$$\delta = \tfrac{1}{2} \quad \text{and} \quad \mathbf{t}_{AB} = \tfrac{1}{2}\mathbf{t}_{AA} = \tfrac{1}{2}\mathbf{t}_{BB}\,.$$

The theory can be extended in an obvious manner to the case of several motif points within the primitive unit cell.

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The Crystal Structure of 1,4-Dithiane*

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The crystal structure of 1,4-dithiane has been determined and refined by least-squares methods, using complete three-dimensional diffraction data from copper X-radiation. The compound is isomorphous with 1,4-diselenane, and hence the molecule has the centro-symmetric chair configuration, as reported by Dothie. The bond distances and standard deviations are: $S–C_1$, 1·801± 0·013 Å; $S–C_2$, 1·821±0·011 Å; $C_1–C_2$, 1·490±0·018 Å.

Introduction

In an electron-diffraction investigation of 1,4-dithiane, $C_4H_8S_2$, Hassel & Viervoll (1947) reported sulfur–carbon distances of approximately 1·81 Å, which is the sum of the accepted single-bond radii of carbon and sulfur (Pauling, 1948), but were unable to differentiate between two different models for the molecule. An X-ray diffraction investigation of 1,4-diselenane (Marsh & McCullough, 1951) showed that this molecule has the expected chair form; however, the average Se–C distance proved to be 2·01 Å—significantly greater than the sum of the single-bond radii of selenium and carbon (1·94 Å). The present X-ray diffraction investigation of crystals of 1,4-dithiane was undertaken to provide a check on the S–C distances, as well as to ascertain the molecular configuration. Recently, Dothie (1953) has reported unit-cell dimensions and space-group symmetry for 1,4-dithiane which require that the molecule be in the centro-symmetric chair configuration.

Experimental

A sample of 1,4-dithiane was recrystallized by slow sublimation in a sealed ampoule. The resulting monoclinic crystals, which were elongated in the *b* direction, were sealed in thin-wall glass capillaries to prevent evaporation during X-ray photography. Two crystals were photographed; one was oriented with its *b* axis parallel to the axis of the capillary and had dimensions of about 0·5×1·5×0·2 mm., while the other had its *c* axis approximately parallel to the axis of the capillary and had dimensions of about 0·3×0·4×0·2 mm. Multiple-film Weissenberg photographs were prepared with unfiltered copper X-radiation for the equator and first four layer lines about the *b* axis, and for the equator and first six layer lines about the *c* axis; by this means, all of the reflections within the sphere of copper radiation were recorded. Out of the total of 618 reflections within the sphere, 548 were strong enough to be observed. Intensities were estimated visually by comparison with a calibrated strip, and a film factor of $3{\cdot}8^{\sec\mu}$ was used to correlate intensities of successive photographs, μ being the equi-inclination angle. No correction was made for absorption.

The space-group symmetry, as determined from the Weissenberg photographs, is that of $C_{2h}^5–P2_1/n$. Approximate unit-cell dimensions and intensity comparisons showed that the compound is isomorphous with 1,4-diselenane (Marsh & McCullough, 1951); there are thus two centro-symmetric molecules in the unit cell, in agreement with the findings of Dothie (1953). Accurate values for the lattice parameters

Table 1. *Lattice parameters*

	1,4-Dithiane		
	This investigation (1)	Dothie (2)	1,4-Diselenane (3)
a	6·763±0·002 Å	6·74 Å	6·97±0·02 Å
b	5·464±0·005 Å	5·46 Å	5·62±0·02 Å
c	7·844±0·003 Å	7·69 Å	8·01±0·02 Å
β	92·67 ±0·04°	91·53°	93·6 ±0·1°
c'	10·12 ±0·008 Å	10·09 Å	—
β'	129·25 ±0·07°	130·37°	—

(λ = 1·5418 for Cu $K\alpha$, 1·54050 for Cu $K\alpha_1$, 1·54434 for Cu $K\alpha_2$)

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Table 2. *Atomic positional parameters for* 1,4-*dithiane*

