Unit Cells and Space Groups of Some Carboxylic Acid Derivatives of 1,2-Dithiolane, 1,2-Dithiane, 1,2-Diselenane and 1,2-Dithiepane

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The X-ray crystallographic survey of saturated cyclic disulphides reported below serves as a preliminary to attempts at complete crystal structure determinations of suitable representatives. Of special interest is the stereochemistry of the disulphide group, particularly in five-membered rings where the CSS/SSC dihedral angle is expected to be considerably smaller than the normal value of about 90°.

The data were obtained from oscillation and Weissenberg photographs of single-crystal specimens, using Cu*Kα* radiation, $\lambda = 1.542$ Å. Axial lengths are believed to be accurate to within 0.5 %. Densities were determined by flotation in suitable solvent mixtures.

1,2-Dithiolane-4-carboxylic acid [1-3] (I). Triclinic, irregularly shaped crystals, with $a = 5.34$ Å, $b = 5.85$ Å, $c = 10.75$ Å, $\alpha = 93\frac{1}{2}°$, $\beta = 89\frac{1}{2}°$, $\gamma = 109\frac{1}{2}°$. There are two molecules per unit cell; density, calc. 1.58, found 1.54 g/cm³. The space group is $C_i^1-P\bar{1}$.

The projection of the structure along the a axis has been solved [4], and the complete structure will be worked out. The a-axis projection indicates that the dithiolane ring is not planar, the CSS/SSC dihedral angle being different from 0°.

Racem - *1,2 - dithiolane - 3,5 - dicarboxylic acid* [2,5-7] (II). Monoclinic prismatic, $a = 8.47$ Å, $b = 18.20$ Å, $c = 10.14$ Å, $\beta = 98°$. Eight molecules per unit cell; density, calc. 1.67, found 1.67 g/cm³. The space group, from systematic absences, is $C_{2h}^5-P2_1/c$, from which follows that the asymmetric unit consists of two molecules.

The crystals were plates {010} sometimes elongated along the c axis.

Racem - *1,2-dithiane - 3,6-dicarboxylic acid* [2,6,8,9] (III). Monoclinic prismatic, $a = 9.62$ Å, $b = 9.26$ Å, $c = 9.70$ Å, $\beta = 102\frac{1}{2}°$. There are four molecules per unit cell; density, calc. 1.64, found 1.65 g/cm³. The space group, from systematic absences and from Patterson and Fourier projections along the b axis, is C_{2h}^6-I2/c. In the conventional $C2/c$ setting, $a = 12.09$ Å, $\beta = 129°$, otherwise as above.

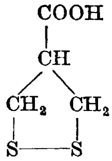
The crystals occurred as thick prisms {110}.

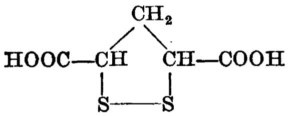
With four molecules per unit cell, each molecule must possess twofold symmetry in the crystals, and were found to lie on twofold axes. The dithiane ring has the chair form, with the substituents in equatorial positions. A detailed structure determination is being made [10].

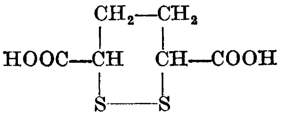
Meso - *1,2 - dithiane - 3,6 - dicarboxylic acid* [2,6,8,9]. Monoclinic prismatic, $a = 6.36$ Å, $b = 13.63$ Å, $c = 10.31$ Å, $\beta = 110°$. Four molecules per unit cell; density, calc. 1.65, found 1.64 g/cm³. The space group, from systematic absences, is $C_{2h}^5-P2_1/c$.

The crystal studied was a thick prism extended along the a axis, bounded by {010}, {001} and {011}, and terminated by {100}.

The *meso* acid, granted that its disulphide group is non-planar. will in the crystals occur in two equivalent mirror image forms, since the space group is not enantiomorphous. In solution, conversion of the dithiane ring, *i. e.*, of one enantiomorph of the *meso* acid into the other, takes place. In view of the relatively high barrier, 10—14 kcal/mole [11], towards rotation through the planar *cis* form of a disulphide group, it may be expected that conversion of the 1,2-dithiane ring takes place less rapidly than the conversion of *cyclo*hexane itself and its derivatives.

