined as follows:

$$R = \frac{\sum_j |F_j^{\text{obs}} - F_j^{\text{calc}}|}{\sum_j |F_j^{\text{obs}}|}$$

All calculations were made on an IBM 7094 computer using the least squares program ORFLS written by Busing, Martin and Levy.<sup>14</sup> The scattering factors used in the calculations were those of Cromer and Waber.<sup>15</sup> Unit weights were assigned to all reflections. A projection of the electron density down the b-axis was calculated for an R of 20% and is shown in Figure 5.

From the set of three-dimensional data collected by counter methods, a three-dimensional Patterson function  $P(u,v,w)$  was synthesized. It was possible, knowing the x and z sulfur atom coordinates, to locate a sulfur-

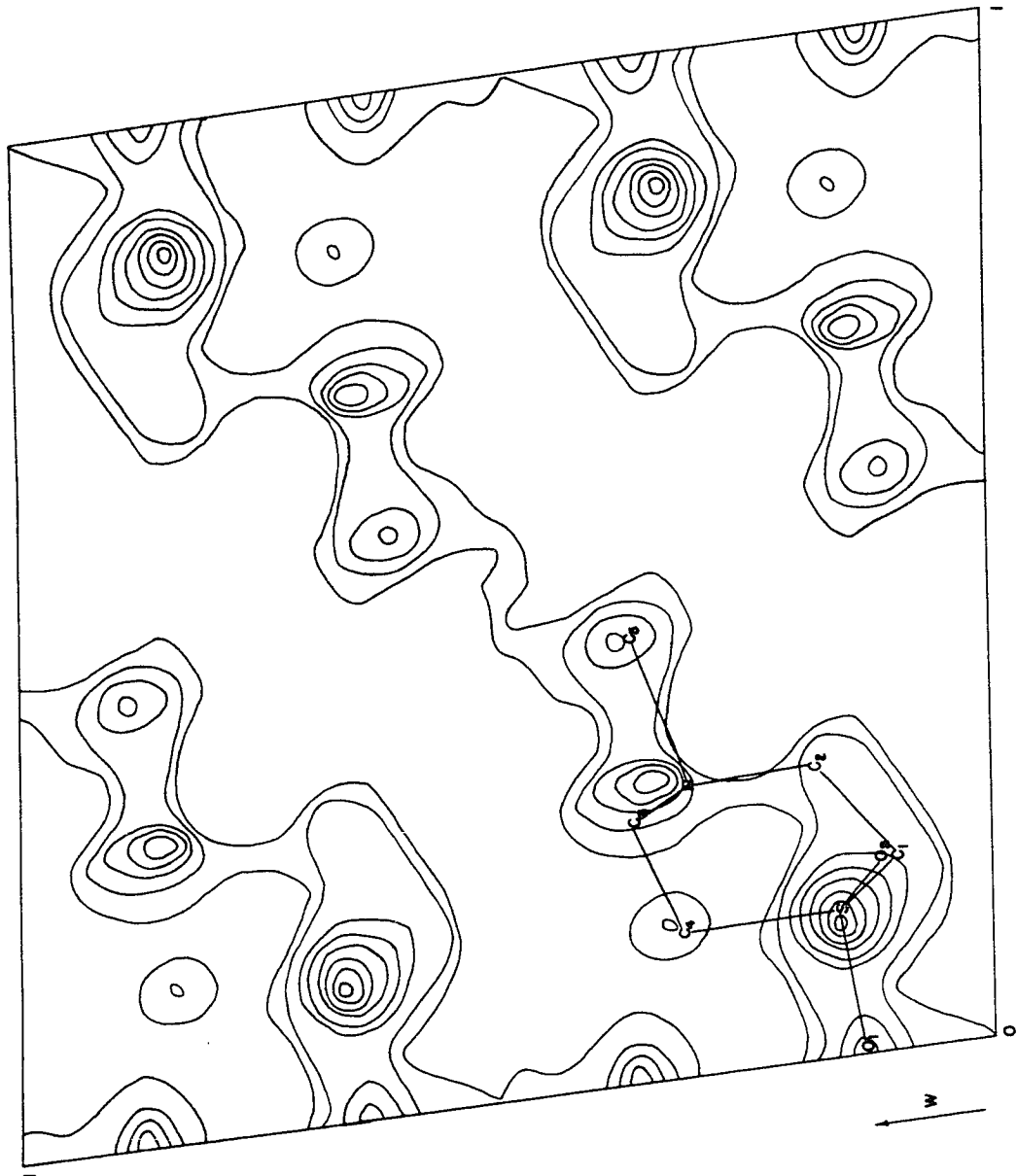


Figure 4. [010] Superposition Function

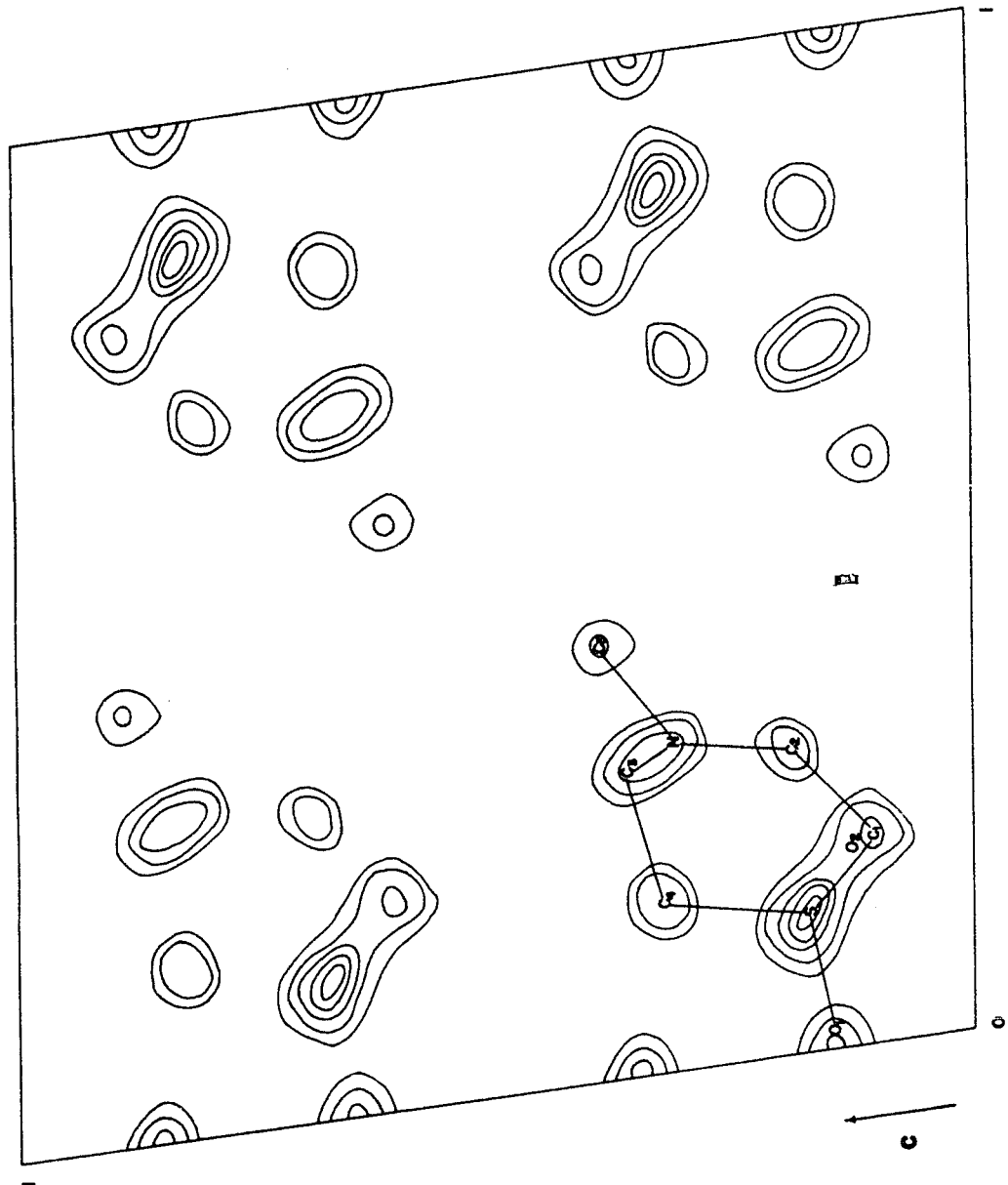


Figure 5. [010] Electron Density Projection

sulfur peak of the type  $(2x, 2y, 2z)$ . Thus, all three sulfur atom coordinates were determined from an examination of Patterson maps. It was not possible to determine the y coordinates of the other atoms from the three-dimensional Patterson function.

A structure factor calculation based on the positions of the sulfur atoms in the unit cell yielded a set of phases which were assigned to the observed structure factors and a three-dimensional electron density was synthesized. The electron density map showed a clear image of the molecule and the y coordinates of the remaining atoms were determined.



### THREE-DIMENSIONAL REFINEMENT

A total of 814 reflections were used in the three-dimensional full-matrix least squares refinement of the structure. The  $x_i$  parameters were adjusted so as to minimize the quantity:

