

The Crystal and Molecular Structures of the 3,6-Dicarboxylic Acids of 1,2-Dithiane and 1,2-Diselenane

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The unit cells of *racem*-1,2-dithiane-3,6-dicarboxylic acid (I) and *racem*-1,2-diselenane-3,6-dicarboxylic acid (II) are: I, $a = 9.62 \text{ \AA}$, $b = 9.26 \text{ \AA}$, $c = 9.70 \text{ \AA}$, $\beta = 102\frac{1}{2}^\circ$; space group $C_{2h}^8 - I2/c$ with $Z = 4$. II, $a = 9.97 \text{ \AA}$, $b = 9.43 \text{ \AA}$, $c = 9.78 \text{ \AA}$, $\beta = 105^\circ$; space group $C_{2h}^8 - C2/c$ with $Z = 4$. The structures have been determined by two-dimensional X-ray methods.

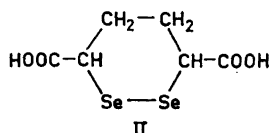
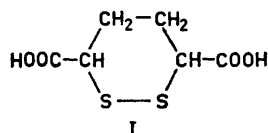
The molecules lie on twofold axes of symmetry in the crystals. The 1,2-dithiane and 1,2-diselenane rings occur in the chair form, and have the carboxyl substituents in equatorial positions. The rotational orientation of the carboxyl groups about the equatorial bonds are different in the two compounds. The dimensions of the disulphide group of the 1,2-dithiane ring were found to be, $S-S = 2.07 \pm 0.02 \text{ \AA}$, $S-C = 1.85 \pm 0.03 \text{ \AA}$, $\angle C-S-S = 99^\circ \pm 1^\circ$, dihedral angle $CSS/SSC = 60^\circ \pm 2^\circ$, and of the diselenide group of the 1,2-diselenane ring, $Se-Se = 2.32 \pm 0.02 \text{ \AA}$, $Se-C = 1.97 \pm 0.02 \text{ \AA}$, $\angle C-Se-Se = 96^\circ \pm 1^\circ$, dihedral angle $CSeSe/SeSeC = 56^\circ \pm 1.5^\circ$. Due to the geometrical requirements of the rings the dihedral angles are smaller than in non-cyclic disulphides and diselenides.

The molecules are arranged into infinite chains through hydrogen bonds between carboxyl groups. The chains are made up of alternately right- and left-handed molecules; the relative location of right- and left-handed molecules of adjacent chains is different in the two compounds.

The dihedral angle between the planes of the bonds of the sulphur atoms in disulphide groups, and of the selenium atoms in diselenide groups, normally has a value of about 90° (*cf.* Ref. 1). The theoretical reasons have been exhaustively discussed by Bergson.²⁻⁶ When the disulphide or diselenide group is part of a ring of small size, the groups are, for steric reasons, forced into smaller dihedral angles. Thus, in the five-membered ring of 1,2-dithiolane-4-carboxylic acid,⁷ the dihedral angle of the disulphide group is about 27° . The present work was carried out in order to arrive at the dihedral angles of disulphide and diselenide groups in saturated six-membered rings.

1,2-Dithiane itself (1,2-dithia-cyclohexane) forms colourless crystals of m.p. slightly above 30° .⁸⁻¹¹ It has been reported to be relatively stable towards

chemical agents,¹¹ but to polymerize on exposure to light.⁸ 1,2-Diselenane (1,2-diselena-cyclohexane) has been described¹² as a yellow powder melting at 41–42°, which may have been a polymer; Bergson³ studied the spectra of chloroform solutions of the monomer obtained by depolymerization of the polymer. The derivatives, *racem*-1,2-dithiane-3,6-dicarboxylic acid^{13,14} (I)



and *racem*-1,2-diselenane-3,6-dicarboxylic acid^{15,16} (II) are quite stable, with no tendency to polymerize. They were first prepared by Fredga^{13–16} and have later been studied by Schotte^{17,18} and Bergson.³ The unit cells and space groups have been published,¹⁹ and a preliminary note on the structure of I.²⁰ Also, some of the results have been mentioned in connection with a later X-ray study in this laboratory of the quasi-racemate of (–)-1,2-dithiane- and (+)-1,2-diselenane-3,6-dicarboxylic acid,²¹ and in review article.¹

