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The Crystal Structure of Dimethanesulphonyl Disulphide

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The chemistry and preparation of dimethanesulphonyl disulphide have been described and discussed by Foss [1], who has also pointed out that chemical properties speak in favour of an unbranched sulphur chain. No detailed studies, however, have yet been reported in the literature of the structure of this compound, or any other tetrathionic compound. Lattice dimensions and space group were determined for potassium tetrathionate by Tunell, Merwin and Ksanda [2], but no structure details are available. On the other hand, extensive analyses of the structures of the trisulphides have been reported by Zachariassen [3], Ketelaar and Saunders [4], Robertson *et al.*[5,6] and Donohue [7,8]. Robertson *et al.* have also given some data and a discussion of possible structures for pentathionates. From cell dimensions extended, unbranched sulphur chains are likely in the structures of pentathionates, and such structures are also the most probable on chemical grounds. The same point of view applies to the tetrathionic compounds, thus to dimethanesulphonyl disulphide $(CH_3SO_2S)_2$, for which some preliminary X-ray data and possible structural arrangement were reported by Sörum and Foss [9].

The present paper concerns the results of a detailed analysis of the crystal structure of this compound by Fourier and least squares methods.

Unit cell and space group

The monoclinic crystals are usually found as needles or plates elongated in one direction. The specimen used in this analysis was obtained from one such plate by cutting and grinding it to approximately circular cross-section of about 0.2 mm diameter. Absorption of the X-rays in the specimen should therefore be negligible. All the X-ray photographs were obtained with Cu-K-radiation. Rotation and Weissenberg photographs were prepared with the crystal rotating around the needle axis (a-axis) and around an axis perpendic-

ular to the most prominent crystal face (b-axis). In the first case Weissenberg photographs were also obtained of the first and the second layer-line. The unit cell dimensions, determined from these photographs, are:

$$a = 5.52 \pm 0.02 \text{ Å} \qquad c = 10.05 \pm 0.02 \text{ Å}$$
$$b = 15.78 \pm 0.02 \text{ Å} \qquad \beta = 97.6° \pm 0.5°$$

corresponding to an axial ratio $a : b : c = 0.349 : 1 : 0.637$, volume $V = 866$ Å^3, specific density of 1.71 g/cm^3 and four molecules per unit cell. The following systematic absences of reflexions are recorded:

$0k0$ when k odd,
$00l$ when l odd,
$h0l$ when l odd,

indicating that the b-axis is a screw axis and the (010) plane a glide plane of symmetry with translation $c/2$. Laue patterns indicate monoclinic holoedry and no signs of polarity of the crystals could be detected. The space group was consequently assumed to be $P\frac{2_1}{c}$ (C_{2h}^5).

Arrangement of the molecules in the unit cell

The direct analysis of this structure by the application of phase relationships for determination of the signs was not successful, probably because of the rather low values of the unitary structure factors. Actually very few of these approach 0.5 in magnitude. The structure has therefore been derived from Patterson synthesis, *i.e.* a projection of vector-density on (100), and some useful informations were obtained by the consideration of characteristic intensity variations of the reflexions. Thus, for example, 011 is too weak to be observed, 022 is the strongest one of the $0kl$'s, and 033 too weak to be observed. This might possibly indicate that the molecules lie approximately parallel and symmetrically to the plane (011) or (01$\bar{1}$) and at a distance of approximately one quarter of a diagonal, in the (100)-projection, from the centres of symmetry. On the other hand, an atom located in such a way in the unit cell that its projection on (100) lies on or near a line connecting the centres of symmetry will make no, or only a small contribution to reflexions for which $k + l$ is odd. The fact that reflexions with $k + l$ odd are on the average as strong as reflexions with $k + l$ even suggests that the approximate centres of the molecules are translated about $|b/4|$ and $|c/4|$ from the centres of symmetry.

Fig. 1. Projected vector-density on (100) for dimethanesulphonyl disulphide. One quarter of the unit cell is shown. The orientation of one sulphur chain and the intramolecular S—S distances are indicated.