$$\sum_j [\sqrt{w_j} (F_j^{\text{obs}} - F_j^{\text{calc}}) - \sqrt{w_j} \sum_i \left( \frac{\partial F}{\partial x_i} \right) \Delta x_i]^2.$$

All calculations were carried out on an IBM 7094 computer using the least squares program ORFLS.

After one cycle of least squares refinement with all atoms assigned isotropic temperature factors of 3.0 and all reflections unit weights, the reliability index R equaled 18%. An additional cycle of refinement, which included refinement of isotropic temperature factors, reduced R to 14%.

Before additional refinement of the structure, individual weights were assigned to the observed reflections after a weighting scheme proposed by Evans.<sup>16</sup> It is well known that each piece of data is not of the same reliability. Seldom, however, are measurements of the standard deviations of the intensities made. When measurements are made by counter methods, a weighting scheme based on observational statistics may be employed. The intensity of a reflection is given by

$$I = q(T-B) = q(1-b)T \quad (1)$$

where,

T = total number of counts under a peak

B = total number of background counts

b = B/T

q = changes in conditions of measurement from one reflection to another.

The integrated intensity is related to the structure factor by the following relationship

$$I = KALp|F|^2 \quad (2)$$

where

|F| = absolute value of the structure factor

Lp = Lorentz, polarization and Tunell factors

A = absorption correction

K = scale factor.

Substituting (2) into (1) and rearranging

$$T = KALp|F|^2 / (q[1-b]) . \quad (3)$$

The standard deviation of the structure factor is given by

$$\sigma_{|F|} = \left( \frac{d|F|}{dP} \right) \sigma_P \quad (4)$$

where

P = (1-b)T = number of counts under a peak.

