bonding, lithium chelation, and other properties of these compounds.

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The Crystal Structure and Molecular Configuration of (+)-*S*-Methyl-L-Cysteine Sulphoxide

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(+)-*S*-methyl-L-cysteine sulphoxide crystallizes in the orthorhombic system, space group $P2_12_12_1$, with a unit cell of dimensions

$$a = 5{\cdot}214 \pm 0{\cdot}002,\ b = 7{\cdot}410 \pm 0{\cdot}002,\ c = 16{\cdot}548 \pm 0{\cdot}008\ \text{Å}\ ,$$

and containing four molecules. The crystal structure was determined in projection by a sign-relation method. Final parameters have been determined by three-dimensional least-squares refinement. The structure represents the first determination of the absolute configuration at an asymmetric sulphur atom. The molecular arrangement in the crystalline state consists of pairs of sheets of molecules parallel to (001) held together by hydrogen bonds between the nitrogen of one molecule and surrounding oxygens of different molecules.

1. Introduction

(+)-*S*-methyl-L-cysteine sulphoxide [(+)MCS, Fig. 1] is one of a range of biologically active organic sulphoxides which have been extracted in recent years from natural sources (Challenger, 1953; Synge & Wood, 1956). In most of these compounds the sulphur is a centre of asymmetry, though not always the only one, and consequently these substances are optically active and exist in at least two isomeric forms whose configurations are unknown. Following the synthesis and resolution of several of these compounds it has been shown that their biological action depends markedly on the configuration used. It is for this reason important that the configurations of these compounds should be established absolutely. Furthermore, the organic sulphoxides represent a class of compounds little studied so far by X-ray methods, and further information about them is desirable. For both these reasons a study, described here, has been made of (+)MCS.

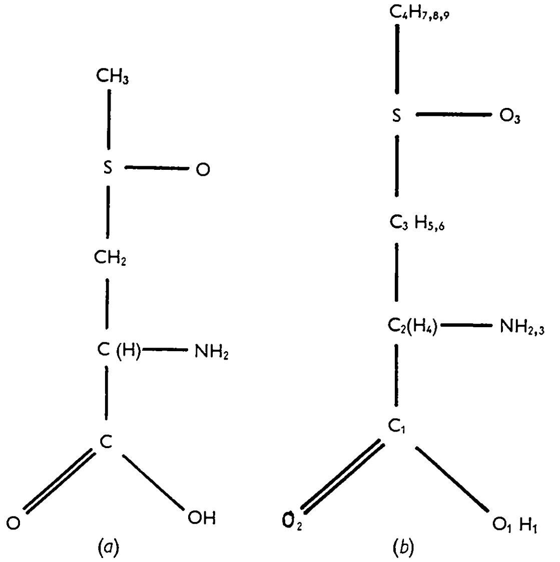

Fig. 1. (*a*) Chemical constitution of (+)-*S*-methyl-L-cysteine sulphoxide. (*b*) Numbering of atoms adopted in text.

2. Experimental

(+)MCS crystallizes from aqueous ethanol as clusters of small colourless laths, elongated along [100] with (001) prominent, and cleaving easily parallel to (100) and to (010).

2·1. *Crystal data*

(+)-*S*-methyl-L-cysteine sulphoxide, $C_4H_9O_3NS$. Molecular weight 151, m.p. 168 °C.

The space group was determined from oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation. Lattice parameters were determined by the method of Farquhar & Lipson (1946).

The unit cell is orthorhombic, with

$$a=5{\cdot}214\pm0{\cdot}002,\ b=7{\cdot}410\pm0{\cdot}002,$$
$$c=16{\cdot}548\pm0{\cdot}008\ \text{Å}\ .$$
$$d_o=1{\cdot}56\ \text{g.cm.}^{-3},\ d_c=1{\cdot}57\ \text{g.cm.}^{-3},\ Z=4\ .$$

Systematic absences—$h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd—uniquely determine the space group $P2_12_12_1$–D_2^4.

Total number of electrons per unit cell = 320.

Absorption coefficient for Cu $K\alpha$ radiation = 40 cm.$^{-1}$.