The Patterson synthesis

With this knowledge of the probable orientation and location of the molecules as backing the further attack on the structure was made by examination of the Patterson projection on (100). The assymmetric part of this projection is shown in Fig. 1. The four sulphur atoms were first assumed to lie approximately in a plane and such that they would fall on a line in the (100)-projection. This assumption led, however, either to unreasonable interatomic distances or to serious contradictions between observed and calculated structure factors. If the four sulphur atoms are placed on a somewhat irregular zigzag line in (100)-projection, the interatomic vectors become more compatible with the maxima of the vector-density projection, and leads simultaneously to an appreciable amelioration of the agreement with observed intensities. The orientation and form of the zigzag sulphur chain is indicated in the vector-

density projection in Fig. 1. The projection of the molecule was then moved along the [011]-direction until a rough agreement with observed structure factors was obtained. The maxima along the line 001/2 in the projection (Fig. 1), some of which are clearly resolved, were also of help in finding the right position of the molecule. With the approximate structure, thus obtained, the signs of the $0kl$ reflexions were calculated and then the first Fourier-projection of electron density on (100).

Fourier and least squares refinement

The first Fourier-projection on (100) showed clearly the positions of the sulphur atoms, though the corresponding maxima were of somewhat uneven heights. The two oxygen atoms attached to the one end sulphur atom were also resolved, but the two other oxygens and the two methyl groups did not show up distinctly. Space considerations led, however, to a probable arrangement of these atoms, and successive calculations of structure factors and the electron density projection improved the resolution of the peaks and the agreement between observed and calculated structure factors. The observed intensities were originally converted to an absolute scale by a method suggested by Wilson [10], as the intensities were determined by visual and relative estimates. The scale factor was readjusted before the final calculation of the electron density projection so as to make $\Sigma|\mathrm{F}(0kl)|$ observed closely equal to $\Sigma|\mathrm{F}(0kl)|$ calculated.

The projection on (100) is shown in Fig. 2, where a little more than a quarter of the unit cell is reproduced in order to illustrate the structure of one complete molecule $(CH_3S_2OS)_2$. The final calculation of the $\mathrm{F}(0kl)$'s resulted in an average discrepancy between observed and calculated values of 18 % for about 170 observed $0kl$-reflexions.

Intensity estimates of about 60 $h0l$-reflexions of a Weissenberg photograph around [010] formed the basis for determination of x-coordinates of the atoms. With the knowledge of the y- and the z-parameters and with assumed interatomic distances (from previous determinations of the structures of similar sulphur compounds), the $F(h0l)$'s could be expressed by one parameter for the displacement of the molecule along the a-axis. The value of this parameter was then chosen so as to give the best possible agreement with experimental data. Two possible arrangement had, however, to be considered. Thus, the direction of the longest extension of the molecule could make either a positive or a negative angle with the c-axis direction. These two possibilities are not widely different since the angle β differs only a few degrees from 90°. In effect, the latter alternative gave only a slightly better agreement with experimental

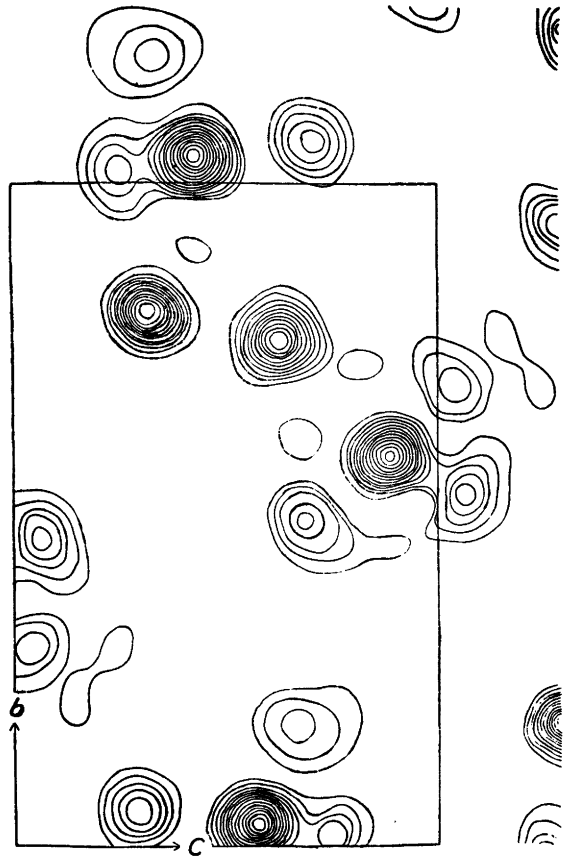

Fig. 2. Projection of electron density on (100) of dimethanesulphonyl disulphide. A little more than one quarter of a unit cell is indicated in order to show the projection of one complete molecule. Contour lines are drawn at intervals of 1 electron per Å^3, beginning with the 3-electron contour.

data than the first alternative in the first calculation of the F($h0l$)'s. The subsequent least squares refinement, by a method including a simplified technique to be described elsewhere [14], led, however, to a substantial improvement in case of the latter alternative, whereas only a slight improvement was obtained in the first case. In addition, some rather unreasonable bond-lengths and bond-angles resulted in the first case, while being within reasonable limits in the latter. Thus, a discrimination between the two alternative structures proved possible and decisive.