From (3),

$$\left( \frac{d|F|}{dP} \right) = q / (2KALp|F|) . \quad (5)$$

From normal counting statistics

$$\sigma_p = [T+B]^{\frac{1}{2}} = [(1+b)T]^{\frac{1}{2}}. \quad (6)$$

Combining (4), (5), and (6)

$$\sigma_{|F|} = \frac{1}{2} [q(1+b)/KALp(1-b)]^{\frac{1}{2}}.$$

The relative weights which were assigned to each reflection were computed according to the following formula:

$$\sqrt{w} = [KALp(1-b)/q(1+b)]^{\frac{1}{2}}.$$

Additional least squares refinement, utilizing this weighting scheme and changing from isotropic to anisotropic temperature factors, reduced the R factor to 8%.

At this stage of refinement a three-dimensional difference map was synthesized in an attempt to locate the eleven hydrogen atoms. From examination of this difference map it was possible to determine the x, y, and z coordinates of all hydrogen atoms. A composite of the three-dimensional difference map as viewed down the b-axis is shown in Figure 6. Isotropic temperature factors ranging from 4.0 to 6.0 were assigned to the hydrogen atoms from an examination of the peaks in the difference map.

The final cycles of least squares refinement were carried out by alternately varying the non-hydrogen atom positional parameters and anisotropic temperature factors as a block and the hydrogen atom positional parameters as a block. The hydrogen atom scattering factors used in the

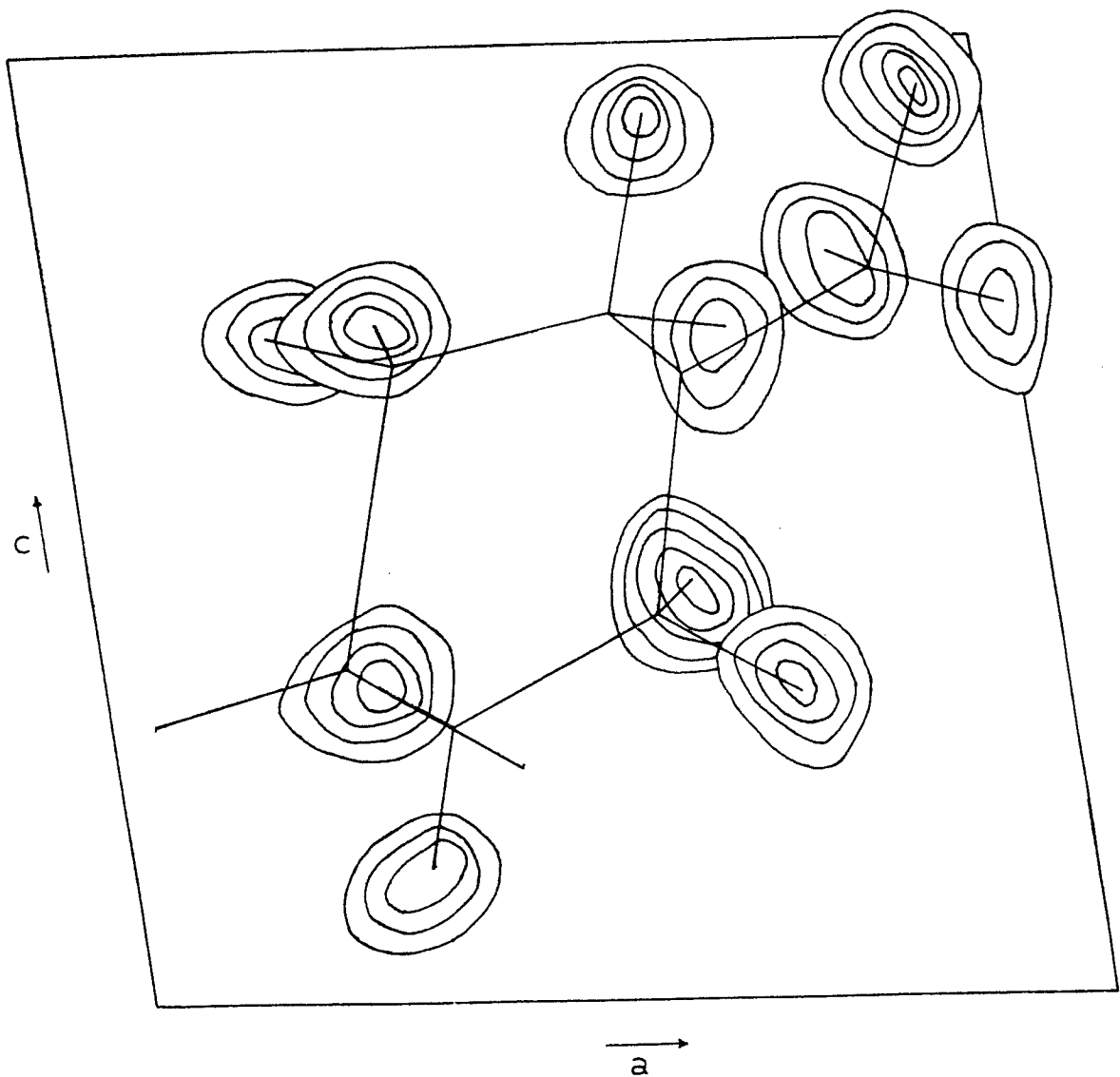


Figure 6. A Composite Difference Map Showing Observed Hydrogen Atom Peaks. Contours are at intervals of 0.1 e.Å<sup>-3</sup> beginning with the 0.2 e.Å<sup>-3</sup> contour.

calculations were those of Stewart, Davidson, and Simpson.<sup>17</sup> An attempt was made to refine on the hydrogen atom temperature factors without success. The final weighted R',

$$R' = \frac{[\sum_j w_j (F_j^{\text{obs}} - s_j F_j^{\text{calc}})^2]^{\frac{1}{2}}}{[\sum_j w_j (F_j^{\text{obs}})^2]^{\frac{1}{2}}},$$

for all 814 reflections was 4.1%, while the conventional R was reduced to 5.5%.