THE STRUCTURE ANALYSES

The compounds crystallize in the space group C_{2h}^6 (No. 15) with four molecules per unit cell, of dimensions:¹⁹

	<i>C</i> -centering		<i>I</i> -centering		<i>b</i>	<i>c</i>
	<i>a</i>	β	<i>a</i>	β		
I	12.08 Å	129°	9.62 Å	102½°	9.26 Å	9.70 Å
II	9.97	105	12.01	127	9.43	9.78

The setting $I2/c$ was used for I and $C2/c$ for II. The projections along the *a* axes then have different symmetries, corresponding to the plane groups *cmm* and *pmg*, respectively. The projections along the *b* and *c* axes have the same symmetries, *p2* and *cmm*, respectively, and the compounds in fact appear isostructural in these projections.

Intensities were estimated visually from zero-level Weissenberg photographs, taken with copper radiation using a double-film technique. The crystals used had cross-sections of about 0.1 × 0.1 mm (the linear absorption coefficient for $CuK\alpha$ radiation is 55 cm⁻¹ for I and 105 cm⁻¹ for II). 55 *h0l* and 56 *hk0* reflections of I were recorded with measurable intensities, out of 57 and 58, respectively, attainable with $CuK\alpha$ radiation; the corresponding figures for II were 49 out of 62 *h0l* and 52 out of 65 *hk0* reflections. The intensities were converted to relative structure factors, which were eventually placed on approximately absolute scale by comparison with the calculated ones. The latter were based on the atomic scattering curves of Berghuis *et al.*²²

Table 1. Atomic coordinates for *racem*-1,2-dithiane-3,6-dicarboxylic acid (I) and *racem*-1,2-diselenane-3,6-dicarboxylic acid (II), in fractions of monoclinic cell edges. Origin at a centre of symmetry.

	I				II		
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
S	0.0885	0.2045	0.3325	Se	0.1024	0.2050	0.3396
C ₃	0.171	0.034	0.292	C ₃	0.170	0.022	0.287
C ₄	0.072	-0.093	0.302	C ₄	0.072	-0.098	0.295
C ₇	0.313	0.024	0.379	C ₇	0.312	0.008	0.375
O ₁	0.396	-0.069	0.342	O ₁	0.410	0.071	0.342
O ₂	0.348	0.096	0.498	O ₂	0.329	-0.067	0.498

for carbon and oxygen, Viervoll and Ögrim²³ for sulphur and Thomas and Umeda²⁴ for selenium; the selenium curve was corrected for dispersion.²⁵ Hydrogen contributions were not included. Summations were made by means of Beavers-Lipson strips, at 6° intervals along all axes.

The molecules lie on twofold axes of symmetry, which pass midway between the two sulphur or selenium atoms and the C₄ and C₅ atoms. The asymmetric units, hydrogen excluded, thus consist of one sulphur or selenium atom, three carbon and two oxygen atoms.

The positions of the sulphur and selenium atoms were found from the *h0l* and *hk0* Patterson maps, and these atoms were used as heavy atoms for location of the carbon and oxygen atoms. The projections were refined by difference syntheses. The final atomic coordinates are given in Table 1, and the observed and calculated *h0l* and *hk0* structure factors are listed in Tables 2 and 3. The reliability index, *R*, with non-observed reflections included when $|F_c|$ exceeds the observable limit, is 0.088 and 0.093, respectively, for the *h0l* and *hk0* zones of I, and 0.089 and 0.068 for the *h0l* and *hk0* zones of II.

