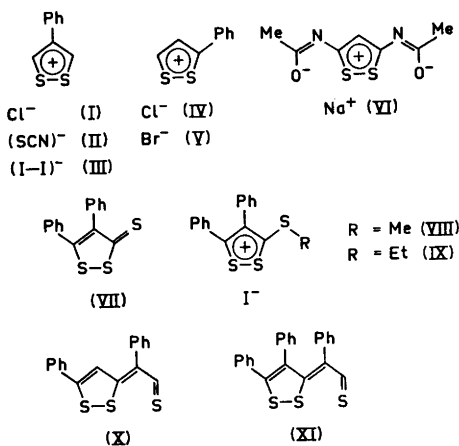


## Crystallographic Data on Miscellaneous Compounds Containing Unsaturated Five-membered Disulphide Rings

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One of us (A. H.)<sup>1</sup> in 1963 reported X-ray crystallographic data on a series of compounds containing unsaturated five-membered disulphide rings. We now extend this survey with unit cell data and space groups for the compounds I–XI which have become available to us since then.



Oscillation and Weissenberg photographs were taken using copper radiation;  $\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$ . The cell dimensions given below are believed to be correct to within 0.5%. Densities were determined by flotation in suitable solvent mixtures.

**4-Phenyl-1,2-dithiolium chloride monohydrate (I).** The salt crystallizes from water as colourless needles and thin flakes elongated along *c* and with {100} predominant. Orthorhombic,  $a = 26.05 \text{ \AA}$ ,  $b = 8.43 \text{ \AA}$ ,  $c = 4.79 \text{ \AA}$ . Four formula units per unit cell; density, calc. 1.47, found 1.46 g/cm<sup>3</sup>. Systematic absences,  $0kl$  for  $k + l$  odd,  $hk0$  for  $h$  odd. The centrosymmetric space group, *Pnma*, has been found to be the correct one through

Fourier projection along the *c*-axis,<sup>2</sup> and the Fourier map shows furthermore that only 50–70% of the water positions are occupied. The salt is isomorphous with the iodide and bromide.

**4-Phenyl-1,2-dithiolium thiocyanate (II).** Crystals from water are brownish and were elongated along the *c*-axis. Orthorhombic,  $a = 25.41 \text{ \AA}$ ,  $b = 8.64 \text{ \AA}$ , and  $c = 4.76 \text{ \AA}$ . Four formula units per unit cell; density, calc. 1.46, found 1.47 g/cm<sup>3</sup>. From systematic absences, the space group is either *Pnma* or *Pn2<sub>1</sub>a*. Fourier projection along the *c*-axis shows that *Pnma* is the correct space group.<sup>2</sup> The salt is isomorphous with the iodide, bromide, and chloride monohydrate.

**4-Phenyl-1,2-dithiolium diiodide (III).** The crystals are thin orange needles and flakes, elongated along *a* with {010} predominant. Orthorhombic,  $a = 6.40 \text{ \AA}$ ,  $b = 8.88 \text{ \AA}$ , and  $c = 24.52 \text{ \AA}$ . Four formula units per unit cell; density, calc. 2.49, found 2.51 g/cm<sup>3</sup>. The space group, from systematic absences, is either *Imma* or *Im2a*. The former space group which has 16 general positions, requires that the asymmetric unit is one quarter of the formula unit, and the latter space group which has 8 general positions, requires that the asymmetric unit consists of one half formula unit. By taking into account that the 4-phenyl-1,2-dithiolium ion, from structure determinations<sup>2</sup> of the iodide, bromide, chloride monohydrate, and thiocyanate, may have two mirror planes, either of the above space groups may be the correct one.

**3-Phenyl-1,2-dithiolium chloride dihydrate (IV).** Crystallization from water yielded colourless crystals elongated along the *b* axis. Monoclinic,  $a = 13.34 \text{ \AA}$ ,  $b = 8.73 \text{ \AA}$ ,  $c = 9.97 \text{ \AA}$ ,  $\beta = 115^\circ$ . Four formula units per unit cell; density, calc. 1.58, found 1.59 g/cm<sup>3</sup>. The systematic absences are those of the space group *P2<sub>1</sub>/c*.

**3-Phenyl-1,2-dithiolium bromide (V).** Light yellow needles from water with *b* as the needle axis. Monoclinic,  $a = 7.92 \text{ \AA}$ ,  $b = 4.99 \text{ \AA}$ ,  $c = 26.08 \text{ \AA}$ ,  $\beta = 96.5^\circ$ . Four formula units per unit cell; density, calc. 1.67, found 1.72 g/cm<sup>3</sup>. Diagrams were taken around the *b*-axis only, and from the systematic absences the space group is either *P2<sub>1</sub>/c* or *P2<sub>1</sub>/c*. With half a molecule water of hydration the calculated density becomes 1.72 g/cm<sup>3</sup> in agreement with the found density. This favours the space group *P2<sub>1</sub>/c* with water on two-fold axis.