The observed and final calculated structure factors are shown in Table 1. The final coordinates and anisotropic temperature factors for the non-hydrogen atoms along with estimated standard deviations are shown in Table 2. Final coordinates and isotropic temperature factors and estimated standard deviations for hydrogen atoms are shown in Table 3.

TABLE 1

Observed and Calculated Structure Factors



TABLE 2

Final Positional and Thermal Parameters for Non-hydrogen Atoms and Their Estimated Standard Deviations

The values in the table have been multiplied by  $10^4$ . The temperature factors are of the form:

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

	X	Y	Z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
S	1282(1)	1099(2)	1689(1)	75(1)	168(1)	40(1)	19(2)	10(1)	- 1(1)
N	3134(3)	-1862(6)	3309(3)	49(3)	224(17)	80(3)	16(5)	13(2)	9(5)
O <sub>1</sub>	0024(3)	1388(6)	1387(2)	91(3)	405(15)	82(3)	77(5)	-12(2)	-21(5)
O <sub>2</sub>	2034(3)	2600(5)	1106(3)	166(4)	159(13)	78(3)	-40(5)	37(3)	24(4)
C <sub>1</sub>	1670(4)	-1744(8)	1438(4)	72(4)	186(19)	65(4)	- 2(6)	- 1(3)	-11(6)
C <sub>2</sub>	2943(4)	-2197(8)	2002(4)	65(4)	184(19)	84(4)	6(6)	16(3)	-35(6)
C <sub>3</sub>	2981(4)	0530(8)	3628(3)	63(4)	298(23)	54(4)	6(6)	16(3)	-22(7)
C <sub>4</sub>	1716(4)	1294(8)	3272(3)	76(4)	232(18)	52(3)	22(7)	17(3)	- 8(6)
C <sub>5</sub>	4297(4)	-2664(9)	3854(4)	77(5)	409(25)	106(5)	32(8)	8(4)	- 2(8)



TABLE 3

## Final Positional and Thermal Parameters for Hydrogen Atoms

The values for the coordinates have been multiplied

by  $10^4$ 

	X	Y	Z	B
H <sub>1</sub>	1503(38)	-2148(81)	0635(43)	6.0
H <sub>2</sub>	1210(36)	-2867(33)	1804(38)	4.5
H <sub>3</sub>	3439(39)	-1063(80)	1694(34)	4.5
H <sub>4</sub>	3151(29)	-3845(81)	1883(28)	4.0
H <sub>5</sub>	1199(32)	0287(69)	3544(29)	5.0
H <sub>6</sub>	1626(29)	2941(75)	3407(28)	4.5
H <sub>7</sub>	3209(32)	0650(66)	4570(34)	4.5
H <sub>8</sub>	3508(36)	1648(78)	3179(35)	5.5
H <sub>9</sub>	4468(36)	-2366(83)	4750(48)	4.0
H <sub>10</sub>	4402(51)	-4136(134)	3566(53)	5.5
H <sub>11</sub>	4922(69)	-1731(145)	3499(67)	5.5

## DISCUSSION

From Figure 7 it is clear that the molecule is in the chair conformation. This would be the expected conformation due to the steric hindrance between the methyl and sulfone groups in the boat conformation. The bond distances and angles involving non-hydrogen atoms are shown in Figure 8. These bond distances and angles along with their estimated standard deviations are reported in Table 4. The bond distances and angles involving the hydrogen atoms and their estimated standard deviations are shown in Table 5. Thermal ellipsoids were calculated for all non-hydrogen atoms and are described in Table 6. All bond distances, bond angles, and thermal ellipsoid calculations were made on an IBM 7094 computer using the program ORFEE written by Busing, Martin, and Levy.<sup>18</sup>

All bond lengths and valency angles associated with the sulfur atom are compared with corresponding values observed for some related compounds in Table 7. The sulfur-carbon bond distances found in the literature vary considerably. Abrahams reports a mean value of 1.82 Å based on six compounds. The values reported in this work for the sulfur-carbon bond length of 1.756 Å and 1.763 Å are somewhat shorter than this value, but in good agreement with the values of 1.73 Å and 1.74 Å recently reported by Desiderato and Sass for cis-2-butene episulfone, and of 1.74 Å reported by Kronfeld and Sass for dibenzothiophenesulfone. These values are also in agreement with the value of 1.75 Å reported by Jeffrey for *R*-isoprenesulfone. All other bond distances and angles in 4-methylthiomorpholene-1,1-dioxide were found to be quite normal.