2·2. *Intensity data*

The intensities were recorded on multiple-film equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. The measurements were made by visual comparison with a calibrated wedge prepared from a strong reflexion from the crystal used for the intensity photographs. All intensity estimations from upper-layer photographs were made on the spots on the contracted side of the film. Three crystals were used, one for oscillation about each of the principal axes. Those for photographs about a and b were cut from a larger lath to about 1 mm. parallel to the axis of oscillation and to about 0·05 mm. square cross section, while for photographs about c the crystal had dimensions of about 0·2 mm. cube.

The majority of the reflexions were recorded on zero, first, second and third layer photographs about a. The lower-sin θ reflexions, which are most affected by change of spot shape on upper layer equi-inclination photographs, were collected on zero and first-layer photographs about b, and on zero-layer photographs about c. In this way 741 reflexions were covered out of about 850 within the sphere of reflexion, and all intensity measurements were made on spots which had not sufferered very great change of shape. Of these 741, 578 were observed to have non-zero F_o's. The intensities were reduced to F_o in the usual way, initial scaling and temperature factors being obtained by Wilson's method (1942).

2·3. *Accuracy of the intensity data*

It was found that neglect of absorption would not introduce in any reflexion an error approaching the 10–20% (see below) likely in visually estimated intensities, and absorption corrections were therefore not applied.

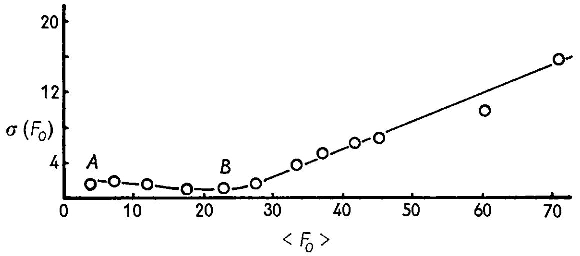

Fig. 2. Variation of standard deviation with magnitude of observed structure factor for $(0kl)$ reflexions.

For weighting purposes in the later least-squares refinement an examination was made of the errors of visual estimation. The reflexions used for this were confined to the $0kl$'s, but the results are probably typical for any layer. Two sets of visual estimates of the intensities of the reflexions in the zone were made quite independently using different crystals of approximately the same dimensions. The wedge used was prepared from the crystal used to take the intensity photographs. The intensities were brought to a common scale, reduced to F_o, and batched in ranges of F_o. A plot of $\sigma(F_o)$ for each range against the mean F_o for the range is shown in Fig. 2. Over the approximately level region AB the standard deviation is about 1·2, while above B it increases approximately linearly with F_o. This indicates that a reasonably satisfactory weighting scheme would probably be represented by a function of the form $\sqrt{w}=1$ for $F_o \le F_o^*$, $\sqrt{w}=F_o^*/F_o$ for $F_o>F_o^*$. For the $0kl$ reflexions, and probably for the $h0l$ reflexions also, F_o^* is about 25. It is likely that the same scheme will be appropriate for the whole of the three-dimensional data, but with a different value of F_o^*. (Strictly it would be better to apply the function to each layer of the reflexion data, varying F_o^* in each layer.) The discrepancy index $\Sigma|I_1-I_2|/\Sigma I_1$ was calculated for the intensities and found to be 0·14.

3. Structure determination

3·1. *The* (100) *projection*

The work on structure determination was begun with the calculation of the (100) Patterson synthesis in an attempt to locate the sulphur atom, but it proved impossible to do this unambiguously. Instead of the possible procedure of calculating further Pattersons in a search for the sulphur a sign relation method (Grant, Howells & Rogers, 1957) was tried. This worked extremely well. Of the 115 $0kl$ reflexions observed, 52, with unitary structure factors $\ge 0{\cdot}2$, were used. The signs of all the 52 were given unambiguously, and none changed sign in the subsequent refinement. Using these 52 terms the electron density projected on (100) was calculated (Fig. 3). There was not the slightest doubt about the interpretation of the map, or the identification of carbon, oxygen and nitrogen atoms. In particular it was possible to distinguish between the oxygen and methyl group at the sulphur atom, and thus to decide immediately the configuration around the sulphur. The sulphur position was checked against the Patterson synthesis and found to be completely consistent with it.