Table 1. Atomic coordinates for dimethanesulphonyl disulphide, given in Å. Estimated limits of error are ± 0.02 Å for the S-atoms and ± 0.04 Å for other atoms.

	S_1	S_2	S_3	S_4	O_1	O_2	O_3	O_4	$(CH_3)_1$	$(CH_3)_2$
x	1.95	1.17	−0.34	0.48	3.34	1.78	−0.77	1.27	0.66	1.67
y	0.31	−1.53	−1.89	−3.24	0.13	0.48	−3.73	−4.03	1.36	−2.32
z	2.88	3.42	1.84	0.56	3.69	1.47	−0.34	1.56	3.35	−0.22

The average discrepancy between observed and calculated structure factors, after the least squares refinement, is 19 % for the $h0l$-reflexions alone. For all the reflexions together this error coefficient is 18 %. It seems not unreasonable to claim that this agreement is sufficient to ensure the correctness of the proposed structure. The refinement could possibly be carried a little further, but the intensities are of moderate accuracy, implying that it would not be justified to attempt any great improvement on the ground of these data.

The obtained atomic coordinates are set out in Table 1, and indicated in Fig. 3 for the structure viewed along the a-axis. Observed and calculated structure factors for about 250 reflexions are listed in Table 3. Bond-lengths, bond-angles and interatomic distances are quoted in Table 2.

The structure of the $(CH_3SO_2S)_2$-molecule

It is evident from Fig. 2 that the molecule of $(CH_3SO_2S)_2$ has an unbranched chain of four sulphur atoms, with two oxygens and one methyl group attached to either end sulphur. These four sulphur atoms are, however, not lying in a plane. On the contrary, planes through the two sulphur atoms in the middle of the chain and one or the other of the end sulphurs respectively, would make an angle of approximately 90° with each other. This means that the one CH_3SO_2-group is twisted about 90° out of the plane through the rest of the sulphur chain. The structure of the molecule, with bond-lengths and angles, is indicated in Fig. 4. It is interesting to note the striking similarity between the structure of this molecule, as viewed along the short axis, and the structure of a pentathionate, which has recently been reported in this journal by Foss, Furberg and Hadler [13]. The arrangement of oxygens, methyl and sulphur around the end sulphur atoms is tetrahedral, though somewhat irregular, as it may be seen from the calculated values for the bond-angles in Table 2.

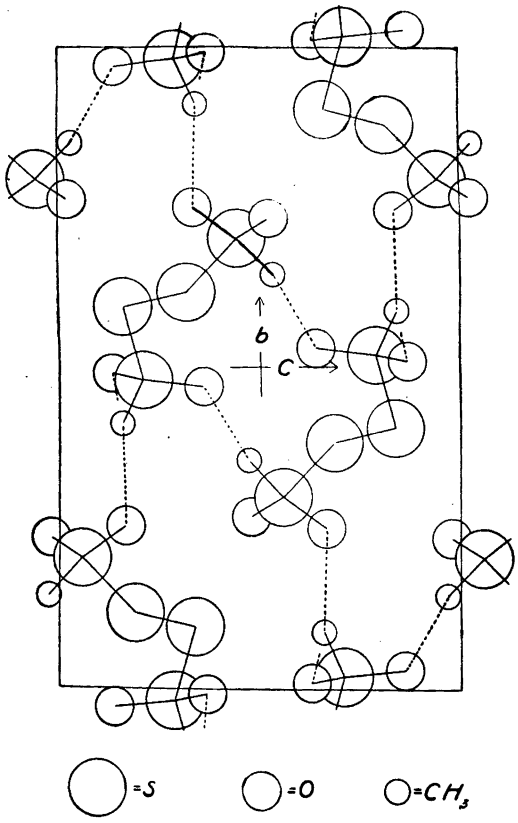

Fig. 3. The structure of dimethanesulphonyl disulphide, viewed in direction of the a*-axis. The centre and the boundaries of the unit cell are indicated. Bonds between the atoms are illustrated by full lines, and dashed lines indicate some short distances, corresponding to weak bonds, between oxygen atoms and methyl groups of different molecules. This weak bond from the O_1 oxygen atom points approximately in the direction of the* a*-axis.*