		Starting parameters	Fouriers on (010) and (001)	Least squares No. 1	Least squares No. 2	Least squares No. 3	Probable error
S	x	0·225	0·217	0·2179	0·2184	0·2184	0·0002
	y	0·167	0·160	0·1586	0·1579	0·1578	0·0003
	z	0·038	0·038	0·0395	0·0397	0·0397	0·0002
C_1	x	0·987	0·996	0·9932	0·9942	0·9953	0·0008
	y	0·183	0·175	0·1784	0·1789	0·1792	0·0009
	z	0·167	0·158	0·1560	0·1555	0·1556	0·0008
C_2	x	0·192	0·186	0·1859	0·1869	0·1875	0·0008
	y	0·835	0·840	0·8449	0·8479	0·8485	0·0008
	z	0·947	0·955	0·9559	0·9554	0·9562	0·0008
R		—	0·19*	0·137†	0·134†	—	—

* Isotropic temperature factor applied to calculated structure factors.
† Anisotropic temperature factor applied to calculated structure factors.

were obtained from photographs prepared in a Straumanis-type single-crystal rotation camera, using Cu $K\alpha$ radiation. These photographs were indexed by comparison with the Weissenberg photographs, and a least-squares adjustment of values of sin θ resulted in the lattice parameters and probable errors which are listed in column (1), Table 1. For comparison, the values reported by Dothie are given in column (2), while the values found by Marsh & McCullough for 1,4-diselenane are given in column (3).

Values for c' and β' in Table 1 refer to the alternate space group setting $P2_1/a$—the setting on which Dothie's measurements were based. Thus, although the agreement between the present values and those of Dothie does not, at first glance, appear to be too satisfactory, it is seen that the source of discrepancy lies in the value of β'. Indeed, if the value of β' as reported by Dothie from optical-goniometric measurements, namely 129·42°, be accepted in preference to the value of 130·37° obtained by him from rotation photographs, the overall agreement of lattice parameters is quite adequate. As a check on the values of β and β', measurements were made of the lattice-row separations on a zero-layer Weissenberg photograph taken about the b axis. The lateral spacing between equivalent lattice rows 180° apart was used for calibration. The resulting values for β and β' were 92·63° and 129·17°, in good agreement with Dothie's goniometric values and with the values obtained from the least-squares analysis of the Straumanis-type photographs.

Refinement of atomic positional parameters

As a starting point for the refinement of the positional parameters for the sulfur atom and the two carbon atoms within the asymmetric unit, the final parameters found for 1,4-diselenane (Marsh & McCullough, 1951) were used to calculate signs of structure factors of the type $hk0$ and $h0l$. Fourier projections and difference maps were then calculated for these two zones, and the resulting improved parameters were used for the first three-dimensional structure-factor calculations. The atomic form factors of James & Brindley (1935) were used for sulfur, while the values of McWeeny (1951) were used for the carbon atoms. The observed data were placed on an absolute scale by application of an empirical scale factor, and the calculated structure factors were corrected by an empirical isotropic temperature factor with $B = 2{\cdot}85$ Å^2. At this stage the correlation factor R was 0·19.

Table 3

	$\Sigma\lvert F_o\rvert$	$\Sigma\lvert F_c\rvert$	$\Sigma\lvert\Delta F\rvert$	R	n
h					
0	1951	2035	306	0·157	42
1	2771	2727	374	0·135	87
2	3556	3468	428	0·120	92
3	3321	3316	401	0·121	85
4	2110	1986	294	0·139	74
5	2147	2177	286	0·133	67
6	920	867	143	0·155	43
7	883	850	107	0·122	33
8	264	280	54	0·205	14
k					
0	2705	2786	257	0·095	57
1	4411	4339	496	0·113	119
2	4341	4131	562	0·129	113
3	2803	2668	423	0·151	93
4	2096	2215	391	0·187	79
5	1055	1020	191	0·181	47
6	512	547	73	0·143	29
l					
0	1650	1712	196	0·119	37
1	3098	3211	509	0·165	79
2	2920	2774	366	0·126	76
3	3133	2976	397	0·128	80
4	2562	2442	328	0·128	72
5	1887	1865	234	0·124	66
6	1268	1266	162	0·128	51
7	802	845	125	0·156	38
8	404	417	43	0·106	24
9	199	198	33	0·166	14
All reflections	17923	17706	2393	0·134	537

Three successive least-squares refinements of the atomic parameters were carried out, using all of the observed data. A weighting system similar to that of Hughes (1941) was used, with the exception that eleven low-order reflections apparently suffering from extinction were given zero weight. The off-diagonal terms in the matrices representing the nine normal equations were neglected; the unit cell is nearly orthogonal, so that even the coupling between the x and z coordinates of the same atom would be expected to be small.