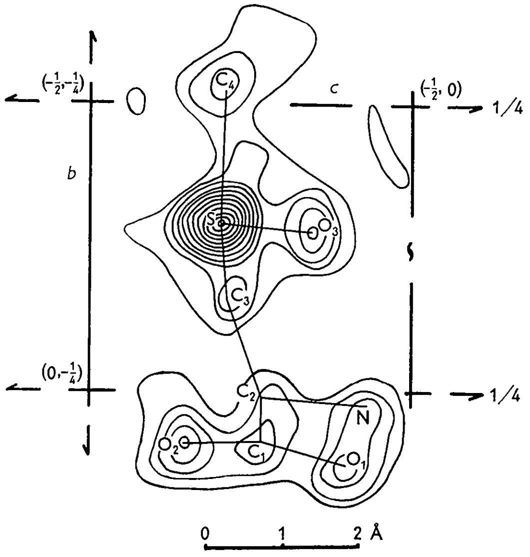

Fig. 3. First electron density projection on (100). Contours at equal but arbitrary intervals.

Structure factors were calculated on the basis of coordinates obtained from the electron-density synthesis, and gave $R=0\cdot28$, for the observed terms only. A second synthesis was calculated and used to refine the atomic coordinates, and this was followed by several cycles of refinement by difference synthesis during which the atomic positions and isotropic sulphur atom temperature factor were corrected in the usual way. The R factor had dropped by this stage to 0·19. The final refinement in this projection was carried out by four cycles of least squares; the DEUCE computer with Dr J. S. Rollett's program for the refinement of positional and anisotropic vibrational parameters was used. No allowance was made for the effect of overlap of atoms, but in this case all the atoms except C_1 and C_2 were reasonably well resolved. In view of the results discussed above the following scheme for the weighting of the observations was adopted: $F_o \leq 25$, $\sqrt{w}=1$; $F_o>25$, $\sqrt{w}=25/F_o$. The refinement was carried out using the 115 observed terms only. All parameters, positional and vibrational, were refined. At the end of the final cycle R was 0·14 for the observed terms and 0·20 overall. It became clear during the course of the refinement that atoms C_2 and C_3 were showing markedly larger amplitudes of vibration parallel to c than were the remaining atoms of the molecule. Of these atoms C_3 has two hydrogens disposed in the (100) projection almost symmetrically about it, and approximately along c, while C_2 has one hydrogen also approximately in the direction of c. It therefore appeared that a part of this apparent anisotropy might be attributable to compensation for the absence of the hydrogens in the assumed structure.

3·2. *The* (010) *projection*

The (010) Patterson synthesis was calculated and the x coordinate of the sulphur atom determined. With the sulphur position found, and the z coordinates of the remaining atoms known from the (100) refinement, it was a simple matter to place the molecule in the (010) projection. The coordinates obtained were used as the starting point for two stages of refinement by electron-density synthesis followed by three difference syntheses, and four cycles of least squares. The distribution of errors in the $h0l$ reflexions was not examined but was expected to be much the same as for the $0kl$'s, and the same weighting scheme was adopted in the least-squares refinement. The final R values were 0·13 for the observed terms and 0·24 overall. The very much larger value when the unobserved reflexions are included is due simply to the larger number, 46, of these in this projection. The final z coordinates for the two projections agreed reasonably well. The poorest agreement was for C_3, which overlaps C_2 in the (010) projection, and which had a difference between the z coordinates of 0·11 Å. The mean difference for the remaining atoms was 0·025 Å.

3·3. *Final refinement*

The parameters obtained from the two-dimensional work were refined to the values finally adopted by five cycles of three-dimensional least-squares, using the program written for the Ferranti Pegasus computer by Dr D. W. J. Cruickshank. The weighting scheme adopted for the two-dimensional work was used in three dimensions, with the exceptions that F_o^* was taken as 20, and that the 004 term, which is probably affected by extinction, was given zero weight. Only the 578 observed terms were used in the refinement.