DISCUSSION OF THE STRUCTURE

The bond-lengths, set out in Table 2, may reasonably be claimed as accurate to within $\pm$ 0.03 Å for the S—S distances and $\pm$ 0.05 Å for the other distances. The diffraction effect of the heavier sulphur atoms may affect the positions of the methyl and oxygen peaks of the projection considerably, especially for the rather close oxygens, and this effect has only been partially removed by the least squares refinement.

The bond-lengths found in this work compare well with those previously reported for sulphur-oxygen compounds. The S—S bonds between the end

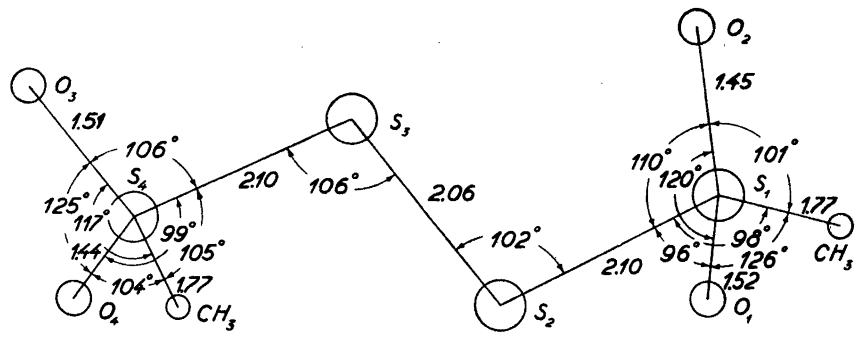

Fig. 4. The structure of the $(CH_3SO_2S)_2$-molecule. Bond-lengths and bond-angles are shown. In this figure the (CH_3SO_2)-group on the left hand side has been turned through an angle of approximately 90° around the line between the two sulphur atoms in the middle of the molecule.

sulphur and the nearest sulphur in the chain are both 2.10 Å, whereas the distance between the two sulphur atoms in the middle of the chain is 2.06 Å. and some significance may be assigned to the difference between these two values. Values ranging from 2.04 Å to 2.16 Å for the S—S distance have been reported in the literature, thus, for example 2.16 Å in trithionate (Zachariassen [3]), 2.07 Å in bisphenylsulphonyl sulphide (Robertson *et al.*[5]), while Warren and Burwell [11], Maxwell and Hendricks [12] determined the S—S distance in elementary sulphur as 2.10 Å. The distance of 2.10 Å, obtained here, may correspond closely to single covalent bond, whereas the slightly shorter S—S distance in the middle of the molecule may indicate some double bond character for that bond.

The S—O distances are on the average 1.48 Å, and thus being close to the value for that bond found in the sulphate ion. The accuracy, attained in this work, does not justify the assignment of any certain significance to the difference of the two S—O bonds, found for both groups, thus, 1.52 Å and 1.45 Å for the first group, 1.51 Å and 1.44 Å for the other group. The sum of the double covalent bond radii for S and O is 1.49 Å and the value of 1.48 Å may, therefore, suggest a considerable double bond character of the S—O bonds. The O—S—O angles are 120° and 125° respectively, thus being close to the expected value for the O—S—O angle of 125.16°, and to the angles found in sulphate and sulphite ions.

The S—CH_3 distances of 1.77 Å are only slightly shorter than the sum of the covalent single bond radii for S and CH_3, thus 1.04 + 0.77 = 1.81 Å.

The distances between non-bonded atoms in the molecule lies within reasonable limits, though the O—O distances of 2.57 Å and 2.62 Å, the O—CH_3

Table 2. Bond lengths, bond angles and some interatomic distances in dimethanesulphonyl disulphide. The limits of error are estimated as ± 0.03 Å for S—S bonds and ± 0.05 Å for other bonds. Errors in the angles are not likely to exceed ± 3°. Values given in brackets refer to distances between atoms of different molecules.