Prior to the second least-squares refinement, an anisotropic temperature factor was applied to the calculated structure factors. This empirical correction was of the form $\exp(-B\sin^2\theta/\lambda^2-\alpha h^2/4a^2-\gamma l^2/4c^2)$, values of B, α, and γ being 2·85 Å^2, −0·46 Å^2, and 0·66 Å^2, respectively. This temperature factor probably has little significance in terms of thermal motions of the atoms; rather, it probably represents absorption and spot-shape effects due to the anisotropic shapes of the crystals and capillaries. Whatever its basis, the improvement in intensity agreement and resulting reduction in probable errors of the atomic parameters warrants its application.

The nine atomic coordinates obtained after each

Table 4. *Observed and calculated structure factors for* 1,4-*dithiane*

h	$F_{\text{obs.}}$	$F_{\text{cal.}}$
h00		
2	12.9	-18.1
4	12.2	13.2
6	<.5	.3
8	<.4	-.1
h01		
$\bar{7}$	5.9	-5.9
$\bar{5}$	11.6	13.4
$\bar{3}$	10.6	-14.5
$\bar{1}$	9.9	18.1
1	9.5	11.0
3	7.8	-7.5
5	9.5	10.5
7	4.5	-4.1
h02		
$\bar{8}$	3.3	-3.2
$\bar{6}$	<.5	.3
$\bar{4}$	3.3	3.5
$\bar{2}$	16.3	-21.2
0	13.1	25.2
2	16.9	-21.4
4	9.2	9.0
6	4.3	-4.0
8	.8	.8
h03		
$\bar{7}$	6.2	-6.3
$\bar{5}$	9.4	8.4
$\bar{3}$	17.6	-18.3
$\bar{1}$	5.1	5.9
1	8.6	-9.3
3	5.8	-4.7
5	1.3	.8
7	3.1	-3.1
h04		
$\bar{8}$	2.7	-3.2
$\bar{6}$	2.3	2.1
$\bar{4}$	1.3	-1.4
$\bar{2}$	6.8	-8.2
0	6.6	6.6
2	11.3	-11.7
4	5.9	4.9
6	4.6	-4.9
h05		
$\bar{7}$	2.3	-2.2
$\bar{5}$	6.5	6.1
$\bar{3}$	7.4	-7.6
$\bar{1}$	7.7	9.1
1	5.5	-6.2
3	4.5	4.2
5	1.5	-1.7
7	<.3	.2
h06		
$\bar{6}$	3.7	3.5
$\bar{4}$	1.1	-1.1
$\bar{2}$	3.1	3.1
0	2.5	2.3
2	.7	-.4
4	4.1	3.9
6	2.1	-1.9
h07		
$\bar{5}$	2.7	2.1
$\bar{3}$	2.2	-1.8
$\bar{1}$	5.4	5.4
1	3.5	-3.7
3	5.1	5.3
5	2.0	-2.0
h08		
$\bar{4}$	2.4	-2.4
$\bar{2}$	3.0	2.8
0	1.8	-2.4
2	.9	1.1
4	.6	.6
h09		
$\bar{3}$	1.1	-.7
$\bar{1}$	.7	.6
1	3.0	-2.9
3	1.8	2.1
h10		
1	7.7	8.9
2	2.8	-1.9
3	4.5	-5.6
4	5.2	5.3
5	6.5	7.0
6	4.7	-4.5