In the temperature factor $\exp[-B(\sin^2 \theta/\lambda^2)]$ applied to the calculated structure factors, *B* (in Å²) is 4.0 for carbon and 5.0 for oxygen in the *h0l* zone of I and 2.7 and 4.0 respectively in the *hk0* zone; *B* = 4.0 for these atoms in the *h0l* zone of II and 3.3 for carbon and 5.0 for oxygen in the *hk0* zone. For sulphur in the *h0l* zone of I, $B = 2.5 + 4.0 \cos^2 \varphi$ where φ is the angle between the normal of the reflecting plane and the direction of maximum vibration of the atom; this direction made an angle of 16° with the *c* axis in the acute angle. For selenium in the *h0l* zone of II, the anisotropy was very pronounced: $B = 2.5 + 10.0 \cos^2 \varphi$ at a corresponding angle of 20°. In the *hk0* zones, maximum vibration of sulphur and selenium occurred along the *b* axis: $B = 2.5 + 0.5 \cos^2 \varphi$ and $4.0 + 1.2 \cos^2 \varphi$, respectively.

The atomic coordinates used for the last structure-factor calculations were corrected on the basis of gradients still present at some atomic positions in the ensuing last difference map for each zone. Two sets of *x* coordinates for each compound were obtained, one from each zone; where the corrected values differed, the final value was taken as the mean of the two, weighted according to their apparent reliability. The last structure-factor coordinates thus differ from those of Table 1 in the following way, in thousandths of cell edges. I,

Table 2. Observed and calculated $h0l$ and $hk0$ structure factors for *racem*-1,2-dithiane-3,6-dicarboxylic acid.

$h0l$ zone				$h0l$ zone				$hk0$ zone			
h	l	F_o	F_c	h	l	F_o	F_c	h	k	F_o	F_c
2	0	21	+ 18	10	$\bar{6}$	22	+ 15	6	2	54	+ 54
4	0	111	-113	2	8	12	- 11	8	2	4	- 4
6	0	36	- 37	4	8	12	+ 16	10	2	12	- 13
8	0	26	- 23	6	$\bar{8}$	16	+ 13	1	3	62	- 60
10	0	20	+ 19	2	$\bar{8}$	16	- 15	3	3	3	+ 1
0	2	78	- 80	4	$\bar{8}$	7	- 7	5	3	40	+ 38
0	4	29	- 25	6	$\bar{8}$	15	+ 19	7	3	39	+ 34
0	6	78	+ 78	8	$\bar{8}$	12	+ 10	9	3	10	- 11
0	8	4	- 7	10	$\bar{8}$	2	- 2	11	3	21	- 17
0	10	3	+ 5	2	10	11	- 14	2	4	13	- 11
2	2	8	- 9	4	10	4	- 4	4	4	3	- 1
4	2	72	+ 69	2	$\bar{10}$	4	+ 4	6	4	< 3	- 3
6	2	43	+ 41	4	$\bar{10}$	4	+ 4	8	4	13	- 11
8	2	10	- 9	6	$\bar{10}$	11	+ 11	10	4	12	+ 11
10	2	30	- 27	8	$\bar{10}$	10	- 10	1	5	56	+ 59
2	$\bar{2}$	69	- 74	2	$\bar{12}$	2	+ 2	3	5	27	- 30
4	$\bar{2}$	36	- 39	4	$\bar{12}$	5	- 8	5	5	45	- 45
6	$\bar{2}$	43	+ 43					7	5	4	- 4
8	$\bar{2}$	34	+ 34					9	5	9	+ 8
10	$\bar{2}$	5	+ 2					2	6	12	- 12
12	$\bar{2}$	8	- 8					4	6	16	+ 17
2	4	65	- 70					6	6	< 3	+ 8
4	4	18	- 18					8	6	4	- 5
6	4	28	+ 23	2	0	23	+ 20	10	6	3	+ 4
8	4	18	+ 24	4	0	116	-123	1	7	26	- 24
10	4	2	+ 4	6	0	37	- 38	3	7	3	- 4
2	$\bar{4}$	43	+ 42	8	0	27	- 27	5	7	19	+ 18
4	$\bar{4}$	29	+ 30	10	0	21	+ 21	7	7	24	+ 23
6	$\bar{4}$	41	+ 43	0	4	18	+ 16	2	8	15	- 14
8	$\bar{4}$	7	- 10	0	6	24	- 27	4	8	17	+ 18
10	$\bar{4}$	48	- 36	0	8	30	- 29	6	8	18	+ 21
12	$\bar{4}$	2	- 1	0	10	24	+ 27	8	8	2	0
2	6	40	+ 47	1	1	15	- 7	1	9	15	+ 16
4	6	35	- 41	3	1	44	+ 50	3	9	5	+ 5
6	6	19	- 21	5	1	14	- 10	5	9	17	- 18
8	6	4	- 4	7	1	21	- 20	7	9	11	- 12
2	$\bar{6}$	16	- 17	9	1	9	- 8	2	10	12	+ 11
4	$\bar{6}$	38	- 38	11	1	3	+ 5	4	10	12	- 13
6	$\bar{6}$	35	- 35	2	2	58	- 60	6	10	15	- 17
8	$\bar{6}$	4	- 1	4	2	2	- 4	3	11	5	+ 6

