

cules in the unit cell gives a calculated density of 1.52 g/cm<sup>3</sup>.

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## Space Groups and Molecular Symmetries of Two Thiocyanates

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The unit cells and space groups of two simple, covalent thiocyanates have been determined from single-crystal oscillation and Weissenberg photographs, using copper radiation,  $\lambda(\text{CuK}\alpha) = 1.542 \text{ \AA}$ .

*Sulphur dithiocyanate*<sup>1</sup>,  $\text{S}(\text{SCN})_2$ . Orthorhombic bipyramidal,  $a = 10.12 \text{ \AA}$ ,  $b = 12.83 \text{ \AA}$ ,  $c = 4.34 \text{ \AA}$ . Four molecules per unit cell; density, calc. 1.75, found 1.76 g/cm<sup>3</sup>. Systematic absences,  $0kl$  when  $k + l$  is odd,  $hk0$  when  $h$  is odd. The unit cell dimensions, the absences, and the relative intensities of the reflections show that the crystals are isomorphous with those of selenium dithiocyanate<sup>2</sup>,  $\text{Se}(\text{SCN})_2$ , and selenium diselenocyanate<sup>3</sup>,  $\text{Se}(\text{SeCN})_2$ . The space group is thus  $D_{2h}^{16} \cdot Pnma$ . From the known structures of the selenium analogues<sup>2,3</sup> it follows that the sulphur dithiocyanate molecule has an unbranched chain structure, with the middle sulphur atom located in a crystallographic mirror plane.

The compound was prepared from sulphur dichloride by reaction with an excess of silver thiocyanate suspended in carbon disulphide, and was recrystallized from the same solvent. Silver thiocyanate was found to react better than mercuric thiocyanate<sup>4</sup>. The crystals occur as plates {010}, bounded by {110} and {111}, and usually very thin. The bulk of crystals became yellow in the

course of a day, due to the formation of an insoluble polymer<sup>1,4</sup>, but individual crystals could be picked which were sufficiently stable.

*Ethylene thiocyanate*,  $(\text{CH}_2\text{SCN})_2$ . Orthorhombic bipyramidal,  $a = 7.39 \text{ \AA}$ ,  $b = 7.81 \text{ \AA}$ ,  $c = 11.48 \text{ \AA}$ . Four molecules per unit cell; density, calc. 1.45, found 1.42 g/cm<sup>3</sup>. Systematic absences,  $0kl$  when  $k$  is odd,  $h0l$  when  $l$  is odd,  $hk0$  when  $h$  is odd. The space group is thus  $D_{2h}^{15} \cdot Pbca$ , which has eightfold general positions, and two fourfold sets of symmetry centres as special positions. With four molecules per unit cell, it follows that the ethylene thiocyanate molecules are centrosymmetric in the crystals. This agrees with the finding from infrared measurements<sup>5</sup> that the compound exists in *trans* configuration in the solid state.

Recrystallized from chloroform, the compound was obtained as plates {010}, or as perfect bipyramids {111} with, also here, {010} developed.

Further work on the crystal structures of the two thiocyanates is intended.

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## "Trans" Naphthodioxan Characterized by its Mercuric Chloride Compound

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In 1950 Furberg and Hassel<sup>1</sup> determined the crystal structure of the lower melting compound (m. p. 111° C) found in the reaction between 2,3-dichloro-1,4-dioxan and ethylene glycol. They found

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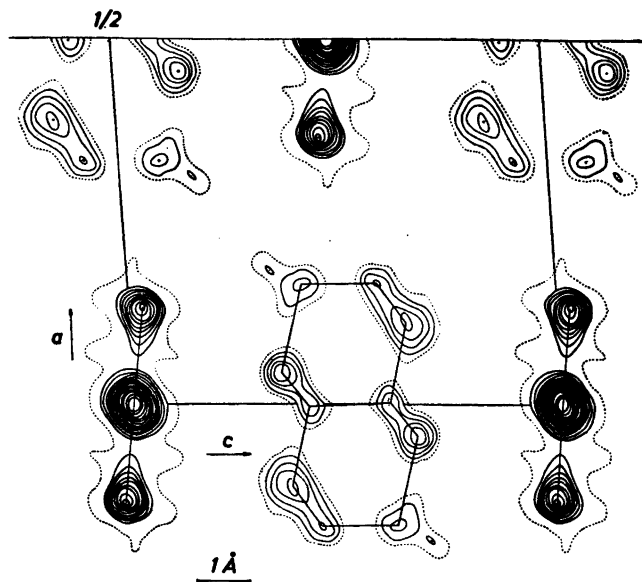


Fig. 1. Electron density map projected along the *b*-axis. Intervals between the contour lines for Hg, Cl, C and O are in the ratio 25:10:4:4.

that this substance is not a naphthodioxan as suggested by Böeseken *et al.*<sup>2</sup>, but bi-1, 3-dioxacyclopentyl(2).

The structure of the higher melting product (m. p. 136° C) had still to be determined although it would of course be expected that this compound is indeed a naphthodioxan and preferably the "trans" form. The crystallographic data did not, however, invite to a direct crystal structure investigation<sup>1</sup>. Later on, it was found that addition compounds of the substance with mercury salts are readily formed<sup>3</sup> which might be suited for X-ray determination of the general shape of the organic molecule. We have chosen the mercuric chloride compound which has one short crystal axis (4.46 Å). Zero order layer line Weissenberg diagrams with rotation about the short axis were taken using the multiple film method. The intensities were estimated visually. The general trend of the intensities is a uniform decrease for increasing Bragg angles, which made us believe that the mercury atoms were in unique positions. Anticipating that the projection would contain the appropriate number of symmetry centres a Fourier projection could be worked out without making

any assumptions regarding the positions of the chlorine, oxygen or carbon atoms. The resulting electron density map is reproduced in Fig. 1. Besides the projection of a linear symmetrical mercuric chloride molecule the map also contains a centrosymmetrical assembly of ten resolved peaks which corresponds satisfactorily to a picture which may be obtained from a naphthodioxan molecule in the "trans" form. The four peaks which in this case must correspond to oxygen atoms are in fact somewhat higher than the six remaining peaks representing carbon atoms.

Without trying to work out further projections which would no doubt exhibit serious overlapping of atoms, we feel entitled to draw the conclusion that the 136° substance is indeed "trans" naphthodioxan.

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