7	3.1	-2.6
8	3.6	3.4
h11		
$\bar{8}$	.6	-1.0
$\bar{7}$	1.3	1.7
$\bar{6}$	<.6	.3
$\bar{5}$	1.0	-.9
$\bar{4}$	5.0	4.7
$\bar{3}$	9.6	10.3
$\bar{2}$	9.0	-10.6
$\bar{1}$	2.7	-3.9
0	14.1	20.9
1	15.9	-20.2
2	10.7	-10.5
3	6.4	8.7
4	6.1	6.2
5	7.7	-8.8
6	1.6	-.9
7	2.3	2.1
8	.9	.3
h12		
$\bar{8}$	3.0	2.9
$\bar{7}$	3.9	-3.5
$\bar{6}$	3.8	-3.3
$\bar{5}$	6.1	5.8
$\bar{4}$	10.3	9.8
$\bar{3}$	9.3	-9.5
$\bar{2}$	5.9	-5.7
$\bar{1}$	4.1	5.2
0	12.6	-18.6
1	2.2	-.9
2	.9	1.1
3	3.9	-3.6
4	1.9	-1.8
5	2.4	2.8
6	4.3	-4.7
7	1.9	-2.0
8	2.4	2.1
h13		
$\bar{8}$	1.4	-1.9
$\bar{7}$	2.0	-1.8
$\bar{6}$	<.6	.5
$\bar{5}$	1.7	1.9
$\bar{4}$	0.9	0.0
$\bar{3}$	0.6	0.0
$\bar{2}$	8.3	-8.0
$\bar{1}$	5.0	-3.3
0	6.8	6.7
1	10.6	-11.5
2	9.1	-9.1
3	9.9	10.3
4	4.0	3.4
5	7.6	-8.4
6	2.7	-2.6
7	3.0	3.2
8	.6	.5
h14		
$\bar{7}$	2.5	-2.3
$\bar{6}$	4.2	-3.7
$\bar{5}$	4.9	3.9
$\bar{4}$	5.9	4.9
$\bar{3}$	7.4	-6.7
$\bar{2}$	13.5	-13.3
$\bar{1}$	4.9	4.2
0	7.7	-10.0
1	4.0	-4.2
2	10.1	9.8
3	1.1	.2
4	1.0	-1.0
5	.6	-.6
6	<.7	-.6
7	1.1	-.7
h15		
$\bar{7}$	3.4	-3.3
$\bar{6}$	1.7	1.7
$\bar{5}$	3.2	2.8
$\bar{4}$	<.6	-.6
$\bar{3}$	6.1	-5.5
$\bar{2}$	.5	-.5
$\bar{1}$	2.8	-2.3
0	1.9	2.3
1	2.5	-2.4
2	2.3	-2.5
3	8.3	8.5
4	2.7	2.4
5	4.2	-4.1
6	1.9	-1.7
7	3.2	3.4
h16		
$\bar{7}$	<.7	-.4
$\bar{6}$	1.5	-1.0
$\bar{5}$	2.6	2.2
$\bar{4}$	4.0	3.3
$\bar{3}$	2.7	-2.0
$\bar{2}$	8.0	-7.6
$\bar{1}$	3.5	4.0
0	5.9	-7.6
1	2.5	-2.4
2	6.7	6.9
3	3.2	3.0
4	2.3	-2.0
5	1.3	-1.0
6	.8	.7
h17		
$\bar{6}$	.8	1.3
$\bar{5}$	4.4	3.9
$\bar{4}$	1.3	-1.0
$\bar{3}$	3.2	-2.9
$\bar{2}$	2.0	1.8
$\bar{1}$	2.3	2.5
0	<.6	-.4
1	1.7	-1.5
2	.7	.5
3	2.1	2.0
4	1.0	1.1
5	2.3	-2.5
h18		
$\bar{5}$	<.5	.1
$\bar{4}$	2.8	1.9
$\bar{3}$	.6	-.6
$\bar{2}$	2.3	-2.2
$\bar{1}$	1.4	1.3
0	4.2	-4.7
1	1.9	-1.8
2	2.3	2.3
3	1.9	1.9
4	2.3	-2.3
h19		
$\bar{3}$	1.9	-1.8
$\bar{2}$	1.0	1.1
$\bar{1}$	2.3	1.9
0	1.7	-1.6
1	.5	.1
2	.5	.5
h20		
0	12.5	-14.5
1	11.2	-11.0
2	4.8	4.1
3	8.4	9.4
4	4.4	-4.9
5	5.1	-4.9
6	.8	-.4
7	2.3	2.1
8	.3	-.1
h21		