It was thought desirable in the following refinement to include the hydrogen contributions to the calculated structure factors, but at the stage reached direct location of the hydrogen atoms was impossible. Hydrogen positions were therefore calculated from known bond distances and angles. For the hydrogens bonded to carbon atoms the usual tetrahedral arrangement was adopted with C–H distances of 1·07 Å. This enabled H_5 and H_6, on C_3, and H_4, on C_2 to be positioned confidently. The hydrogens H_7, H_8, H_9 of the methyl group could not be fixed in this way and were not included in the refinement. To enable the remaining three hydrogens to be placed the molecule

Table 1. *Measured and calculated structure factors*

Unobserved terms are indicated by —.

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
0	0	2	20	23
0	0	4	83	91
0	0	6	42	42
0	0	8	15	11
0	0	10	40	40
0	0	12	—	0
0	0	14	12	11
0	0	16	4	5
0	0	18	—	1
0	0	20	6	5
0	1	1	26	28
0	1	2	42	49
0	1	3	49	51
0	1	4	31	30
0	1	5	22	21
0	1	6	24	23
0	1	7	28	29
0	1	8	5	3
0	1	9	14	14
0	1	10	16	16
0	1	11	8	7
0	1	12	17	17
0	1	13	27	29
0	1	14	17	17
0	1	15	—	1
0	1	16	9	7
0	1	17	12	13
0	1	18	8	6
0	1	19	6	3
0	1	20	—	2
0	1	21	—	1
0	2	0	13	15
0	2	1	48	55
0	2	2	8	6
0	2	3	37	35
0	2	4	25	23
0	2	5	7	2
0	2	6	6	5
0	2	7	29	26
0	2	8	14	12
0	2	9	4	2
0	2	10	20	19
0	2	11	10	9
0	2	12	20	18
0	2	13	—	3
0	2	14	22	19
0	2	15	—	1
0	2	16	8	6
0	2	17	—	3
0	2	18	6	2
0	2	19	—	1
0	2	20	—	4
0	2	21	4	3
0	3	1	64	67
0	3	2	19	19
0	3	3	44	42
0	3	4	5	2
0	3	5	6	3
0	3	6	15	13
0	3	7	12	8
0	3	8	13	12
0	3	9	20	19
0	3	10	—	4
0	3	11	11	6
0	3	12	6	4
0	3	13	—	7
0	3	14	10	9
0	3	15	—	1
0	3	16	—	2
0	3	17	6	4
0	3	18	6	5
0	3	19	—	2
0	3	20	—	1
0	4	0	20	21
0	4	1	17	15
0	4	2	8	7
0	4	3	14	13
0	4	4	17	16
0	4	5	14	14
0	4	6	—	0
0	4	7	10	9
0	4	8	10	6
0	4	9	8	7
0	4	10	10	8
0	4	11	25	26
0	4	12	8	5
0	4	13	—	3
0	4	14	8	6
0	4	15	16	13
0	4	16	8	5
0	4	17	6	5
0	4	18	—	2
0	4	19	—	2
0	5	1	—	4
0	5	2	30	29
0	5	3	14	10
0	5	4	19	19
0	5	5	6	6
0	5	6	8	7
0	5	7	14	14
0	5	8	18	15
0	5	9	6	3
0	5	10	12	11
0	5	11	—	3
0	5	12	13	11
0	5	13	5	3
0	5	14	12	9
0	5	15	—	3
0	5	16	—	3
0	5	17	—	2
0	5	18	3	6
0	6	0	11	10
0	6	1	12	11
0	6	2	—	3
0	6	3	12	10
0	6	4	6	4
0	6	5	8	7
0	6	6	9	7
0	6	7	7	4
0	6	8	6	3
0	6	9	8	6
0	6	10	12	9
0	6	11	10	9
0	6	12	—	2
0	6	13	—	1
0	6	14	6	1
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0	7	5	—	3
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0	7	8	10	8
0	7	9	—	0
0	7	10	—	1
0	7	11	—	1
0	7	12	6	7
0	7	13	—	2
0	7	14	3	2
0	8	0	8	6
0	8	1	13	9
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0	8	3	3	2
0	8	4	8	7
0	8	5	14	11
0	8	6	10	8
0	8	7	—	1
0	8	8	—	1
0	8	9	—	1
0	8	10	6	7
0	8	11	6	5
0	9	1	10	9
0	9	2	—	3
0	9	3	6	7
0	9	4	4	2
0	9	5	—	2
0	9	6	—	1
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1	0	2	4	1
1	0	3	14	13
1	0	4	9	8
1	0	5	32	33
1	0	6	31	30
1	0	7	19	17
1	0	8	10	10
1	0	9	25	26
1	0	10	27	27
1	0	11	25	27
1	0	12	3	5
1	0	13	—	2
1	0	14	—	0
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1	0	16	—	2
1	0	17	9	7
1	0	18	—	1
1	0	19	6	6
1	0	20	—	1
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1	1	10	9	9
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1	1	13	6	6
1	1	14	7	6
1	1	15	8	7
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1	1	17	—	1
1	1	18	6	6
1	1	19	4	3
1	1	20	4	2
1	1	21	—	1
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2	4	14	—	3
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2	4	17	—	4
2	4	18	—	2
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2	5	1	—	2
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6	4	0	1	0