$h0l$ zone, Δx : $C_3 + 2, C_4 - 2$; Δz : $O_2 + 1$; $hk0$ zone, Δx : $C_3 - 2, C_4 + 1, O_2 + 2$; Δy : $C_3 - 1, C_7 + 2$. II, $h0l$ zone, Δx : $Se + 0.1, C_3 + 1, C_4 + 3, C_7 - 1, O_1 + 1$; Δz : $Se - 0.6, C_3 + 2, C_7 - 2$; $hk0$ zone, Δx : $Se + 0.3, C_3 - 2, C_4 - 2, C_7 + 4, O_1 + 1, O_2 + 1$; Δy : $C_3 - 1, C_4 + 2, O_1 + 3, O_2 + 1$; where + means that the coordinates of Table 1 are numerically smaller.

Estimates of standard deviations of atomic coordinates were obtained from the root-mean-square gradients in the final difference maps and the curvatures of the peaks in the electron density maps.^{26,27} Where overlapping

Table 3. Observed and calculated $h0l$ and $hk0$ structure factors for *racem*-1,2-disele-
nane-3,6-dicarboxylic acid.

$h0l$ zone				$h0l$ zone				$hk0$ zone			
h	l	F_o	F_c	h	l	F_o	F_c	h	k	F_o	F_c
2	0	36	+ 31	2	8	8	- 5	8	2	43	- 44
4	0	207	-197	4	8	13	+ 15	10	2	29	- 32
6	0	81	- 81	6	8	< 4	- 4	1	3	138	-131
8	0	7	+ 4	2	$\bar{8}$	24	- 12	3	3	51	+ 50
10	0	55	+ 55	4	$\bar{8}$	< 6	0	5	3	88	+ 82
12	0	17	+ 13	6	$\bar{8}$	21	+ 25	7	3	22	+ 20
0	2	121	-128	8	$\bar{8}$	7	- 5	9	3	32	- 31
0	4	72	- 69	10	$\bar{8}$	6	- 9	11	3	17	- 18
0	6	100	+104	2	10	< 5	- 9	2	4	19	- 19
0	8	< 6	+ 4	4	10	< 3	+ 5	4	4	43	- 42
0	10	< 6	+ 1	2	$\bar{10}$	< 6	- 5	6	4	< 8	0
0	12	< 3	0	4	$\bar{10}$	7	- 4	8	4	< 8	+ 6
2	2	80	+ 76	6	$\bar{10}$	8	+ 13	10	4	16	+ 14
4	2	143	+134	8	$\bar{10}$	7	+ 7	1	5	97	+103
6	2	5	+ 11	2	$\bar{12}$	< 4	+ 1	3	5	49	- 52
8	2	63	+ 65	4	$\bar{12}$	< 4	- 5	5	5	88	- 83
10	2	13	- 15	6	$\bar{12}$	< 3	- 2	7	5	< 8	- 2
2	$\bar{2}$	167	-188					9	5	32	+ 32
4	$\bar{2}$	12	- 7					11	5	12	+ 13
6	$\bar{2}$	125	+125					2	6	16	- 16
8	$\bar{2}$	33	+ 31					4	6	< 8	+ 1
10	$\bar{2}$	30	- 27					6	6	< 12	+ 12
12	$\bar{2}$	17	- 18					8	6	< 8	+ 2
2	4	147	-134					10	6	< 5	+ 3
4	4	13	+ 16					1	7	44	- 41
6	4	94	+ 91					3	7	16	+ 12
8	4	17	+ 20					5	7	44	+ 42
10	4	29	- 32					7	7	12	+ 9
2	$\bar{4}$	59	+ 60					9	7	20	- 21