	S_1	S_2	S_3	S_4	O_1	O_2	O_3	O_4	$(CH_3)_1$	$(CH_3)_2$
S_1		2.10	3.24		1.52	1.45			1.77	
S_2	2.10		2.06	3.32	2.72	2.93			2.94	
S_3	3.24	2.06		2.10			2.91	2.72		3.08
S_4		3.32	2.10				1.51	1.44	2.94	1.77
O_1	1.52	2.72				2.57			(3.17)	
O_2	1.45	2.93			2.57					(3.18)
O_3			2.91	1.51				2.62	2.50	2.80
O_4			2.72	1.44			2.62		(3.21)	2.54
$(CH_3)_1$	1.77	2.95			2.94 (3.17)	2.50		(3.21)		
$(CH_3)_2$			3.08	1.77		(3.18)	2.80	2.54		

$\angle S_1-S_2-S_3 = 102°$, $\angle S_2-S_3-S_4 = 106°$, $\angle O_1-S_1-S_2 = 96°$,
$\angle O_2-S_1-S_2 = 110°$ $\angle CH_3-S_1-S_2 = 98°$, $\angle O_1-S_1-O_2 = 120°$,
$\angle CH_3-S_1-O_1 = 126°$, $\angle CH_3-S_1-O_2 = 101°$, $\angle O_3-S_4-S_3 = 106°$,
$\angle O_4-S_4-S_3 = 99°$, $\angle CH_3-S_4-S_3 = 105°$, $\angle O_3-S_4-O_4 = 125°$,
$\angle CH_3-S_4-O_3 = 117°$, $\angle CH_3-S_4-O_4 = 104°$

distances of 2.50 Å and 2.54 Å appear to be rather short. There are significant differences in the distances between $O_1-(CH_3)$ and $O_2-(CH_3)$ for the first group, $O_3-(CH_3)$ and $O_4-(CH_3)$ for the other group. These differences are of the order of 0.3—0.4 Å and may be attributed to steric hindrances.

The molecules are stacked together in pairs around the centres of symmetry, with the direction of their longest extension alternating in the [011] and the [01$\bar{1}$] direction, as may be seen from Fig. 3. The distances between the atoms of different molecules are all above the sum of the van der Waal's radii, except for some distances between oxygen atoms and methyl groups. Such distances are indicated by dashed lines in Fig. 3. The sum of the normal van der Waal's radii for O and CH_3 is 2.0 + 1.4 = 3.40 Å and such distances are usually not found shorter than 3.32 Å. The values of 3.17 Å, 3.18 Å and 3.21 Å found in this structure, are significantly shorter than previous values for this distance, and this observation forces one to conclude that weak bonds, possibly hydrogen bonds, are exerted between oxygen atoms and methyl groups belonging to different molecules. These weak bonds, in addition to normal van der Waal's attraction are holding the molecules together in the crystal.

Table 3. Observed and calculated structure factors for dimethanesulphonyl disulphide. The average discrepancy between observed and calculated values is 18%.

$h\,k\,l$	$F_{obs.}$	$F_{calc.}$	$h\,k\,l$	$F_{obs.}$	$F_{calc.}$
100	52	+50	$\bar{4}04$	—	+18
200	45	−34	$\bar{5}04$	—	−12
300	16	+21	$\bar{6}04$	22	+35
400	39	−36	106	34	+41
500	—	−11	206	73	−76
600	—	−15	306	—	−8
102	35	+27	406	26	+32
202	27	+32	506	13	−2
302	34	−35	$\bar{1}06$	12	−4
402	—	−4	$\bar{2}06$	39	+35
502	12	−18	$\bar{3}06$	—	−12
602	14	+12	$\bar{4}06$	—	−1
$\bar{1}02$	17	+23	$\bar{5}06$	15	−23
$\bar{2}02$	13	−5	$\bar{6}06$	21	−23
$\bar{3}02$	13	−15	108	38	−52
$\bar{4}02$	11	+6	208	—	+5
$\bar{5}02$	23	−30	308	11	−17
$\bar{6}02$	27	−33	$\bar{1}08$	38	−40
104	61	−65	$\bar{2}08$	66	−56
204	28	−31	$\bar{3}08$	29	+23
304	28	−34	$\bar{4}08$	37	+32
404	41	−45	$\bar{5}08$	14	−6
504	17	−24	1010	15	−21
$\bar{1}04$	68	+67	2010	14	−13
$\bar{2}04$	102	+85	3010	22	+13
$\bar{3}04$	78	+80			
$\bar{1}010$	14	−13	0131	25	−18
$\bar{2}010$	48	+47	0151	30	+22
$\bar{3}010$	28	+34	0171	—	−6
1012	16	+25	0191	7	+4
2012	14	+3	021	39	+36
$\bar{1}012$	—	+1	041	18	−21
$\bar{2}012$	19	−20	061	70	−74
$\bar{3}012$	42	−42	081	76	−72
020	31	+26	0101	28	−14
040	26	+40	0121	—	+2
060	22	−20	0141	43	−45
080	74	+67	0161	25	−28
0100	74	+64	0181	24	−24
0120	18	−15	022	100	−95
0140	20	−16	042	12	+17

