

## Remarks on the Stereochemistry of Disulphide Compounds

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Theoretical considerations predict<sup>1</sup> that compounds of the disulphide type,  $\text{X—S—S—X}$ , are non-planar. The dihedral angle, *i. e.*, the angle between the X—S groups as seen projected on a plane normal to the S—S bond, is expected to be around  $90^\circ$ , due to interaction of the electron clouds of the two sulphur atoms.

## STRUCTURE OF COMPOUNDS OF THE DISULPHIDE TYPE

Pertinent data are available for hydrogen disulphide<sup>2</sup>, disulphur dichloride<sup>3,4</sup>, diphenyl diselenide<sup>5,6</sup> which is isomorphous with diphenyl disulphide<sup>5,7</sup>, di-*p*-bromophenyl disulphide<sup>8</sup>, dimethanesulphonyl disulphide<sup>9</sup> and barium tetrathionate dihydrate<sup>10</sup>. In every case, the disulphide group is non-planar, with a dihedral angle close to the predicted value.

A non-planar, symmetrical X—S—S—X group possesses a twofold axis of symmetry, but no centre, whereas a planar, *trans* group has a centre. Unit cell and space group data, but no detailed structure analysis, are available for dibenzoyl disulphide<sup>5</sup>, di-*p*-chlorophenyl diselenide<sup>11</sup>, disulphur and diselenium dibenzenesulphinates and di-*p*-toluenesulphinates<sup>12</sup>, and potassium, rubidium and ammonium tetrathionate<sup>13,14</sup>. No molecular symmetry is required in any of the crystals. In view of the crystallographic experience that a molecular centre of symmetry, if present, usually will coincide with a crystallographic centre of symmetry, whereas this only occasionally happens with twofold axes, the evidence is thus in favour of non-planar disulphide groups in the above compounds.

The space group of dibenzoyl disulphide and diselenide<sup>5</sup> and *bis*(dimethylthiocarbamyl) disulphide<sup>15</sup> is probably  $C_{2v}^6—C2/c$ , with four molecules per unit cell. Here, a twofold axis or a centre is required as molecular symmetry. By inference, it appears likely that the molecular symmetry element is a twofold axis and not a centre.

It may be stated that no exceptions to the principle of non-planarity have so far been established for compounds of the disulphide type.

The unit cells and space groups of disulphur and diselenium dibenzenesulphinate, referred to above, were determined some time ago, and are reported here. Oscillation and Weissenberg photographs were taken with  $\text{FeK}\alpha$  radiation,  $\lambda = 1.934 \text{ \AA}$ , and densities were measured by a flotation method. The values given below for axial lengths are believed to be accurate to within 0.5 %.

*Disulphur dibenzenesulphinate*<sup>16</sup>,  $\text{S}_2(\text{SO}_2\text{C}_6\text{H}_5)_2$ . Monoclinic prismatic;  $a = 12.30 \text{ \AA}$ ,  $b = 6.09 \text{ \AA}$ ,  $c = 20.72 \text{ \AA}$ ,  $\beta = 109^\circ$ . There are four molecules per unit cell; density, calc. 1.57, found 1.57. Absent reflections,  $h0l$  when  $l$  is odd,  $0k0$  when  $k$  is odd. Space group,  $C_{2h}^2 - P2_1/c$ . The crystals appear as flat prisms, elongated along the  $b$  axis, and with  $\{10\bar{1}\}$  predominant.

The crystals have been described by Groth<sup>17</sup>. With Groth's  $a$  and  $c$  axes doubled, his data correspond to a cell in which the  $b$  face is centered. The translation of the glide plane is along Groth's  $a$  axis.

*Diselenium dibenzenesulphinate*<sup>18</sup>,  $\text{Se}_2(\text{SO}_2\text{C}_6\text{H}_5)_2$ . Monoclinic prismatic;  $a = 5.54 \text{ \AA}$ ,  $b = 14.25 \text{ \AA}$ ,  $c = 23.18 \text{ \AA}$ ,  $\beta = 108^\circ$ . Four molecules per unit cell; density, calc. 1.68, found 1.65. Absent reflections,  $h0l$  when  $l$  is odd,  $0k0$  when  $k$  is odd. Space group,  $C_{2h}^2 - P2_1/c$ . The crystals appear as prisms  $\{011\}$ , and there is a tendency to twinning on (001).