4	$\bar{4}$	67	+ 66					2	8	14	- 13
6	$\bar{4}$	24	+ 25					4	8	27	+ 28
8	$\bar{4}$	34	- 31					6	8	20	+ 20
10	$\bar{4}$	29	- 26					8	8	11	+ 10
12	$\bar{4}$	10	+ 11					1	9	22	+ 27
2	6	27	+ 31					3	9	9	- 7
4	6	61	- 70					5	9	20	- 21
6	6	21	- 24					7	9	< 6	- 4
8	6	15	+ 18					2	10	8	+ 8
2	$\bar{6}$	9	- 13					4	10	16	- 19
4	$\bar{6}$	41	- 43					6	10	10	- 13
6	$\bar{6}$	< 6	- 2					1	11	6	0
8	$\bar{6}$	25	+ 26					3	11	6	+ 4
10	$\bar{6}$	4	+ 5					5	11	4	- 3

$hk0$ zone			
h	k	F_o	F_c
2	0	37	+ 37
4	0	194	-195
6	0	73	- 72
8	0	10	+ 1
10	0	44	+ 43
12	0	13	+ 12
0	2	24	- 34
0	4	79	+ 78
0	6	8	- 9
0	8	32	- 38
0	10	27	+ 36
0	12	< 4	- 6
1	1	24	+ 19
3	1	24	+ 29
5	1	43	- 45
7	1	< 7	- 2
9	1	11	+ 11
11	1	< 7	0
2	2	82	- 83
4	2	75	+ 76
6	2	94	+ 86

occurred, the s.d. was taken as up to twice that which would otherwise have applied. The s.d. thus arrived at, and used for calculation of s.d. of bond lengths and angles, were 0.005 — 0.008 Å for the sulphur coordinates and 0.02 — 0.04 Å for the lighter atom coordinates in I, and 0.005 — 0.01 Å for selenium and 0.02 — 0.05 Å for the lighter atoms in II.

The $hk0$ projections do not give the signs of the x and y coordinates, and there was thus an ambiguity in the sign of the y coordinates with respect to which atoms belong to the same molecule. For atoms of the ring part of the molecules, and for the carboxyl group of I, only the signs listed in Table I give reasonable molecular dimensions. The signs of the y coordinates of the carboxyl group of II of the chosen ring part, were picked out from Fourier maps of the $0kl$ zone of II, first based on 27 $0kl$ reflections with phases corresponding to the selenium contributions alone, and next on 39 out of 40 observed $0kl$ reflections (out of 60 attainable) with phases calculated from all atoms except the carbon atom of the carboxyl group (C_7) the y sign of which was difficult to ascertain from the first map.