$\bar{8}$	3.0	3.4
$\bar{7}$	1.8	1.9
$\bar{6}$	3.6	-3.5
$\bar{5}$	4.2	-4.5
$\bar{4}$	7.3	8.2
$\bar{3}$	4.0	3.9
$\bar{2}$	4.2	-3.2
$\bar{1}$	6.5	-5.4
0	11.3	-10.1
1	4.5	-3.1
2	.8	-1.1
3	2.3	1.5
4	.8	1.1
5	4.1	-3.7
6	4.5	-4.9
7	1.6	1.2
8	1.9	2.7
h22		
$\bar{8}$	1.3	1.2
$\bar{7}$	<.5	.1
$\bar{6}$	.6	.1
$\bar{5}$	1.3	1.0
$\bar{4}$	.5	-.8
$\bar{3}$	5.4	5.0
$\bar{2}$	5.5	6.3
$\bar{1}$	4.1	-2.9
0	8.8	-6.2
1	15.7	-15.0
2	8.2	6.8
3	9.8	9.2
4	3.3	-3.0
5	8.0	-9.2
6	1.1	1.5
7	3.2	2.6
8	<.4	-.3
h23		
$\bar{8}$	.9	1.4
$\bar{7}$	1.9	2.3
$\bar{6}$	3.5	-3.5
$\bar{5}$	2.4	-2.3
$\bar{4}$	7.5	7.1
$\bar{3}$	7.5	6.4
$\bar{2}$	11.3	-10.4
$\bar{1}$	1.9	-1.5
0	14.0	-12.5
1	4.5	4.0
2	7.8	6.3
3	3.0	1.8
4	1.9	-1.5
5	0.6	0.0
6	1.9	-2.5
7	1.7	1.3
h24		
$\bar{7}$	2.8	-2.9
$\bar{6}$	.9	-.6
$\bar{5}$	2.4	2.3
$\bar{4}$	1.8	.9
$\bar{3}$	3.9	-3.8
$\bar{2}$	3.2	2.8
$\bar{1}$	3.7	-3.4
0	1.6	-1.6
1	6.1	5.5
2	5.9	4.2
3	9.9	9.9
4	1.9	-1.4
5	5.7	-6.0
6	1.8	2.0
7	3.9	3.5
h25		
$\bar{7}$	<.5	.6
$\bar{6}$	2.4	-2.3
$\bar{5}$	2.2	-2.1
$\bar{4}$	4.5	3.8
$\bar{3}$	3.3	2.5
$\bar{2}$	10.4	-10.5
$\bar{1}$	3.6	-3.3
0	8.5	-8.4
1	2.5	2.2
2	8.6	8.7
3	1.4	-1.5
4	2.3	-1.4
5	1.0	.6
6	.7	.4
h26		
$\bar{6}$	2.0	-1.4
$\bar{5}$	3.4	3.7
$\bar{4}$	<.5	.2
$\bar{3}$	4.2	-4.2
$\bar{2}$	1.6	-1.4
$\bar{1}$	.7	.8
0	1.9	-1.1
1	1.7	-1.9
2	<.5	-.1
3	4.3	4.8
4	2.0	-1.6
5	3.2	-3.2
6	<.5	.6
h27		
$\bar{5}$	1.2	-.9
$\bar{4}$	3.2	2.7
$\bar{3}$	.5	.5
$\bar{2}$	4.1	-4.2
$\bar{1}$	2.3	-2.2
0	5.0	-6.3
1	.9	1.1
2	3.7	4.1
3	1.7	-2.0
4	2.5	-2.4
5	<.5	.5
h28		
$\bar{4}$	.9	.9
$\bar{3}$	2.0	-2.2
$\bar{2}$	1.0	-1.0
$\bar{1}$	2.3	2.4
0	<.5	.9
1	.5	-.7
2	<.5	-.4
3	<.6	.6
h29		
$\bar{2}$	1.2	-1.4
$\bar{1}$	<.5	-.2
0	2.3	-2.4
1	1.2	1.1
2	.7	1.6
h30		
1	7.1	-7.8
2	.5	-.2
3	6.2	5.8
4	.4	.4
5	8.0	-8.9
6	<.5	-.6
7	3.5	3.2
h31		
$\bar{7}$	.5	0.0
$\bar{6}$	<.5	-.4
$\bar{5}$	1.0	-.8
$\bar{4}$	4.9	-5.8
$\bar{3}$	.5	.2
$\bar{2}$	10.1	10.7
$\bar{1}$	1.4	-1.7
0	15.9	-18.9
1	1.7	-.7
2	12.3	11.3
3	2.4	2.0
