fatty leaves or thin plates {001}. There is perfect cleavage along (001) and along planes parallel to the *ab* diagonals.

*Sodium p-toluenethiosulphonate dihydrate*, $C_7H_7SO_2SNa \cdot 2H_2O$. Monoclinic prismatic, $a = 13.59$ Å, $b = 6.47$ Å, $c = 12.95$ Å, $\beta = 91\frac{1}{2}°$. Four formula units per unit cell; density, calc. 1.44, found 1.43 g/cm³. Systematic absences, $h0l$ when $l$ is odd, $0k0$ when $k$ is odd. The space group is thus $C_{2h}^5 - P2_1/c$.

The dihydrate [3,5] was obtained by crystallization from 96 % ethanol at low room temperature, and occurred as plates {100} which were often prismatic along the *b* axis. There is a pronounced tendency of cleavage along the plate face. In air, the crystals keep well at temperatures below 10° C, but give off the water of crystallization rapidly above 20° C.

A salt, originally [6] listed as sodium *p*-toluenethiosulphonate dihydrate but later [2] reported to be the monohydrate, was described by Weibull [2,6] as monoclinic prismatic with $a : b : c = 0.8869 : 1 : 2.774$ and $\beta = 103° 52'$. With the transformation, $\bar{1}00/0\bar{1}0/\frac{1}{2},0,\frac{1}{2}$, Weibull's data become $a : b : c = 0.8869 : 1 : 1.351$; $\beta = 94.6°$, which do not agree with the X-ray data for the dihydrate nor the anhydrous salt. A monohydrate has not been observed in the present work. Weibull's transformed data are almost identical with those which apply to potassium *p*-toluenethiosulphonate monohydrate.

Further work on the crystal structures of some of the salts will be made, with a view of determining the length of a thiosulphonate sulphur-sulphur bond. As pointed out earlier [7], this bond is probably a predominantly double bond.


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Received June 13, 1956.

## Structure of Thiuret Hydroiodide


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Thiuret hydroiodide, or 3,5-diimino-1,2,4-dithiazolidine hydroiodide, occurs on oxidation of dithiobiuret with iodine [1], and is a five-membered cyclic disulphide [1,2].

The unit cells and space groups of some simple 1,2,4-dithiazolidine derivatives, including thiuret hydroiodide, were reported by one of us in a preceding note [3]. The preliminary results of a complete crystal structure determination of thiuret hydroiodide are given here. The disulphide group has been found to lie across a crystallographic mirror plane of symmetry, and is thus exactly planar. This appears to be the first crystal structure determination reported for a cyclic disulphide, and the first recorded instance of a planar disulphide group.

Open-chain disulphides, X—S—S—X, have always been found to be non-planar *cf.*[4] with a dihedral angle of about 90° between the X—S—S and S—S—X planes, there being a barrier to internal rotation about an S—S bond of from 10 to 14 kcal/mole [5-7]. The formation of a five-membered cyclic disulphide requires the rotation of the S—S bond to a dihedral angle of nearly 0°, where the barrier probably has its highest value. The nevertheless relatively high stabilities of unsaturated five-membered cyclic disulphides, such as 1,2-dithiacenaphthene [8] and the trithiones [9,10], and of 1,2,4-dithiazolidine derivatives with double-bonded substituents in the 3 and 5 positions, must be due to some extent to resonance stabilization of the ring, a resonance involving the unshared *p* electron pairs of the sulphur atoms. The barrier to internal rotation about an S—S bond being thought to be due principally to the mutual repulsion of these electron pairs [11], one on each sulphur atom, their participation in $\pi$ bonding with the adjacent carbon atoms would tend to lower the barrier height.