THE 1,2-DITHIANE AND 1,2-DISELENANE RINGS

The bond lengths and angles in the molecules, from the coordinates in Table 1, are listed in Table 4, together with estimated standard deviations. Drawings of the molecules as seen along the c crystal axes are shown in Fig. 1.

The S—S bond length, 2.07 Å, does not differ significantly from the average, 2.038 ± 0.007 Å, reported from crystal structure determinations of six non-cyclic organic disulphides: N,N'-diglycyl-L-cystine dihydrate²⁸ (2.04 ± 0.005 Å), hexagonal L-cystine²⁹ (2.032 ± 0.004 Å), L-cystine dihydrochloride³⁰ (2.044 ± 0.01 Å), L-cystine dihydrobromide³¹ (2.024 ± 0.014 Å), formamidinium disulphide dibromide monohydrate³² (2.044 ± 0.01 Å) and the diiodide monohydrate³² (2.044 ± 0.02 Å). Incidentally, in all these six compounds the disulphide group lies across a crystallographic twofold axis of symmetry. In orthorhombic S_8 and rhombohedral S_6 the S—S bonds are 2.059 ± 0.002 Å and 2.057 ± 0.018 Å, respectively.³³ In the only five-membered saturated

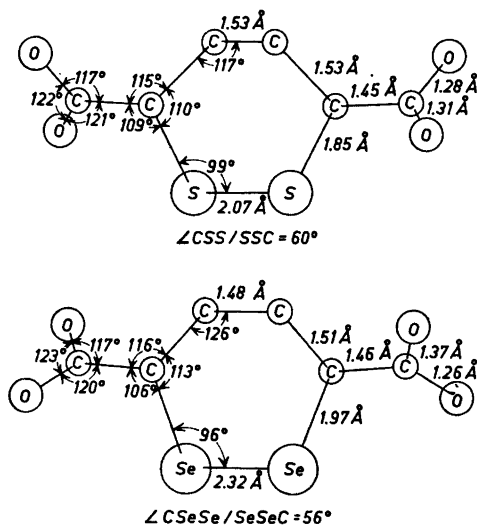


Fig. 1. 1,2-Dithiane-3,6-dicarboxylic acid (above) and 1,2-diselenane-3,6-dicarboxylic acid (below) as seen along the c crystal axes.

Table 4. Molecular dimensions.

1,2-Dithiane-3,6-dicarboxylic acid.

$S_1-S_2 = 2.069 \pm 0.015 \text{ \AA}$	$\angle S_1-S_2-C_3 = 98.9 \pm 1.0^\circ$
$S_2-C_3 = 1.85 \pm 0.03$	$\angle S_2-C_3-C_4 = 109.9 \pm 2.1$
$C_3-C_4 = 1.53 \pm 0.04$	$\angle C_3-C_4-C_5 = 116.5 \pm 2.7$
$C_4-C_5 = 1.53 \pm 0.06$	Dihedral angle
	$C_6S_1S_2/S_1S_2C_3 = 60.3 \pm 2^\circ$
$C_3-C_7 = 1.45$	$\angle O_1-C_7-O_2 = 122.1$
$C_7-O_1 = 1.28$	$\angle C_3-C_7-O_1 = 116.6$
$C_7-O_2 = 1.31$	$\angle C_3-C_7-O_2 = 120.8$
$\angle S_2-C_3-C_7 = 109.0 \pm 2.0^\circ$	$\angle C_4-C_3-C_7 = 115.0 \pm 2.5^\circ$

1,2-Diselenane-3,6-dicarboxylic acid.