4	8.2	-8.1
5	1.6	-.8
6	1.4	1.0
7	1.3	.7
h32		
$\bar{7}$	4.7	4.7
$\bar{6}$	.6	-.7
$\bar{5}$	6.9	-7.1
$\bar{4}$	<.5	.4
$\bar{3}$	10.3	11.2
$\bar{2}$	2.3	-1.9
$\bar{1}$	7.1	-5.9
0	1.9	-.8
1	1.9	2.1
2	3.5	1.6
3	4.1	3.8
4	.8	.4
5	3.4	-3.5
6	.5	-.2
7	2.9	2.6
h33		
$\bar{7}$	<.4	-.2
$\bar{6}$	.6	-.5
$\bar{5}$	<.5	.3
$\bar{4}$	.8	.3
$\bar{3}$	.5	-.3
$\bar{2}$	9.3	8.9
$\bar{1}$	.6	-.5
0	8.1	-7.1
1	.7	-1.1
2	12.2	11.1
3	2.5	1.8
4	5.0	-4.1
5	1.3	-1.1
6	3.4	3.6
7	1.2	.7
h34		
$\bar{7}$	2.3	3.1
$\bar{6}$	<.3	-.1
$\bar{5}$	4.8	-4.8
$\bar{4}$	1.2	1.1
$\bar{3}$	9.5	8.6
$\bar{2}$	1.8	-1.2
$\bar{1}$	5.5	-5.4
0	2.9	-2.2
1	7.1	5.8
2	2.5	1.0
3	<.4	-.1
4	1.5	-.5
5	.5	.9
6	.5	-.3
h35		
$\bar{6}$	1.9	-2.3
$\bar{5}$	.9	.9
$\bar{4}$	.8	.7
$\bar{3}$	.5	-.3
$\bar{2}$	.5	.4
$\bar{1}$	1.0	.5
0	3.0	-2.9
1	.8	-1.1
2	3.7	3.2
3	<.5	.8
4	3.4	-3.1
5	1.0	-1.1
6	2.1	2.3
h36		
$\bar{6}$	<.6	-.1
$\bar{5}$	2.7	-3.0
$\bar{4}$	1.0	.6
$\bar{3}$	2.3	2.5
$\bar{2}$	.9	-1.0
$\bar{1}$	5.4	-5.5
0	1.7	-1.4
1	3.0	2.9
2	.8	.8
3	3.6	-4.0
4	1.1	-.5
5	.8	1.2
h37		
$\bar{4}$	1.0	1.2
$\bar{3}$	.5	-.7
$\bar{2}$	2.2	-2.5
$\bar{1}$	.4	.1
0	<.5	.3
1	<.5	-.1
2	.5	-.8
3	<.4	.6
4	1.5	-1.6
h38		
$\bar{3}$	.9	.8
$\bar{2}$	.6	-.7
$\bar{1}$	1.5	-1.7
0	<.4	-.5
1	1.9	2.4
2	.4	.6
h40		
0	7.5	-9.3
1	4.8	5.5
2	6.6	6.3
3	4.3	-4.6
4	3.9	-3.4
5	1.7	2.2
6	1.3	.2
h41		
$\bar{7}$	2.6	2.3
$\bar{6}$	1.9	1.5
$\bar{5}$	3.5	-4.4
$\bar{4}$	4.3	-4.5
$\bar{3}$	3.9	4.9
$\bar{2}$	2.1	1.4
$\bar{1}$	2.5	3.3
0	3.4	4.2
1	.8	-1.1
2	2.3	1.4
3	2.4	2.9
4	1.6	-.4
5	2.5	-3.3
6	2.8	2.7
7	.4	1.7
h42		
$\bar{6}$	<.5	-.3
$\bar{5}$	.9	-.8
$\bar{4}$	.7	-1.6
$\bar{3}$	2.9	-3.0
$\bar{2}$	5.5	5.2
$\bar{1}$	1.9	1.7
0	6.3	-6.7
1	8.3	7.4
2	6.4	5.9
3	4.0	-3.8
4	3.4	-3.2
5	3.7	4.7
6	1.8	1.2
h43		
$\bar{6}$	1.2	1.8
$\bar{5}$	3.5	-3.5
$\bar{4}$	4.0	-3.5
$\bar{3}$	4.7	5.0
$\bar{2}$	4.4	4.7
$\bar{1}$	2.9	-3.3
0	5.1	5.3
1	2.3	1.8
2	1.8	-2.4
3	.6	.7
4	<.5	.8
5	.5	-.7
6	2.0	1.4
h44		
$\bar{6}$	<.5	-.9
$\bar{5}$	.9	-.8