The yellow crystals of thiuret hydroiodide, $S_2(C{:}NH)_2NH \cdot HI$, occur as prisms, bounded by {001} and {011} and showing perfect cleavage along the *c* plane. The four-molecule unit cell has the dimensions [3], $a = 5.38$ Å, $b = 9.24$ Å, $c = 13.98$ Å, and the space group is $D_{2h}^{16} - Pnma$. The intensities of the $0kl$ reflections were

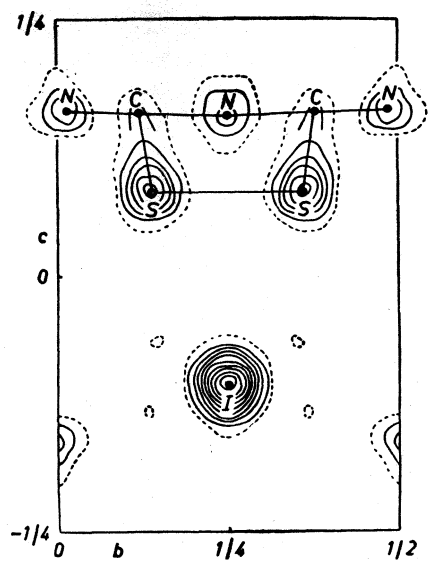


*Fig. 1. Electron density projection of thiuret hydroiodide along the* a *axis, showing two asymmetric units. The 4-electron line is dashed. Contour intervals: 10 e · Å$^{-2}$ for the iodide ion, 4 e · Å$^{-2}$ for the sulphur atoms and 2 e · Å$^{-2}$ for the carbon and nitrogen atoms.*

estimated visually from zero layer Weissenberg photographs about the *a* axis. A crystal with cross-section 0.07 × 0.08 mm was used, and copper radiation. A Patterson synthesis based on the 0*kl* data gave the *y* and *z* coordinates of the iodide ion and the sulphur atom of the asymmetric unit, and subsequent Fourier syntheses lead to the electron density map reproduced in Fig. 1.

At the present stage of refinement, the *y* and *z* coordinates are as listed in Table 1. These coordinates, with appropriate temperature and scale factors, give a reliability factor of $R = 14.4$ % for the 0*kl* reflections.

The sulphur *y* coordinate and the iodide *z* coordinate give a S—S bond length of 2.05 Å and a closest I—I approach of 4.82 Å, respectively. The former of these distances agrees well with the S—S bond length in orthorhombic sulphur [12], 2.04 Å, and the latter is 0.5 Å larger than twice the ionic radius of iodine [13].

*Table 1. Atomic coordinates, in fractions of corresponding cell edges. Origin at a centre of symmetry.*

| | *y* | *z* |
|---|---|---|
| I | 0.250 | —0.107 |
| $N_1$ | 0.250 | 0.156 |
| S | 0.139 | 0.081 |
| C | 0.120 | 0.160 |
| $N_2$ | 0.014 | 0.162 |

The 1,2,4-dithiazolidine ring is intersected by a crystallographic mirror plane, which passes through the nitrogen atom and midway between the sulphur atoms, and it follows that the disulphide group, including the two sulphur atoms and the adjacent carbon atoms, is planar. The ring as a whole, however, need not be planar, and as far as can be judged from the 0*kl* electron density map, the nitrogen atom of the 1,2,4-dithiazolidine ring is displaced from the plane of the sulphur and carbon atoms.

The work will be continued, and details published later. Also, it is intended to study the crystal structures of 1,2-dithiacyclohepta-3,6-diene derivatives [14,15], with a view of determining the degree of planarity of the disulphide group in unsaturated seven-membered rings.

*Note added in proof, Sept. 3, 1956.* — Refinement by difference syntheses of the *a* axis projection of thiuret hydroiodide has led to a reliability factor of $R = 7.6$ % and a S—S bond length of 2.09 Å.

The authors wish to express their thanks to *Norges Almenvitenskapelige Forskningsråd* for a grant.

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Received June 13, 1956.

# X-Ray Crystallographic Data on Certain Five-membered Cyclic Disulphides

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A survey has been made of unit cells and space groups of some simple 1,2,4-dithiazolidine derivatives. The compounds studied are, xanthan hydride [1-3] (3-imino-1,2,4-dithiazolidine-5-thione), rhodan hydrate [4,5] (3-imino-1,2,4-dithiazolidine-5-one), and three thiuret (3,5-diimino-1,2,4-dithiazolidine) hydrohalides. The latter compounds are oxidation products of dithiobiuret; the hydrochloride [6] and hydroiodide [7] have been mentioned in literature earlier, but apparently not the hydrobromide. The hydrobromide and hydroiodide used in the present work were obtained by adding an excess of aqueous potassium bromide or iodide to a warm aqueous solution of the hydrochloride.