$Se_1-Se_2 = 2.321 \pm 0.015 \text{ \AA}$	$\angle Se_1-Se_2-C_3 = 95.7 \pm 0.8^\circ$
$Se_2-C_3 = 1.97 \pm 0.02$	$\angle Se_2-C_3-C_4 = 113.4 \pm 1.6$
$C_3-C_4 = 1.51 \pm 0.04$	$\angle C_3-C_4-C_5 = 125.5 \pm 2.5$
$C_4-C_5 = 1.48 \pm 0.07$	Dihedral angle
	$C_6Se_1Se_2/Se_1Se_2C_3 = 55.9 \pm 1.5^\circ$
$C_3-C_7 = 1.46$	$\angle O_1-C_7-O_2 = 122.9$
$C_7-O_1 = 1.26$	$\angle C_3-C_7-O_1 = 120.4$
$C_7-O_2 = 1.37$	$\angle C_3-C_7-O_2 = 116.5$
$\angle Se_2-C_3-C_7 = 105.7 \pm 1.6^\circ$	$\angle C_4-C_3-C_7 = 116.3 \pm 2.1^\circ$

cyclic disulphide for which data are available, 1,2-dithiolane-4-carboxylic acid,⁷ $S-S = 2.096 \pm 0.009 \text{ \AA}$.

The dihedral angles of the disulphide groups in the above non-cyclic disulphides range from 105° in formamidinium disulphide diiodide monohydrate³² to 74° in hexagonal L-cystine²⁹; in S_8 and S_6 they are $98.9 \pm 0.7^\circ$ and $74.5 \pm 2.5^\circ$, respectively.³³ Apart from the dihedral angle of $26.6 \pm 1^\circ$ in 1,2-dithiolane-4-carboxylic acid,⁷ and the dihedral angles of zero in unsaturated five-membered cyclic disulphides, the dihedral angle of $60.3 \pm 2^\circ$ in the 1,2-dithiane ring is the smallest yet reported. The strain due to the deviation from the normal, larger dihedral angle is, however, fairly small, probably³⁴ only a few kcal/mole.

Crystal structure determinations of two non-cyclic organic diselenides, diphenyl diselenide³⁵ and di-*p*-chlorophenyl diselenide,³⁶ have been carried out: there $Se-Se = 2.29 \pm 0.01 \text{ \AA}$ and $2.333 \pm 0.015 \text{ \AA}$, respectively. In α -monoclinic³⁷ and β -monoclinic³⁸ Se_8 , $Se-Se = 2.34 \text{ \AA}$. The present result, 2.32 \AA , thus lies in the range of earlier values. The smallest dihedral angle about a diselenide group earlier reported is 74.5° in di-*p*-chlorophenyl diselenide.³⁶

The $S-S-C$ and $Se-Se-C$ bond angles of 99° and 96° , respectively, in the six-membered rings, are smaller than in the first five of the six-non-cyclic disulphides referred to above, where the average $S-S-C$ angle is $103.8 \pm 0.4^\circ$ (in the last one, $99 \pm 2^\circ$) and in the two non-cyclic diselenides where the $Se-Se-C$ angles are 106° and 101° . Values of $99.0 \pm 0.6^\circ$ and $97.6 \pm 3.5^\circ$, respectively, have been reported for the sulphur and selenium valency angles in crystals of 1,4-dithiane³⁹ and 1,4-diselenane.⁴⁰

The S—S and Se—Se bond lengths, $2.078 \pm 0.016 \text{ \AA}$ and $2.332 \pm 0.007 \text{ \AA}$, found²¹ for the same molecules from an X-ray study of the quasi-racemate of (–)-1,2-dithiane- and (+)-1,2-diselenane-3,6-dicarboxylic acid, agree well with the present results.