*Sodium 3,5-diacetylrimino-1,2-dithiole trihydrate* (VI), crystallizes from dilute sodium hydroxide solution in one orthorhombic and one monoclinic crystal modification, both colourless. The orthorhombic crystals are needles elongated along the *c*-axis; they become opaque and disintegrate after a few hours in air. The cell dimensions are,  $a = 16.18 \text{ \AA}$ ,  $b = 12.00 \text{ \AA}$ ,  $c = 6.94 \text{ \AA}$ . Four formula units per unit cell; density, calc. 1.44, found 1.41 g/cm<sup>3</sup>. The space group, from systematic absences, is *Cmcm*, *Cmc2<sub>1</sub>*, or *C2cm*. Fourier projection along the *c*-axis, and least squares refinement of the *hk0* data,<sup>2</sup> strongly indicate that the correct space group is *Cmcm*. Only about 50 % of a rather loosely bonded water molecule, in addition to two water molecules more firmly bound, is present. This probably accounts for the instability of the crystals.

The monoclinic crystals are laths developed along the *b*-axis, with  $a = 11.68 \text{ \AA}$ ,  $b = 10.13 \text{ \AA}$ ,  $c = 12.19 \text{ \AA}$ , and  $\beta = 111^\circ$ . Four molecules per unit cell; density, calc. 1.44, found 1.43 g/cm<sup>3</sup>. The space group, from systematic absences, is *P2<sub>1</sub>/n*.

*4,5-Diphenyl-1,2-dithiole-3-thione* (VII). The compound crystallizes from ethanol as orange-red orthorhombic prisms, with  $a = 16.36 \text{ \AA}$ ,  $b = 27.21 \text{ \AA}$ , and  $c = 6.02 \text{ \AA}$ . Eight molecules per unit cell; density, calc. 1.42, found 1.43 g/cm<sup>3</sup>. The space group, from systematic absences, is *Pbca*.

*3-Methylmercapto-4,5-diphenyl-1,2-dithiolium iodide* (VIII). Orange-red orthorhombic prisms from ethanol, with  $a = 18.91 \text{ \AA}$ ,  $b = 18.76 \text{ \AA}$ ,  $c = 9.40 \text{ \AA}$ . Eight formula units per unit cell; density, calc. 1.71, found 1.68 g/cm<sup>3</sup>. The space group, from systematic absences, is *Pbca*.

*3-Ethylmercapto-4,5-diphenyl-1,2-dithiolium iodide* (IX). Orange-red orthorhombic prisms from ethanol, with  $a = 19.33 \text{ \AA}$ ,  $b = 18.08 \text{ \AA}$ ,  $c = 10.52 \text{ \AA}$ . Eight molecules per unit cell; density, calc. 1.42, found 1.43 g/cm<sup>3</sup>. The space group, from systematic absences, is *Pbca*.

*Meribicyclo-3,5-epidithio-1,4-diphenyl-2,4-pentadienethione-1* (X). Irregularly developed orange crystals, triclinic, with  $a = 10.18 \text{ \AA}$ ,  $b = 8.52 \text{ \AA}$ ,  $c = 10.29 \text{ \AA}$ ,  $\alpha = 118.8^\circ$ ,  $\beta = 94.3^\circ$ ,  $\gamma = 101.1^\circ$ . Two molecules per unit cell; density, calc. 1.38, found 1.39 g/cm<sup>3</sup>. A Patterson projection along *b* indicates that the space group is *P1*.

*Meribicyclo-3,5-epidithio-1,2,4-triphenyl-2,4-pentadienethione-1* (XI). Black needles elongated along the *b*-axis, with  $a = 6.24 \text{ \AA}$ ,

$b = 15.05 \text{ \AA}$ ,  $c = 9.83 \text{ \AA}$ ,  $\beta = 91.5^\circ$ . Two molecules per unit cell; density, calc. 1.40, found 1.40 g/cm<sup>3</sup>. The space group is probably *P2<sub>1</sub>*; the higher space group *P2<sub>1</sub>/m* compatible with the systematic absences, would require a molecular mirror plane which appears unlikely.

The authors wish to thank Dr. H. Bootsma, Haile Selassie I University, Addis Ababa, Ethiopia, for samples of VII, VIII, and IX, Cand. real. S. Hauge, this Institute, for samples of I, IV, and V, Dr. E. Klingsberg, American Cyanamid Company, for samples of II, III, X, and XI, and Dr. U. Schmidt, University of Freiburg, for a sample of 3-acetylrimino-5-acetamido-1,2-dithiole from which VI was prepared.

1. Hordvik, A. *Acta Chem. Scand.* **17** (1963) 1809.
2. Work, to be published, by A. Hordvik and co-workers (R. M. Baxter, F. Grundtvig, H. M. Kj\o ge and E. Sletten).

Received March 26, 1966.

## Unit Cell and Space Group Data on Certain Pyranose Sugars

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Structure investigations of pyranose sugars<sup>1-8</sup> have confirmed Hassel and Ottar's assumption<sup>9</sup> that the pyranose ring is chair formed. It follows that each pyranose isomer may occur in two different conformations one formed by the other through a conversion of the ring.

Different instability factors have been suggested in order to predict which of the conversion forms of a pyranose isomer will occur, and according to this the predicted normal conformations for various pyranose sugars have been listed by Reeves.<sup>10</sup>

From Reeves' stability scheme both conversion forms of  $\beta$ -lyxose seem probable, because the difference between their instability factors is small. In this connection it is interesting to note that the conversion form of  $\beta$ -lyxose which has been found to occur<sup>6</sup> in the crystal is the one with smallest instability factors.