was assumed to be in the *zwitterion* ($-N^+H_3$) form, as is usual with α-amino acids, with the three hydrogens arranged approximately tetrahedrally round the C_2–N bond and with N–H distances of 1·0 Å. The molecular arrangement in the crystalline state (Fig. 5) is such that each nitrogen has five oxygens at distances of less than 2·9 Å. Of these, three are to neighbouring molecules and have C_2–N ⋯ O angles of 111°, 111°, and 126°, and the remaining two are intramolecular with the corresponding angles, at 63° and 88°, departing further from the tetrahedral value. This kind of arrangement is similar to that reported for some other α-amino acids (e.g. Schoemaker *et al.*, 1950; Schoemaker *et al.*, 1953), and it would seem correct to ascribe the three intermolecular N ⋯ O distances to hydrogen bonding, and the intramolecular ones to electrostatic attraction. The three remaining hydrogen atoms were therefore placed in accordance with this arrangement. Four cycles of refinement were carried out during which three positional and six vibrational parameters were refined for each atom except the hydrogens.

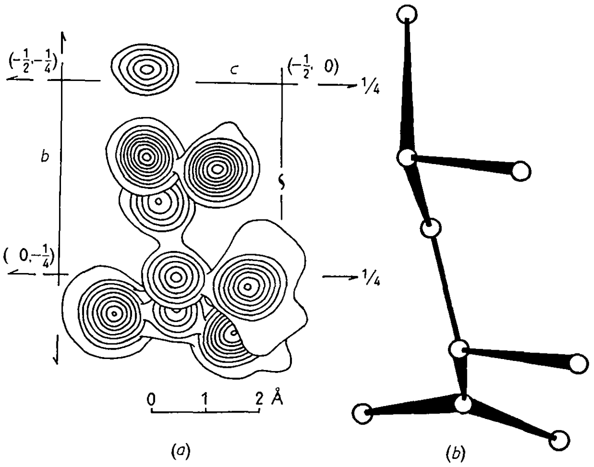

Fig. 4. (*a*) Final composite electron density synthesis. Contours are at 1 e.Å^{-3} intervals starting at 1 e.Å^{-3} except around the sulphur where the interval is 3 e.Å^{-3}. (*b*) Molecular conformation in crystalline state, showing absolute configuration of molecule.

The largest coordinate shift in the last cycle was 0·0029 Å to O_1, which is 0·22 of a standard deviation, and the mean shift was 0·0008 Å, or 0·05 of a standard deviation. The final *R* value was 0·128 for the observed terms only and 0·180 overall. The final observed and calculated structure factors are listed in Table 1, and final values of the coordinates together with the standard deviations estimated from the coefficients of the normal equations of the least-squares, in Table 2. The final electron-density map is shown in Fig 4(*a*).

4. Discussion

4·1. *Absolute configuration*

The conformation which the molecule adopts in the crystalline state is shown in Fig. 4(*b*), which portrays the absolute configuration of the L_s amino acid group, and therefore the configuration of the whole molecule. The configuration at the (+)-*S* atom is S in Cahn, Ingold & Prelog's notation (1956). The chemical implications of the work have been set out elsewhere (Hine & Rogers, 1956).