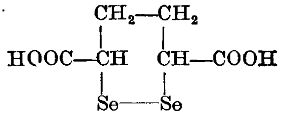

(I)


(II)


(III)

Racem - *1,2 - diselenane - 3,6 - dicarboxylic acid* [12,13] (IV). Monoclinic, probably prismatic, $a = 9.97$ Å, $b = 9.43$ Å, $c = 9.78$ Å, $\beta = 105°$. There are four molecules per unit cell; density, calc. 2.26, found 2.27 g/cm^3. Systematic absences, hkl when $h + k$ is odd, $h0l$ when l is odd. Similarities with the dithiane analogue, particularly of the $h0l$ zones of reflections, indicate that the space group is the centrosymmetric one, C_{2h}^6-C2/c. In the $I2/c$ setting, $a = 12.01$ Å, $\beta = 127°$. As in the case of the dithiane analogue, the crystals occur as prisms {110}.

The *racem* 1,2-dithiane- and 1,2-diselenane-3,6-dicarboxylic acids thus crystallize in the same space group, with very similar unit cell dimensions, but, once the a axes and β angles are chosen so as to conform dimensionally, the C- and I-centered settings are interchanged in the two crystals. Thus, the photographs of the $0kl$ zones of reflections have different symmetries, corresponding to the plane groups *cmm* and *pmg*, respectively. The difference corresponds to interchange of locations of twofold screw axes and symmetry centres at $x = \frac{1}{4}$ and $\frac{3}{4}$, and to different arrangements of the molecules relatively to each other as seen along the a axes. Otherwise, the two structures should be very similar.



(IV)

(+) - *1,2 - diselenane - 3,6 - dicarboxylic acid* [12,13]. Orthorhombic sphenoidal, $a = 9.57$ Å, $b = 9.91$ Å, $c = 9.50$ Å. Four molecules per unit cell; density, calc. 2.23, found 2.21 g/cm^3. The systematic absences are those of the space group $D_2^4-P2_12_12_1$.

The crystals occurred as flat prisms extended along the c axis, with {100} dominant. {110} and {101} were also observed. There is a pronounced tendency of cleavage along the c plane.

Racem - *1,2-dithiepane - 3,7 - dicarboxylic acid* [2,14,15] (V). Monoclinic prismatic, $a = 12.97$ Å, $b = 8.20$ Å, $c = 8.90$ Å, $\beta = 96°$. There are four molecules per unit cell; density, calc. 1.57, found 1.57 g/cm^3. The space group is $C_{2h}^5-P2_1/c$, from systematic absences.

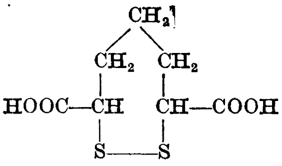
The crystals were mostly poorly developed; the one studied was a prism extended along the b axis.

Meso - *1,2 - dithiepane - 3,7 - dicarboxylic acid* [2,14,15]. Monoclinic, $a = 25.91$ Å, $b = 5.82$ Å, $c = 13.21$ Å, $\beta = 91\frac{1}{2}°$. Eight molecules per unit cell; density, calc. 1.48, found 1.49 g/cm^3. Systematic absences, hkl when $h + k$ is odd, $h0l$ when l is odd. The morphology of the crystals indicates that a twofold axis is present, and thus that the space group is the centrosymmetric one, C_{2h}^6-C2/c.

The sample consisted of prisms elongated along the b axis and bounded by {100} and {201}.

The disulphide group of the 1,2-dithiepane ring almost certainly being non-planar, two enantiomorphous forms of the *meso* acid occur in the crystals. Analogous considerations as to interconversion of the enantiomorphs in solution should apply as indicated above for *meso*-1,2-dithiane-3,6-dicarboxylic acid.