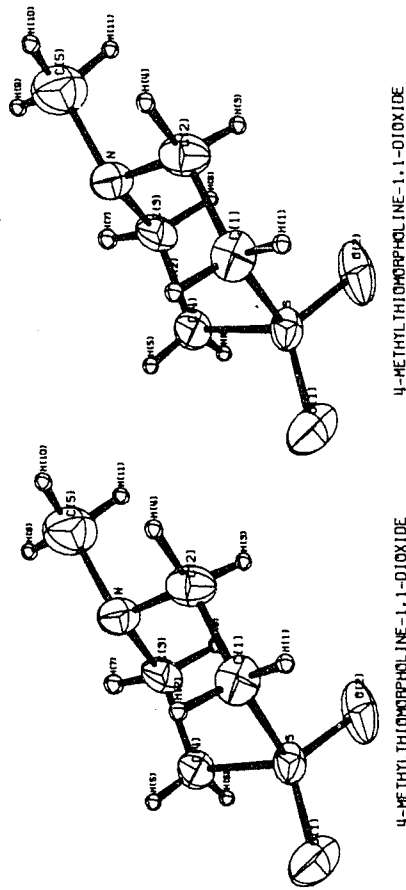


Figure 7. 4-methylthiomorpholine-1,1-dioxide  
(Stereo Pair)



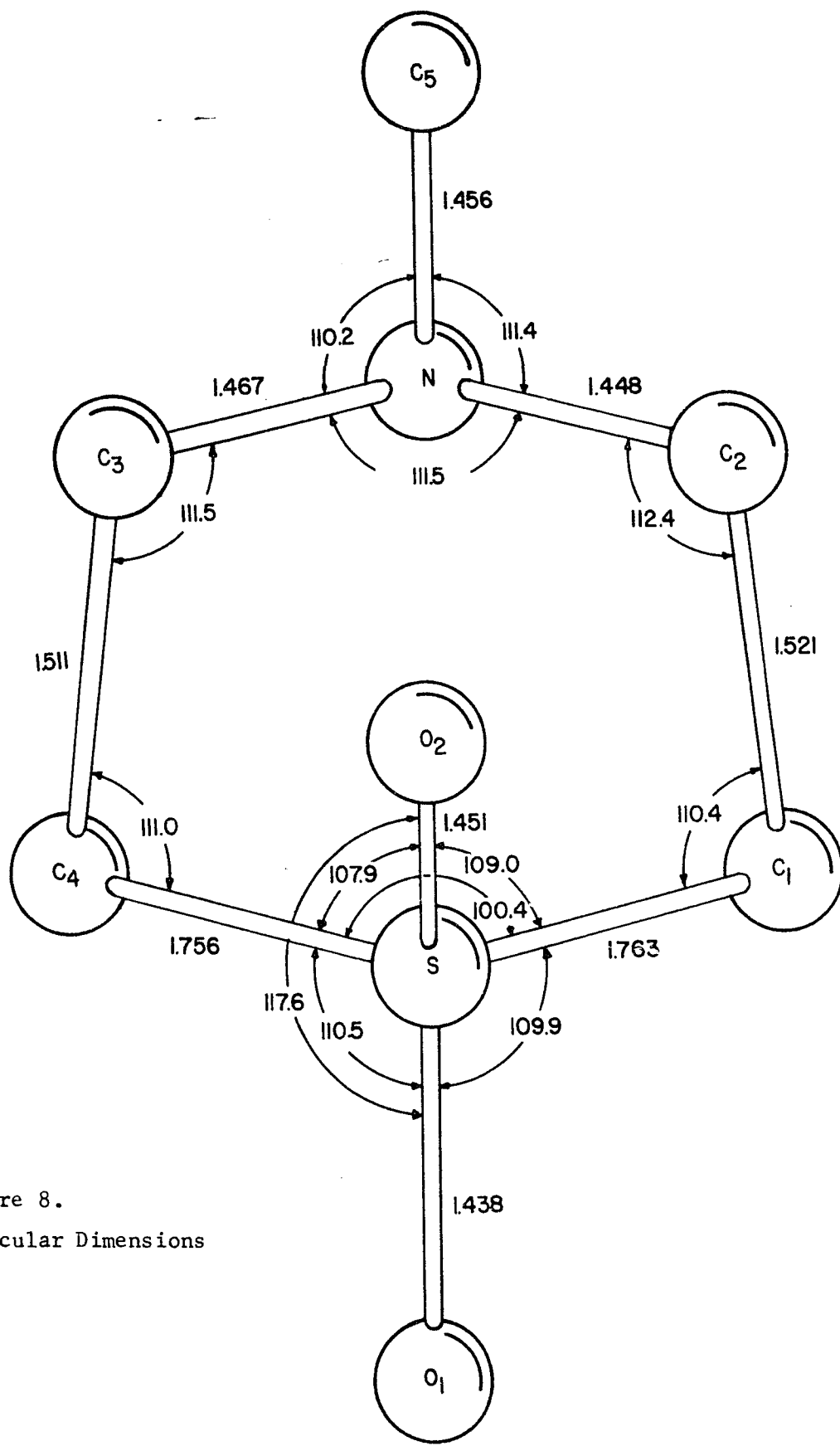


Figure 8.  
Molecular Dimensions

TABLE 4

Bond Distances and Angles Involving Non-hydrogen  
Atoms and Their Estimated Standard Deviations