4·2. *Crystal structure*

The molecular arrangement adopted in the crystalline state is shown diagrammatically in Fig. 5. The molecules lie in well defined twin sheets parallel to (001), with the nitrogen and two of the three oxygens of each molecule directed inwards. The arrangement is such that each nitrogen has three oxygens from three different adjacent molecules (oxygens O_1', O_1'', O_3' in Fig. 5) arranged approximately at the three vertices of a tetrahedron around the nitrogen and with the α-carbon at the fourth vertex. The N ⋯ O distances are 2·89, 2·81 and 2·83 Å respectively. This arrangement is completely compatible with the existence of hydrogen bonding between the nitrogen and oxygens.

It is apparent that the molecules in each sheet are held together by means of the three intermolecular

Table 2. *Atomic coordinates and standard deviations*

Atom	*x* (Å)	*y* (Å)	*z* (Å)	σ(*x*) (Å)	σ(*y*) (Å)	σ(*z*) (Å)
C_1	−0·2026	+0·6639	−1·9814	0·020	0·017	0·017
C_2	+1·2450	+0·0475	−1·9655	0·022	0·018	0·016
C_3	+1·1730	−1·4062	−2·2988	0·022	0·022	0·018
C_4	+2·1705	−3·9295	−2·5368	0·022	0·016	0·017
O_1	−0·5848	+1·1145	−0·8909	0·014	0·011	0·012
O_2	−0·7063	+0·7277	−3·0857	0·014	0·013	0·013
O_3	+3·4951	−2·0209	−1·2234	0·014	0·010	0·011
N	+1·8945	+0·2187	−0·6078	0·015	0·013	0·014
S	+2·7964	−2·2274	−2·5202	0·005	0·004	0·004
H_1	+1·655	−0·540	−0·040	—	—	—
H_2	+1·532	+1·020	−0·160	—	—	—
H_3	+2·870	+0·022	−0·675	—	—	—
H_4	+1·885	+0·525	−2·713	—	—	—
H_5	+0·672	−1·882	−1·478	—	—	—
H_6	+0·629	−1·490	−3·213	—	—	—
H_7	—	—	—	—	—	—
H_8	—	—	—	—	—	—
H_9	—	—	—	—	—	—

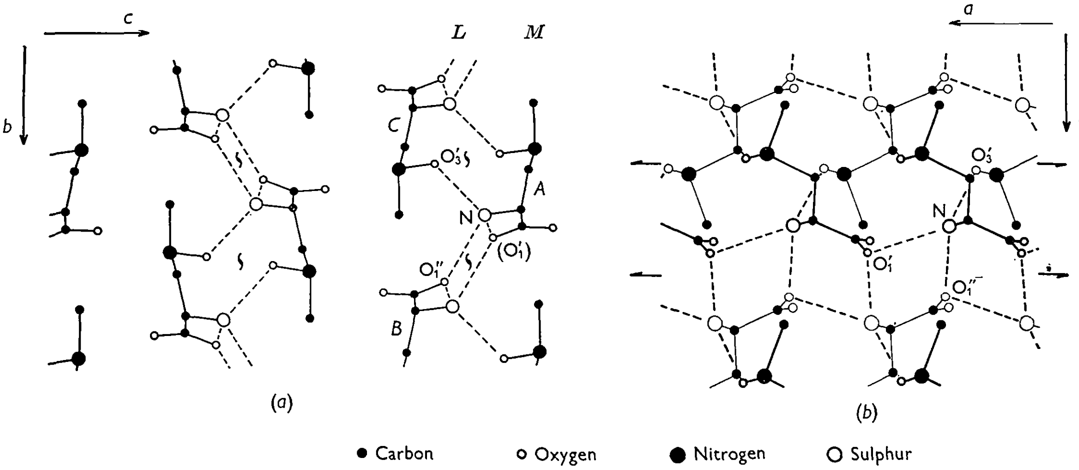

Fig. 5. Schematic diagram of the crystal structure. Broken lines indicate the hydrogen bonds. Only the screw axes parallel to a are shown. (a) Shows the structure viewed down [100]. (b) Shows only the molecules of the twin sheet marked LM in (a) viewed down [001]; those in sheet M are drawn heavier.

hydrogen bonds. Of these bonds, one is to oxygen O_1' of the carboxyl group of the molecule one cell translation parallel to a above, while the second is to O_1'' of a screw-related molecule B, giving a spiral of hydrogen bonds around the screw axis. In this way the O_1 oxygen participates in two hydrogen bonds: one with the nitrogen of the molecule immediately below, and one with the nitrogen of a screw-related molecule. The third hydrogen bond occurs between the nitrogen of molecule A and the sulphoxide oxygen of molecule C. It is clear that the sulphoxide group has rotated around the S–C_3 bond for this purpose.