$\bar{4}$	.7	.1
$\bar{3}$	1.6	1.9
$\bar{2}$	1.8	2.0
$\bar{1}$	2.3	2.1
0	2.4	-2.8
1	3.1	2.3
2	2.5	3.2
3	5.1	-4.8
4	2.2	-2.0
5	2.4	2.7
6	1.2	1.4
h45		
$\bar{5}$	1.4	-2.1
$\bar{4}$	1.2	-1.5
$\bar{3}$	2.2	2.7
$\bar{2}$	4.8	5.3
$\bar{1}$	2.5	-2.8
0	2.7	3.4
1	1.9	2.1
2	4.0	-4.4
3	2.2	-1.3
4	<.5	.4
5	1.0	.6
h46		
$\bar{5}$	1.1	-1.7
$\bar{4}$	<.5	.6
$\bar{3}$	1.8	2.1
$\bar{2}$	.5	-.6
$\bar{1}$	<.5	-.2
0	<.5	-.4
1	.5	.7
2	<.5	.5
3	2.4	-2.4
4	1.0	-1.0
h47		
$\bar{2}$	1.4	1.8
$\bar{1}$	.9	-1.5
0	2.0	3.2
1	1.2	1.5
2	.8	-1.9
h50		
1	1.6	1.6
2	1.0	1.2
3	<.5	.2
4	1.9	-2.1
5	1.8	1.5
h51		
$\bar{5}$	1.0	.7
$\bar{4}$	<.6	.9
$\bar{3}$	2.5	-3.3
$\bar{2}$	<.7	-.7
$\bar{1}$	3.2	3.3
0	2.3	2.4
1	5.4	5.7
2	<.7	-.8
3	4.5	-4.0
4	1.0	1.5
5	3.4	3.5
h52		
$\bar{5}$	.5	.5
$\bar{4}$	2.9	-3.5
$\bar{3}$	1.8	-1.6
$\bar{2}$	2.9	3.1
$\bar{1}$	<.6	.5
0	4.3	4.5
1	<.6	-.7
2	1.9	-1.1
3	1.3	-.5
4	<.6	.3
5	1.2	.3
h53		
$\bar{5}$	<.5	-.8
$\bar{4}$	.9	-.7
$\bar{3}$	<.6	0.0
$\bar{2}$	.9	-1.5
$\bar{1}$	1.7	1.7
0	<.6	.2
1	4.3	4.1
2	2.5	-2.0
3	4.9	4.3
4	<.6	.2
5	5.0	3.6
h54		
$\bar{5}$	<.5	.3
$\bar{4}$	1.9	-2.3
$\bar{3}$	1.5	-1.4
$\bar{2}$	4.5	4.9
$\bar{1}$	<.8	.4
0	4.1	4.3
1	1.3	-1.3
2	4.0	-3.6
3	1.2	-.3
4	.7	.7
h55		
$\bar{4}$	<.7	-.1
$\bar{3}$	1.4	2.1
$\bar{2}$	<1.0	.2
$\bar{1}$	1.0	.5
0	1.0	.4
1	1.1	1.4
2	1.3	-.4
3	3.3	-3.4
4	1.1	.5
h56		
$\bar{3}$	<.8	0.0
$\bar{2}$	2.5	3.2
$\bar{1}$	1.1	1.2
0	3.0	3.4
1	<1.0	-.1
2	2.3	-2.9
h60		
0	5.2	5.8
1	<.5	.8
2	2.9	-3.1
3	.7	-.7
4	2.0	2.6
h61		
$\bar{4}$	<.5	-.1
$\bar{3}$	2.4	-2.6
$\bar{2}$	.5	.9
$\bar{1}$	1.9	2.2
0	<.6	.1
1	<.6	.9
2	1.2	-.6
3	1.4	-1.3
4	.5	-.4
h62		
$\bar{4}$	<.4	-.7
$\bar{3}$	<.5	.2
$\bar{2}$	3.0	-3.2
$\bar{1}$	.8	.8
0	3.4	3.6
1	<.5	.5
2	3.9	-3.7
3	1.5	-1.4
4	1.9	1.9
h63		
$\bar{3}$	3.0	-3.5
$\bar{2}$	.9	1.0
$\bar{1}$	1.4	1.5
0	.8	1.0
1	1.4	-1.7
2	1.6	-.9
3	.6	-.7
h64		
$\bar{3}$	<.5	.1
$\bar{2}$	1.1	-1.4
$\bar{1}$	<.6	-.2
0	1.4	1.3
1	<.5	.9
2	2.3	-2.3
h65		
$\bar{1}$	1.5	1.9
0	1.2	1.3
1	.8	-1.4