It appears that disulphur and diselenium dibenzenesulphinate are not isomorphous, and crystallize differently from the  $p$ -toluene analogues, which are mutually isomorphous<sup>18</sup>.

#### SPACE GROUP AND TWINNING OF SODIUM TETRATHIONATE DIHYDRATE

As has been pointed out recently<sup>18</sup> with reference to organic disulphides, there are two enantiomorphous forms of non-planar disulphide groups. The crystals of diphenyl disulphide and diselenide<sup>5-7</sup> and probably di- $p$ -tolyl disulphide<sup>7</sup> are based on enantiomorphous space groups. The number of molecules in the unit cells do not exceed the number of general positions of the space groups, and a unit cell thus contains only one of the two enantiomorphous forms. This appears to be true also for sodium tetrathionate dihydrate.

As reported earlier<sup>14</sup>, the crystals of sodium tetrathionate dihydrate are monoclinic, with the unit cell dimensions,  $a = 14.46 \text{ \AA}$ ,  $b = 6.37 \text{ \AA}$ ,  $c = 5.44 \text{ \AA}$ ,  $\beta = 105.5^\circ$ . There are two molecules per unit cell. Absent reflections,  $hkl$  when  $h + k$  is odd. Granted that the sulphur chain of the ion is non-planar in this salt as has been found in barium tetrathionate dihydrate<sup>10</sup>, the space group is  $C_2^3 - C2$ , which requires that the tetrathionate ion possesses a twofold axis of symmetry.

The space group,  $C_2^3 - C2$ , is enantiomorphous, and a unit cell contains only one of the two enantiomorphous forms of the tetrathionate ion. The crystals are always submicroscopically twinned<sup>14</sup>, with (100) as a twin plane. They appear to consist of submicroscopic lamellae of alternating  $d$  and  $l$  crystals. On zero layer Weissenberg photographs about the  $b$  axis, equivalent  $h0l$  reflections from  $d$  and  $l$  lamellae occur with the same intensity. This type of twinning is analogous to that<sup>19</sup> of inactive  $\beta$ -phenylglyceric acid of m.p.  $141^\circ$ .

#### POSSIBLE EXISTENCE OF STABLE ISOMERS

The enantiomorphous forms of disulphide compounds should be expected to isomerize very rapidly in solutions at room temperature, the barrier restricting rotation about a sulphur-sulphur bond being<sup>1</sup> in the neighbourhood of

5 kcal./mole. The same should apply to the enantiomorphous *trans* forms of trisulphide and pentathionic compounds<sup>20</sup>.

The isomerization of the tetrathionate ion probably occurs by rotation through the planar *trans* form, since in the planar *cis* form, with a dihedral angle of 0°, the approach of the oxygen atoms of the two sulphonate groups would be too close, or require an excessive bending of bonds. In dimethyl disulphide<sup>21</sup>, the carbon-carbon distance in the planar *cis* form may be calculated as roughly 3.1 Å. The van der Waals radius of methyl and methylene groups being<sup>22</sup> about 2.0 Å, it appears that isomerization by rotation through planar *cis* forms is unfavourable also for organic disulphides. With large organic groups attached to sulphur, as in the case of di-*tert*-butyl disulphide<sup>23</sup>, spatial interference between the groups give rise to an increased value, above 100°, of the dihedral angle, and rotations through planar *cis* forms should not be expected to take place.

In cyclic disulphides with not too large rings, isomerization by rotation through planar *trans* forms would also be impossible. Thus, stable rotational isomers of disulphide compounds might perhaps occur among cyclic disulphides, having, preferably, bulky substituents on the carbon atoms next to sulphur.

#### SUMMARY

The available data concerning the structure of disulphide compounds are in accordance with a non-planar distribution of valencies about the sulphur-sulphur bond.

The twinning of sodium tetrathionate dihydrate crystals is discussed in connection with the occurrence of two enantiomorphous forms of the tetrathionate ion.

It is pointed out that stable rotational isomers of cyclic disulphides may exist.

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