The distances between adjacent twin sheets of molecules involve only typical van der Waals distances. With the exception of contacts between C_4 and O_2, and between C_3 and O_2, of 3·18 and 3·32 Å respectively, all are greater than 3·4 Å. The arrangement is completely consistent with the observed easy cleavage parallel to (100) and to (010), and with the relatively low melting point of 168 °C. The important intermolecular N $\cdots$ O distances and angles are listed in Table 3(b).

Table 3(a). *Intramolecular interatomic distances and angles*

	Distance	Std. dev.		Angle	Std. dev.
S–C_4	1·814 Å	0·017 Å	C_4–S–O_3	107·5°	0·7°
S–O_3	1·488	0·012	C_4–S–C_3	96·7	1·0
S–C_3	1·833	0·022	C_3–S–O_3	104·4	0·8
C_2–C_3	1·493	0·028	S–C_3–C_2	114·9	1·4
C_2–N	1·515	0·022	C_3–C_2–N	109·3	1·3
C_1–C_2	1·574	0·029	C_3–C_2–C_1	109·6	1·5
C_1–O_1	1·240	0·021	C_2–C_1–O_1	114·6	1·4
C_1–O_2	1·215	0·022	C_2–C_1–O_2	114·3	1·4
N–O_3	2·821	0·018	C_1–C_2–N	111·1	1·3
N–O_1	2·651	0·020	O_1–C_1–O_2	130·7	1·5
			C_2–N–O_3	87·6	1·0
			C_2–N–O_1	62·7	1·0
			O_1–N–O_2	140·9	0·5
			S–O_3–N	92·0	0·6
			C_1–O_1–N	71·5	1·2

Table 3(b). *Intermolecular interatomic distances and angles*

	Distance	Std. dev.		Angle	Std. dev.
N $\cdots$ O_1'	2·892 Å	0·020 Å	C_2–N–O_1'	110·7°	1·0°
N $\cdots$ O_1''	2·808	0·017	C_2–N–O_1''	126·4	0·9
N $\cdots$ O_3'	2·826	0·018	C_2–N–O_3'	110·6	1·0

4·3. *Molecular dimensions*

The intramolecular distances and angles in (+)MCS are listed, with estimated standard deviations, in Table 3(a) and shown in Fig. 6. The distances and angles are generally in good agreement with the values obtained for other comparable sulphoxides and amino acids (for a review of sulphoxide data see Abrahams, 1956; and for amino acids see Hahn, 1957). The data available for organic sulphoxides are unfortunately

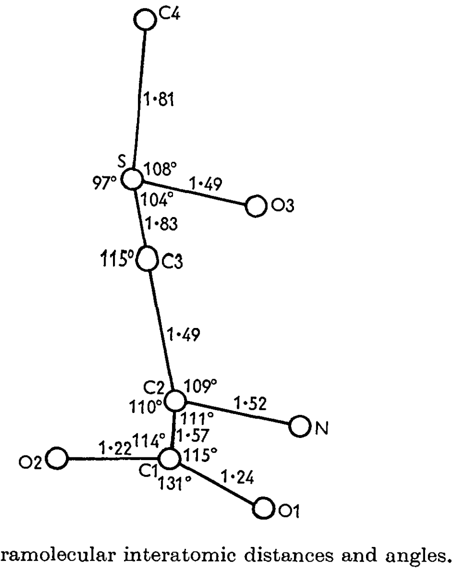

Fig. 6. Intramolecular interatomic distances and angles.