S -O <sub>1</sub>	1.438(3) Å
S -O <sub>2</sub>	1.451(3) Å
S -C <sub>1</sub>	1.763(5) Å
S -C <sub>4</sub>	1.756(4) Å
C <sub>1</sub> -C <sub>2</sub>	1.521(5) Å
C <sub>2</sub> -N	1.448(5) Å
C <sub>3</sub> -C <sub>4</sub>	1.511(5) Å
C <sub>3</sub> -N	1.467(5) Å
C <sub>5</sub> -N	1.456(5) Å
O <sub>1</sub> -S -O <sub>2</sub>	117.6(2) °
O <sub>1</sub> -S -C <sub>4</sub>	110.5(2) °
O <sub>1</sub> -S -C <sub>1</sub>	109.9(2) °
O <sub>2</sub> -S -C <sub>4</sub>	107.9(2) °
O <sub>2</sub> -S -C <sub>1</sub>	109.0(2) °
C <sub>1</sub> -S -C <sub>4</sub>	100.4(2) °
S -C <sub>1</sub> -C <sub>2</sub>	110.4(3) °
S -C <sub>4</sub> -C <sub>3</sub>	111.0(3) °
C <sub>1</sub> -C <sub>2</sub> -N	112.4(3) °
C <sub>4</sub> -C <sub>3</sub> -N	111.5(3) °
C <sub>2</sub> -N -C <sub>3</sub>	111.5(3) °
C <sub>2</sub> -N -C <sub>5</sub>	111.4(3) °
C <sub>3</sub> -N -C <sub>5</sub>	110.2(3) °

TABLE 5

Bond Distances and Angles Involving Hydrogen  
Atoms and Their Estimated Standard Deviations

$C_1-H_1$	.914(4) Å
$C_1-H_2$	.971(5) Å
$C_2-H_3$	.970(5) Å
$C_2-H_4$	1.011(5) Å
$C_3-H_5$	1.041(4) Å
$C_3-H_6$	1.065(4) Å
$C_4-H_7$	.919(4) Å
$C_4-H_8$	.988(5) Å
$C_5-H_9$	1.000(5) Å
$C_5-H_{10}$	.936(5) Å
$C_5-H_{11}$	1.025(5) Å
$H_1-C_1-H_2$	100.5(3) °
$H_3-C_2-H_4$	116.8(3) °
$H_5-C_3-H_6$	110.7(3) °
$H_7-C_4-H_8$	119.7(4) °
$H_9-C_5-H_{10}$	119.0(4) °
$H_{10}-C_5-H_{11}$	104.1(4) °
$H_9-C_5-H_{11}$	103.5(4) °

TABLE 6

R. M. S. Displacements ( $\times 10^4$ ) Along the Principal Axes of the Thermal Ellipsoids and the Angles Between these Axes and the a, b, and c\* Axes

		a	b	c*
S	1534(15) Å	80°	75°	161°
	1670(22) Å	104°	157°	108°
	2259(15) Å	162°	73°	96°
N	1692(61) Å	155°	115°	91°
	2008(62) Å	66°	148°	110°
	2233(49) Å	97°	72°	160°
O <sub>1</sub>	1889(44) Å	136°	116°	122°
	2224(46) Å	104°	124°	38°
	3154(45) Å	131°	46°	73°
O <sub>2</sub>	1430(70) Å	103°	27°	66°
	2205(43) Å	98°	116°	27°
	3322(41) Å	164°	99°	103°
C <sub>1</sub>	1748(80) Å	96°	11°	98°
	1942(59) Å	63°	79°	29°
	2295(64) Å	152°	91°	62°



Table 6 - continued

		a	b	c*
C <sub>2</sub>	1595(87) Å	73°	30°	114°
	2056(68) Å	17°	107°	86°
	2385(59) Å	93°	114°	155°
C <sub>3</sub>	1657(68) Å	62°	73°	146°
	2055(60) Å	29°	94°	62°
	2343(84) Å	95°	18°	73°
C <sub>4</sub>	1666(68) Å	66°	66°	145°
	1982(69) Å	71°	39°	57°
	2319(62) Å	149°	61°	101°
C <sub>5</sub>	2142(75) Å	155°	112°	102°
	2551(63) Å	96°	105°	16°
	2769(77) Å	114°	27°	79°

TABLE 7

Sulfur Valency Angles and Bond Distances in  $\text{CH}_3\text{NC}_4\text{H}_8\text{SO}_2$   
 Compared with Values in Related Compounds

0-S-O	117.6(.2)°	$\text{CH}_3\text{NC}_4\text{H}_8\text{SO}_2$
	119.3(.9)°	$(\text{CH}_3\text{SO}_2)_3\text{CH}$ (Silverton, Gibson, Abrahams, 1965) <sup>20</sup>
	120.4(.4)°	$(p\text{-Cl C}_6\text{H}_4)_2\text{SO}_2$ (Sime, Abrahams, 1960) <sup>21</sup>
	120.4(.7)°	$((\text{CH}_3)_2\text{C}_2\text{H}_2\text{SO}_2)$ (Desiderato and Sass, 1967)
0-S-C	110.5(.2)°	$\text{CH}_3\text{NC}_4\text{H}_8\text{SO}_2$
	109.9(.2)°	
	107.9(.2)°	
	109.0(.2)°	
	107 (1)°	$(\text{CH}_3\text{SO}_2)_3\text{CH}$
	106 (1)°	
	107 (1)°	
	111 (1)°	
	107.3(.3)°	$(p\text{-ClC}_6\text{H}_4)_2\text{SO}_2$
	108.0(.3)°	
	109 (5)°	$(p\text{-BrC}_6\text{H}_4)_2\text{SO}_2$ (Abrahams, 1956)
	105 (3)°	$(\text{CH}_3)_2\text{SO}_2$ (Abrahams, 1956)
C-S-C	100.4(.2)°	$\text{CH}_3\text{NC}_4\text{H}_8\text{SO}_2$
	105 (1)°	$(\text{CH}_3\text{SO}_2)_3\text{CH}$
	100 (5)°	$(p\text{-BrC}_6\text{H}_4)_2\text{SO}_2$
	99.6(2)°	$\beta\text{-CH}_3\text{C}_4\text{H}_5\text{SO}_2$ (Jeffrey, 1953)

