Remarks on the Stereochemistry of Disulphide Compounds

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Theoretical considerations predict that compounds of the disulphide type, 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°, 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, disulphur dichloride, diphenyl diselenide which is isomorphous with diphenyl disulphide, di-p-bromophenyl disulphide, dimethanesulphonyl disulphide and barium tetrathionate dihydrate. 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, di-p-chlorophenyl diselenide, disulphur and diselenium dibenzenesulphinate and di-p-toluenesulphinate, and potassium, rubidium and ammonium tetrathionate. 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 dibenzyl disulphide and diselenide and bis(dimethylthiocarbamyl) disulphide is probably $C_{2h}^6-C2'/c$, 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 dibenzensulphinate, referred to above, were determined some time ago, and are reported here. Oscillation and Weissenberg photographs were taken with FeKα radiation, λ = 1.934 Å, and densities were measured by a flotation method. The values given below for axial lengths are believed to be accurate to within 0.5%.

**Disulfur dibenzensulphinate** 14, S₂(SO₄C₆H₅)₂. Monoclinic prismatic; a = 12.30 Å, b = 6.09 Å, c = 20.72 Å, β = 109°. 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, C₂₃—P2₁/c. The crystals appear as flat prisms, elongated along the b axis, and with [101] predominant.

The crystals have been described by Groth 15. 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 dibenzensulphinate** 14, Se₂(SO₄C₆H₅)₄. Monoclinic prismatic; a = 5.54 Å, b = 14.25 Å, c = 23.18 Å, β = 108°. 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, C₂₃—P2₁/c. The crystals appear as prisms {011}, and there is a tendency to twinning on (001).

It appears that disulphur and diselenium dibenzensulphinate are not isomorphous, and crystallize differently from the p-toluene analogues, which are mutually isomorphous 15.

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

As has been pointed out recently 18 with reference to organic disulphides, there are two enantiomorphous forms of non-planar disulphide groups. The crystals of diphenyl disulphide and diselenide 5—7 and probably di-p-tolyl disulphide 7 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 14, the crystals of sodium tetrathionate dihydrate are monoclinic, with the unit cell dimensions, a = 14.46 Å, b = 6.37 Å, c = 5.44 Å, β = 105.5°. 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 19, the space group is C₂₃—C2, which requires that the tetrathionate ion possesses a twofold axis of symmetry.

The space group, C₂₃—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 14, 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 19 of inactive β-phenylglyceric acid of m.p. 141°.

**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 1 in the neighbourhood of

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5 kcal./mole. The same should apply to the enantiomorphous trans forms of trisulphide and pentathionic compounds 30.

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 31, 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 22 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 33, 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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