Table 3 continued.

h k l	$F_{obs.}$	$F_{calc.}$	*h k l*	$F_{obs.}$	$F_{calc.}$
0160	15	−15	062	9	−2
0180	20	−19	082	42	−45
0200	8	+8	0102	16	−17
002	34	−38	0122	14	−13
004	30	−25	0142	29	+31
006	57	+61	0162	—	−1
008	34	−43	012	40	+39
0010	21	−30	032	27	−29
0012	—	−4	052	—	−4
011	—	−1	072	—	+4
031	56	−60	092	15	+17
051	36	+37	0112	34	+30
071	16	−20	0132	18	−19
091	—	+7	0152	—	−2
0111	36	−39	0172	25	+30
0192	13	+20	054	—	+1
013	49	+48	074	9	+16
033	—	+6	094	57	−65
053	23	+27	0114	12	+5
073	22	−29	0134	16	−17
093	33	+27	0154	12	+14
0113	36	+37	0174	16	−28
0133	31	+35	015	18	−15
0153	16	−16	035	35	−38
0173	26	−29	055	35	−33
0193	21	+9	075	—	+13
023	6	+6	095	—	+5
043	14	−13	0115	20	−21
063	40	+43	0135	—	−5
083	—	−6	0155	—	+12
0103	—	+7	0175	19	+26
0123	35	+26	025	21	−24
0143	—	+3	045	33	−33
0163	39	+35	065	41	+56
024	16	−20	085	11	+4
044	16	+16	0105	12	−7
064	27	+28	0125	12	−12
084	—	−4	0145	26	−19
0104	15	−16	0165	16	+23
0124	14	−14	0185	8	−8
0144	16	+18	026	20	+16
0164	11	+3	046	33	−40
0184	8	−4	066	33	−36

Table 3 continued.

h k l	$F_{obs.}$	$F_{calc.}$	*h k l*	$F_{obs.}$	$F_{calc.}$
014	26	−9	086	31	+34
034	16	−19	0106	—	+7
0126	14	+13	0108	22	−26
0146	30	−26	0128	24	+26
016	15	+16	0148	9	+4
036	27	+25	018	14	−8
056	—	+8	038	24	−30
076	27	+18	058	14	−12
096	—	−4	078	—	−6
0116	50	+58	098	15	−16
0136	14	+9	0118	17	−17
0156	15	+12	0138	27	−28
0176	14	+6	0158	19	−20
017	—	−1	019	14	−15
037	48	+42	039	14	−6
057	22	+22	059	37	−47
077	33	+36	079	—	−12
097	19	−21	099	14	−16
0117	14	−15	0119	—	+16
0137	—	+1	0139	17	+17
0157	14	−11	029	19	−15
027	40	+35	049	—	+6
047	—	+1	069	—	+9
067	14	−15	089	9	−5
087	24	−24	0109	16	−18
0107	14	+17	0129	18	+11
0127	25	+30	0210	15	+19
0147	12	−22	0410	10	−9
028	14	+17	0610	17	+23
048	19	+17	0810	18	+13
068	14	+13	01010	15	−14
088	—	−3			
0110	15	−20	0911	15	+12
0310	15	+9	0211	18	−21
0510	10	+12	0411	10	+4
0710	—	+18	0611	10	−8
0910	—	−1	0811	16	+10
01110	10	+8	0212	9	−4
0111	10	+14	0412	19	−32
0311	15	+12	0612	18	−28
0511	10	−11	0312	20	+29
0711	19	+32			

SUMMARY

The structure of dimethanesulphonyl disulphide has been determined in detail from X-ray intensity data by Fourier and least squares methods.

Atomic coordinates, bond-angles and interatomic distances are given, the structure is described and discussed. It is shown that the $(CH_3SO_2S)_2$ molecule has an unbranched zigzag sulphur chain. Weak hydrogen bonds between oxygen atoms and methyl groups appear to be acting as intermolecular forces in this structure.

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