Table 7 - continued

S-O	1.438(3) Å	$\text{CH}_3\text{NC}_4\text{H}_8\text{SO}_2$
	1.451(3) Å	
	1.435(10) Å	$(\text{CH}_3\text{SO}_2)_3\text{CH}$
	1.436(17) Å	$\beta\text{-CH}_3\text{C}_4\text{H}_5\text{SO}_2$
	1.430(2) Å	$(\text{CH}_3)_2\text{SO}_2$
S-C	1.763(5) Å	$\text{CH}_3\text{NC}_4\text{H}_8\text{SO}_2$
	1.756(4) Å	
	1.830(1) Å	$(\text{CH}_3\text{SO}_2)_3\text{CH}$
	1.730(2) Å	
	1.750(2) Å	$\beta\text{-CH}_3\text{C}_4\text{H}_5\text{SO}_2$
	1.800(2) Å	$(\text{CH}_3)_2\text{SO}_2$
	1.73 Å	$((\text{CH}_3)_2\text{C}_2\text{H}_2\text{SO}_2)$

An [010] projection of the unit cell indicating the crystal packing is shown in Figure 9. A stereoscopic drawing of this same projection is shown in Figure 10. Both Figure 10 and Figure 7 were drawn on a CalComp plotter using the program ORTEP written by Carroll Johnson.<sup>19</sup> All intermolecular distances of 4 Å or less were calculated and are shown in Table 8. There were no contacts shorter than the normally accepted van der Waals contacts.

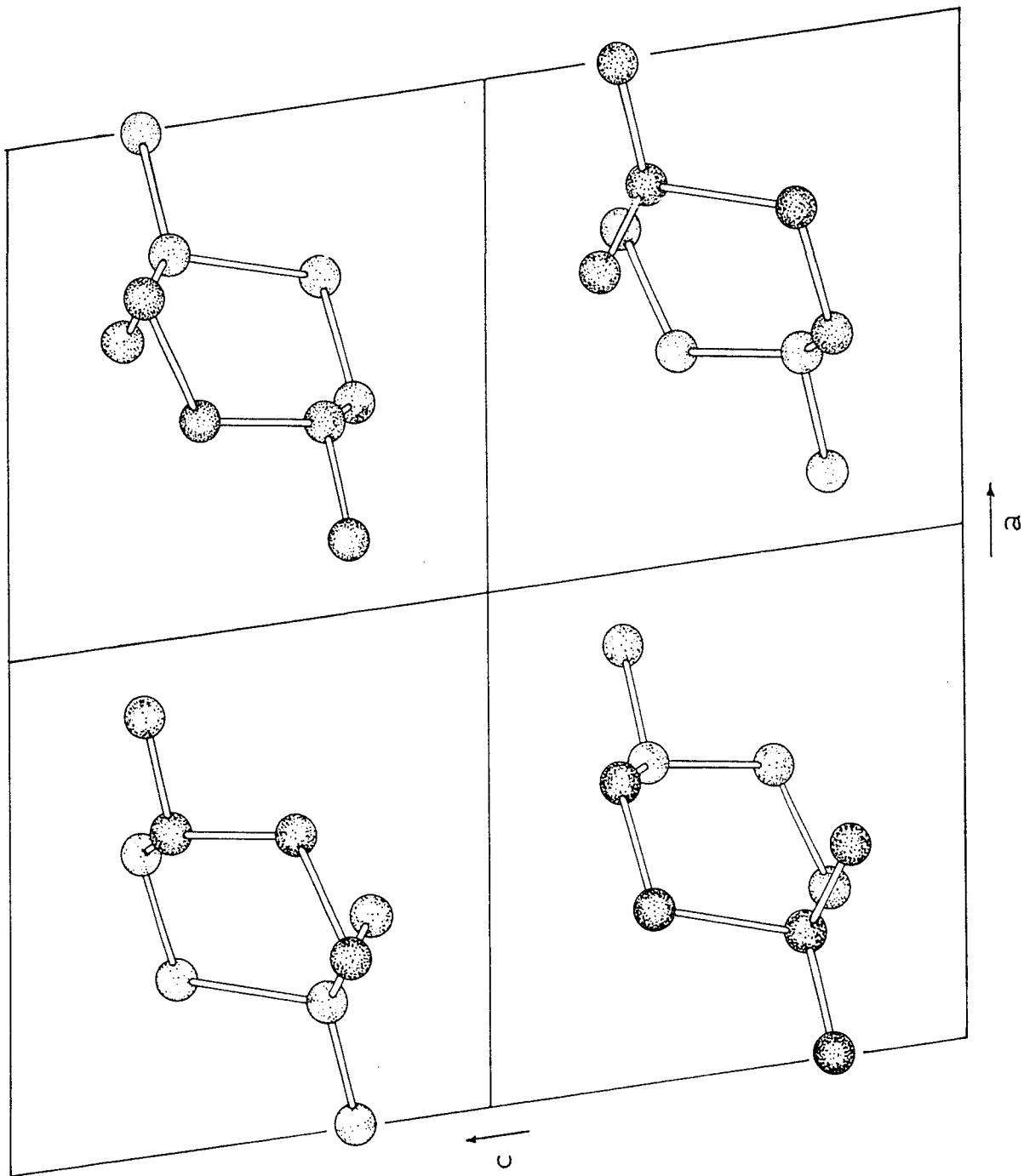
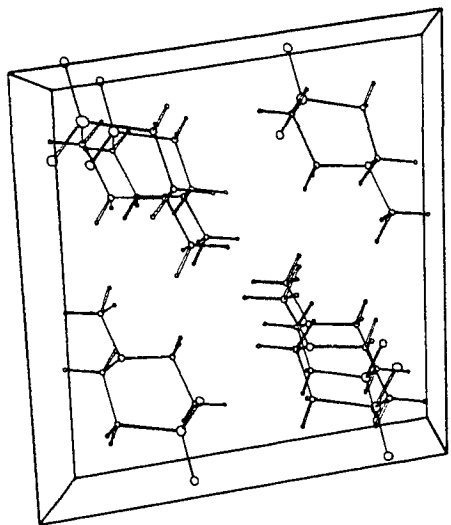
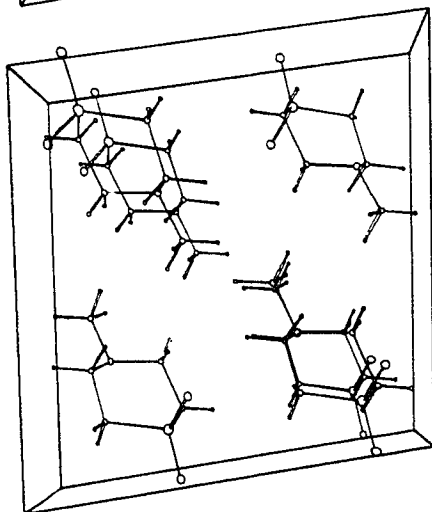