THE CARBOXYL GROUPS

These are attached to the 1,2-dithiane and 1,2-diselenane rings in equatorial positions. The groups are planar within the accuracy, the deviation of the middle atom, C₇, from the least squares planes of the groups being 0.04 Å in I and 0.03 Å in II. The rotational position of the carboxyl group about the C₃—C₇ bond, relative to the ring, is different in the two compounds, as can

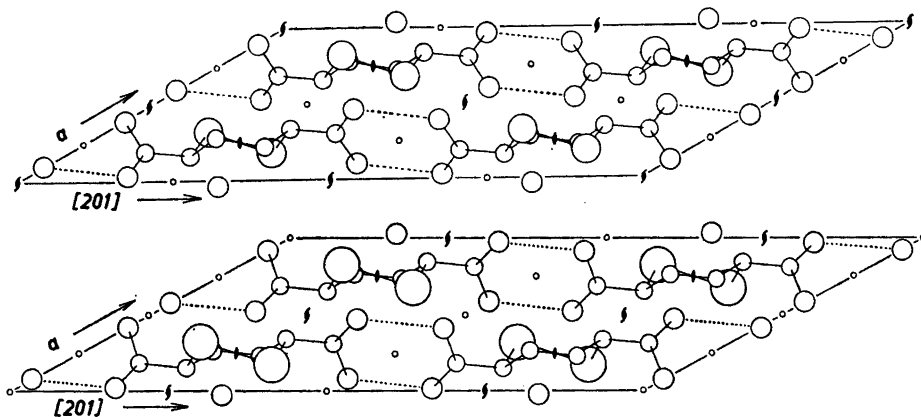


Fig. 2. The different packings of parallel hydrogen-bonded chains of alternatingly right- and left-handed molecules in the crystals of *racem*-1,2-dithiane-3,6-dicarboxylic acid (above) and *racem*-1,2-diselenane-3,6-dicarboxylic acid (below) as seen along the *b* axes.

be seen from Fig. 1, and from the opposite signs of the *y* coordinates of O₁ and O₂ in I relative to II (Table 1). If the carboxyl group in II had the same orientation as in I, the non-bonded Se...O₂ distance would become too short (about 2.7 Å). In I, the S...O₂ distance is 2.83 Å and there adequately long.

THE PACKING IN THE CRYSTALS

The change in the orientation of the carboxyl group is probably a contributing cause to a difference in packing of the molecules in the two crystals. The compounds crystallize in the same space group and the unit cells can be chosen so as to conform dimensionally, but then one cell is *I*-centered while the other is *C*-centered. This corresponds to an interchange of locations of twofold screw axes and symmetry centres at $x = \frac{1}{4}$. With symmetry centre

at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ in II as in I, instead of screw axis at $\frac{1}{4}, y, \frac{1}{4}$, the distance from Se of one molecule, to O₁ of a molecule across the centre, would be 2.73 Å. Likewise, with screw axis at $\frac{1}{4}, y, \frac{1}{2}$ in II as in I, instead of symmetry centre at $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$, the distance from Se to O₂ of a molecule across the screw axis would be 2.66 Å, also too short. The corresponding intermolecular S...O₁ and S...O₂ distances in I, with these symmetry centres and screw axes placed as in II, would be 2.72 Å and 2.46 Å; the latter one would certainly be too short.

The least squares planes of the carboxyl groups pass close to the symmetry centre at $\frac{1}{2}, 0, \frac{1}{2}$ (0.01 Å from the centre in I and 0.06 Å in II). There are O—H...O hydrogen bonds, of lengths 2.69 Å in I and 2.67 Å in II, between carboxyl groups of different molecules across this centre of symmetry, and the molecules are thus joined into infinite chains. This is the usual arrangement in crystals of dicarboxylic acids.^{41,42} The chains run parallel to [201] and are made up of alternately right- and left-handed molecules.

The molecules of one chain are transferred into molecules of an adjacent chain through the screw axes and symmetry centres mentioned above, which alternate in the same direction as the chains and are located between these. The difference in centering of the unit cells, *i.e.*, the interchange of the screw axes and symmetry centres, results in a different relative location of right- and left-handed molecules of adjacent chains.

The shortest non-bonded S...S and Se...Se distances are 3.87 Å between sulphur atoms in I over symmetry centre at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, and 3.81 Å between selenium atoms in II over symmetry centre at $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$.

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