Corrections to above table.—$F(124)_{\text{cal.}}$ should −5·5, $F(\bar{1}41)_{\text{cal.}}$ should be −3·3, $F(353)_{\text{cal.}}$ should be −4·3.

Table 5. *Bond distances and angles*

1,4-Dithiane		1,4-Diselenane	
S–C_1	1·801±0·013 Å	Se–C_1	1·99±0·06 Å
S–C_2	1·821±0·011	Se–C_2	2·04±0·09
C_1–C_2	1·490±0·018	C_1–C_2	1·54±0·06
S–S (non-bonded)	3·452±0·007	Se–Se (non-bonded)	3·66±0·03
S–C_1–C_2	112·8±0·9°	Se–C_1–C_2	108·5±4·5°
S–C_2–C_1	112·6±0·9	Se–C_2–C_1	107·8±6·0
C_1–S–C_2	99·0±0·6	C_1–Se–C_2	97·6±5·5

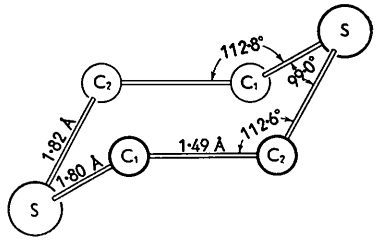

Fig. 1. The 1,4-dithiane molecule.

step of the refinement are given in Table 2. In addition, the probable errors in these parameters, as calculated from the residuals and the diagonal terms of the normal equations of the final least-squares adjustment, are listed in the last column of Table 2. In the last two least-squares refinements, eight very weak terms were omitted whose calculated structure factors were so small as to make the signs doubtful. Structure factors were not recalculated after the last least-squares adjustment. No attempt was made to find the positions of the four hydrogen atoms within the asymmetric unit.

The R factor obtained after the second least-squares treatment, 0·134, was calculated only for the observed reflections; furthermore, the eleven low-order reflections apparently suffering from extinction were also omitted from the calculation. In an attempt to confirm the presence of extinction in these eleven reflections, a photograph was prepared of a powdered sample of 1,4-dithiane sealed in a glass capillary. There were not enough separate lines in the medium-angle region of this photograph to permit a good correlation of intensity data with the Weissenberg photographs; a rough correlation, however, indicated that the relative intensities of the eleven reflections in question were significantly greater on the powder film than on the single-crystal photographs.

As an indication of the agreement between observed and calculated structure factors, there are listed in Table 3 the values of R, together with the values of $\Sigma|F_o|$, $\Sigma|F_c|$, and $\Sigma||F_o|-|F_c||$, obtained for all reflections (n in number) having h, k, or l in common; these values are listed for each such h, k, or l. As might be expected, the $h0l$ data show the lowest R value; for this zone, the atomic structure factors involve a single cosine term, whereas the structure factors for all other reflections involve the product of two trigonometric terms.

Observed and calculated structure factors are recorded in Table 4.

The interatomic bond distances and angles are listed in Table 5, together with the corresponding values for 1,4-diselenane (see also Fig. 1). The uncertainties are standard deviations, as calculated from the residuals of the least-squares treatment of the atomic positional parameters.

The average Se–C distance in 1,4-diselenane, 2·01 Å, is 0·07 Å longer than the sum of the covalent radii of selenium and carbon (Pauling, 1948); furthermore, an electron-diffraction investigation of dimethyl selenide, which is being undertaken in these Laboratories, also indicates a Se–C distance appreciably longer than predicted (Goldish, Hedberg, Marsh & Schomaker, 1955). No such effect is noted for 1,4-dithiane, where the average S–C distance of 1·81 Å is equal to the sum of the covalent radii of sulfur and carbon. The value of 1·81 Å was also found by Hassel & Viervoll (1947) in an electron-diffraction investigation of 1,4-dithiane in the vapor state. Hassel & Viervoll report a C–C distance of 1·54 Å (no uncertainty given), the normal single-bond distance, whereas the value found in this investigation, 1·49 Å, is somewhat shorter. In view of the relatively large standard deviation in the C–C bond distance, it is not felt that this discrepancy is necessarily of significance.

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