Figure 9. [010] Projection of the Unit Cell



PACKING DIAGRAM



PACKING DIAGRAM

Figure 10. Crystal Packing: viewed down the b-axis  
(Stereo Pair)

TABLE 8

Non-hydrogen Atom Intermolecular Contacts Less Than 4.0 Å

S -O <sub>1</sub>	(1)	3.809(3) Å
O <sub>1</sub> -O <sub>1</sub>	(1)	3.477(4) Å
O <sub>1</sub> -C <sub>1</sub>	(1)	3.438(4) Å
C <sub>3</sub> -O <sub>2</sub>	(2)	3.291(5) Å
C <sub>4</sub> -O <sub>2</sub>	(2)	3.180(4) Å
O <sub>1</sub> -S	(3)	3.926(3) Å
O <sub>1</sub> -N	(3)	3.820(4) Å
O <sub>1</sub> -O <sub>1</sub>	(3)	3.856(4) Å
O <sub>1</sub> -C <sub>1</sub>	(4)	3.491(5) Å
O <sub>1</sub> -C <sub>4</sub>	(4)	3.557(5) Å
C <sub>1</sub> -O <sub>2</sub>	(4)	3.378(5) Å
C <sub>2</sub> -O <sub>2</sub>	(4)	3.335(5) Å

Numbers in Parenthesis Refer to the Following Positions:

- (1)  $\bar{x}, \bar{y}, \bar{z}$
- (2)  $x, \frac{1}{2}-y, \frac{1}{2}+z$
- (3)  $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$
- (4)  $x, y-1, z$

## REFERENCES

- (1) R. Desiderato and R. L. Sass, Acta Cryst., 23, 430 (1967).
- (2) L. E. Sutton, Tables of Interatomic Distances, The Chemical Society, London, 1958.
- (3) S. C. Abrahams, Quart. Rev. Chem. Soc., 10, 407 (1956).
- (4) L. R. Kronfeld and R. L. Sass, Acta Cryst., to be published (1968).
- (5) R. L. Sass and C. S. Yoo, Private Communication, 1967.
- (6) G. A. Jeffrey, Acta Cryst., 4, 58 (1951).
- (7) D. E. Sands, Z. Kristallogr., 124, 220 (1967).
- (8) J. Ladell, Norelco Reporter, 12, 32 (1965).
- (9) M. J. Buerger, Crystal Structure Analysis, John Wiley and Sons, Inc., New York, 1960, p. 152.
- (10) W. L. Bond, Acta Cryst., 12, 375 (1959).
- (11) L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithica, 1948, p. 189.
- (12) C. A. Beevers and J. H. Robertson, Acta Cryst., 3, 164 (1950).
- (13) H. Lipson and C. A. Taylor, Fourier Transforms in X-Ray Diffraction, Bell and Sons, Ltd., London, 1958.
- (14) W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.
- (15) D. T. Cromer and J. T. Waber, Acta Cryst., 18, 104 (1965).
- (16) H. T. Evans, Acta Cryst., 14, 689 (1961).
- (17) R. F. Stewart, E. R. Davidson, and W. T. Simpson, J. Chem. Phys., 42, 3175 (1965).
- (18) W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.
- (19) C. K. Johnson, ORNL-TM-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.



- (20) J. V. Silverton, D. T. Gibson, and S. C. Abrahams, Acta Cryst.,  
19, 651 (1965).
- (21) J. G. Sime and S. C. Abrahams, Acta Cryst., 13, 1 (1965).