In the course of the work, data were obtained also for meso-*a,a'-dibromo-adipic acid* (m. p. 193 °C). The crystals were monoclinic prismatic, and occurred as prisms {011} terminated by {101}, with $a = 5.00$ Å, $b = 10.42$ Å, $c = 9.78$ Å, $\beta = 111°$. There are two molecules per unit cell; density, calc. 2.12, found 2.12 g/cm^3. The space group from systematic absences, is $C_{2h}^5-P2_1/c$, from which follows that the molecules are centrosymmetric in the crystals.



(V)

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Structure of Crystalline 1,2-Dithiolane-4-carboxylic Acid

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As part of a program for the study of crystal structures of five-, six- and seven-membered cyclic disulphides, with the view of obtaining information about the stereochemistry of the disulphide group in the rings, unit cell and space group determinations have recently been made of some 1,2,4-dithiazolidine derivatives [1] and of some 1,2-dithiolane-, 1,2-dithiane-, 1,2-diselenane- and 1,2-dithiepane-carboxylic acids [2]. Also, the detailed structure of thiuret (3,5-diimino-1,2,4-dithiazolidine) hydroiodide has been worked out [3,4]. The present note gives the preliminary results of a crystal structure determination of 1,2-dithiolane-4-carboxylic acid [5,6].

The crystals are triclinic, with the unit cell dimensions [2], $a = 5.34$ Å, $b = 5.85$ Å, $c = 10.75$ Å, $\alpha = 93\frac{1}{2}°$, $\beta = 89\frac{1}{2}°$, $\gamma = 109\frac{1}{2}°$. The space group is $C_i^1-P\bar{1}$, and there are two molecules per unit cell. The intensities of the $0kl$ reflections were estimated visually from Weissenberg photographs taken with Cu*K* radiation, and were converted to relative structure factors in the usual way. The positions of the two sulphur atoms were found from a F_0^2 synthesis of the $0kl$ data, and a subsequent F_0 synthesis with signs based on the sulphur contributions showed the outline of the molecule and gave approximate coordinates for the carbon and oxygen atoms. After a few F_0 and (F_0-F_c) refinements the $0kl$ electron density map is as shown in Fig. 1, and the y and z coordinates as listed in Table 1. The reliability index R is at this stage 15.7 %.

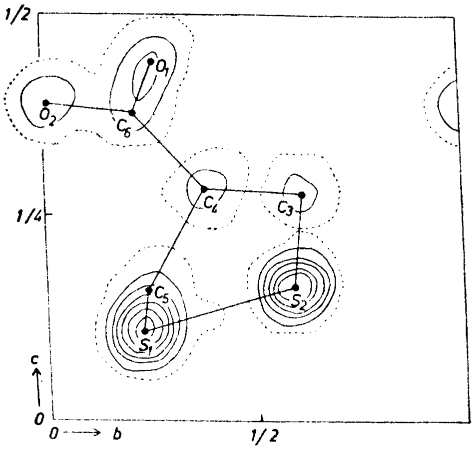

Fig. 1. Electron density projection of 1,2-dithiolane-4-carboxylic acid along the *a* axis, showing one asymmetric unit (one molecule). Contours at intervals of 3 e · Å^{-2}, beginning with 3 e · Å^{-2} (dashed).

Provided that the chemically equivalent S_1-C_5 and S_2-C_3 bonds and $S_1-S_2-C_3$ and $S_2-S_1-C_5$ bond angles do not have too different dimensions, the *a*-axis projection shows that the disulphide group of the 1,2-dithiolane ring is not planar. If, pending the determination of the x coordinates through a projection along another axis, the assumption is made that the S—C bond lengths are equal and approximately 1.81 Å, and that the S—S—C bond angles are equal, the y and z coordinates of the sulphur atoms and the C_3 and C_5 atoms lead to a disulphide group with dimensions approximately as follows: S—S bond length = 2.09 Å, S—S—C bond angles = 95°, and CSS/SSC dihedral angle = 20°.

The carboxyl groups of different molecules appear to be arranged around symmetry centres at $z = \frac{1}{2}$, and non-bonded S—S contacts only to occur across the c plane at $z = 0$.