rather sparse: of the compounds listed by Abrahams all are symmetrical, i.e. of the form X–S(0)–X, and only one, diphenyl sulphoxide (Abrahams & Grenville-Wells, 1956) has been examined by X-ray diffraction. For the compounds listed the angle X–S–O is nearly constant at about 106°, while X–S–X varies from about 93° to 114°. (+)MCS is of the form X–S(0)–X', where X' represents the group $CH_2.CH(NH_2).COOH$ and is considerably larger than X, the CH_3 group. This seems to have made little difference to the angles involved: X–S–O = 108°, X'–S–O = 105°, X–S–X' = 97°. The S–C bonds, with lengths of $1{\cdot}81_4$ Å and $1{\cdot}83_3$ Å seem to be completely single in character. It had been thought that the S–O bond might, by reason of its environment, show an increase in length over the value of $1{\cdot}473 \pm 0{\cdot}015$ Å for diphenyl sulphoxide (Abrahams & Grenville-Wells, 1956). This, however, seems not to have occurred; the value of 1·488 Å, with a standard deviation of 0·012 Å, for (+)MCS is not significantly different.

The geometry of the remainder of the molecule requires some discussion. The C_2–N^+H_3 bond at 1·52 Å is in good agreement with previous values (Hahn, 1957), as are the C_1–C_2–N^+H_3, and C_3–C_2–N^+H_3 angles at 111° and 109° respectively. The –N^+H_3 group is elevated out of the plane of the carboxyl group by 7°. The C_2–C_3 bond of length 1·49 Å is not significantly different from the 1·51 Å in serine (Schoemaker *et al.*, 1953), but it may be significantly different from 1·54 Å (Cruickshank, 1949), and in this is completely consistent with the shortening of this bond in many amino acids containing an odd number of carbon atoms in the chain. The dimensions of the C_1–C_2 bond and of the carboxyl group do, however, show some departures from the expected values. The C_1–C_2 bond in α-amino acids shows a significant decrease from the accepted C–C single bond of $1{\cdot}54_5$ Å to an average of about $1{\cdot}51_3$ Å. This shortening seems partly to be reduced in chains containing an odd number of carbon atoms. Thus in serine the C_1–C_2 bond is of length 1·528 Å and in alanine (Donohue, 1950) 1·536 Å; in threonine (Schoemaker *et al.*, 1950) it is 1·517 Å and in norleucine (Mathieson, 1953) 1·49 Å. In (+)MCS, however, this bond is of length 1·57 Å with a standard deviation of 0·030 Å. This is almost two standard deviations longer than $1{\cdot}51_3$ Å and probably can safely be regarded as significantly different, and therefore that the structure is showing hyperconjugation with C_1–C_2 lengthened and C_2–C_3 shortened. In this connection, however, the possibility must be considered that atom C_2 is displaced from its correct position by an amount approaching two standard deviations. An examination of the progress of the refinement gives no grounds for thinking this: the refinement proceeded steadily, and the final shift was less than 0·1 of the standard deviation. Furthermore, the shift required to lengthen C_2–C_3 and shorten C_1–C_2 would lengthen the C_2–N^+H_3 bond and distort the angles at C_2. It can therefore be concluded with some certainty that the shortening of C_2–C_3 from $1{\cdot}54_5$ Å is real. The same considerations may be applied to the placing of C_1. If, by analogy with other comparable structures, C_1–C_2 is expected to be about 1·54 Å, then a change of about one standard deviation would be required in the position of C_1 to correct the observed bond length to the expected value. This would also have the effect of reducing the O_1–C_1–O_2 angle from the rather large 131° to about 127°, which is typical of many amino acids, and of increasing C_1–O_1 by about one standard deviation from 1·24 to 1·26 Å, and C_1–O_2 from 1·22 to 1·24 Å, both of which are very close to values obtained in other amino acids. The O_1–O_2 distance of 2·23 Å is quite usual. Furthermore the position given for C_1 in Table 2 is 0·035 Å away from the best plane through O_1, O_2, C_1, C_2 while O_1, O_2, C_2 are only about a third of this distance away. There are grounds, therefore for thinking that the final position quoted in Table 2 for C_1 may be in error by about one standard deviation.

Work is at present proceeding on the structure of (−)-*S*-methyl-L-cysteine sulphoxide with the objects of (*a*) confirming the allocation of configuration at the sulphur atom, (*b*) examining the dimensions of the amino-acid part of the molecule, and (*c*) examining the effect of the change of configuration at the sulphur upon the crystal structure. Further work is proposed upon related sulphoxides and sulphoximines.

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