Oscillation and Weissenberg photographs were taken using copper radiation, $\lambda(CuK\alpha) = 1.542$ Å. The axial lengths given below are believed to be correct to within 0.5 %. Densities were determined by flotation in bromoform-carbon tetrachloride mixtures.

*Xanthan hydride*, $S_2(C{:}NH)(C{:}S)NH$. Monoclinic prismatic, $a = 4.05$ Å, $b = 10.59$ Å, $c = 12.78$ Å, $\beta = 97°$. Four molecules per unit cell; density, calc. 1.83, found 1.84 g/cm³. Systematic absences, $h0l$ when $l$ is odd, $0k0$ when $k$ is odd. The space group is thus $C_{2h}^5-P2_1/c$.

From 60 % acetic acid the compound crystallized as long prisms, extended along the $a$ axis and flattened along the $b$ axis.

*Rhodan hydrate*, $S_2(C{:}NH)(C{:}O)NH$. Monoclinic, $a = 12.50$ Å, $b = 5.24$ Å, $c = 14.67$ Å, $\beta = 95\frac{1}{2}°$. Eight molecules per unit cell; density, calc. 1.86, found 1.87 g/cm³. Systematic absences, $hkl$ when $h + k$ is odd, $h0l$ when $l$ is odd. The space group is thus either $C_{2h}^6-C2/c$ or $C_s^4-C/c$.

From water, the compound crystallized as flat prisms, extended along the $b$ axis and with {100} predominant. There is perfect cleavage along (001). The morphology of the crystals indicates the presence of a twofold axis and thus the correctness of the centrosymmetric space group, $C_{2h}^6-C2/c$.

*Thiuret hydrochloride*, $S_2(C{:}NH)_2NH \cdot HCl \cdot \frac{1}{2}H_2O$. Monoclinic, $a = 19.58$ Å, $b = 5.47$ Å, $c = 14.34$ Å, $\beta = 114\frac{1}{2}°$. Eight formula units per unit cell; density, calc. 1.70, found 1.71 g/cm³. Systematic absences, $hkl$ when $h + k$ is odd, $h0l$ when $l$ is odd. Space group, $C_{2h}^6-C2/c$ or $C_s^4-C/c$.

The density, and the statement by Preisler and Bateman [6] that 5 % water remain after drying over calcium chloride, point to the presence of half a mole of crystal water per mole of hydrochloride.

From water, the compound crystallized as prisms extended along the $b$ axis. As in the case of rhodan hydrate, the morphology is in favour of the former of the two possible space groups. The water molecules would then lie on twofold axes.

*Thiuret hydrobromide*, $S_2(C{:}NH)_2NH \cdot HBr$. Monoclinic prismatic, $a = 5.11$ Å, $b = 12.76$ Å, $c = 10.47$ Å, $\beta = 110°$. Four formula units per unit cell; density, calc. 2.22, found 2.22 g/cm³. Systematic absences, $h0l$ when $l$ is odd, $0k0$ when $k$ is odd. The space group is thus $C_{2h}^5-P2_1/c$.

The compound crystallized from water as large plates {010} or as prisms extended along the $a$ axis with, also here, {010} predominant.

*Thiuret hydroiodide*, $S_2(C{:}NH)_2NH \cdot HI$. Orthorhombic bipyramidal, $a = 5.38$ Å, $b = 9.24$ Å, $c = 13.98$ Å. Four formula units per unit cell; density, calc. 2.50, found 2.49 g/cm³. Systematic absences, $0kl$ when $k + l$ is odd, $hk0$ when $h$ is odd. Of the two space groups compatible with these absences, the centrosymmetric one, $D_{2h}^{16}-Pnma$, has been found to be the correct one through Patterson and Fourier projections along the $a$ axis [8]. The thiuret-$H^+$ ion lies across a crystallographic mirror plane of symmetry, and also the iodide ion is located in the mirror plane.

From water, the compound crystallized as prisms extended along the $a$ axis and bounded by {001} and {011}. There is perfect cleavage along (001), and a rather pronounced tendency of irregular growth and twinning.

Further work on the crystal structures of some of the compounds will be made.