The Structure of 3-Acetamido-1,2,4-dithiazole-5-thione

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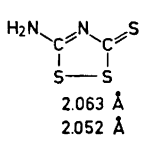
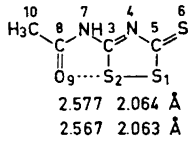
Two independent structure studies of xanthan hydride (I) have been reported,[1,2] and the lengths of the sulphur-sulphur bond in I from these studies are 2.063(5) and 2.052(4) Å, respectively.



(I)



(II)

We have carried out a structure investigation of the acetyl derivative of xanthan hydride, 3-acetamido-1,2,4-dithiazole-5-thione (II), in order to find out whether the O···S contact in II affects the sulphur-sulphur bond there. The preliminary results from this investigation are given.

The O···S contacts in the two crystallographically independent molecules of II are 2.577(3) and 2.567(3) Å, respectively, and the corresponding S–S bond lengths are 2.0644(15) and 2.0632(13) Å. Thus, when compared with I, the O···S contacts in II are seen to have no significant lengthening effect on the S–S bonds.

Other bond lengths in the two independent molecules of II, mentioned in the same order as above, are, S(2)–C(3) 1.758(3) and 1.752(3) Å, C(3)–N(4) 1.314(5) and 1.311(4) Å, N(4)–C(5) 1.350(5) and 1.347(5) Å, C(5)–S(6) 1.666(4) and 1.665(4) Å, C(5)–S(1) 1.753(3) and 1.752(4) Å, C(3)–N(7) 1.356(5) and 1.363(5) Å, N(7)–C(8) 1.381(5) and 1.390(5) Å, C(8)–C(10) 1.480(7) and 1.488(6) Å, and C(8)–O(9) 1.227(5) and 1.222(5) Å.

Crystals of II from 60 % acetic acid are light yellow prisms and belong to the orthorhombic space group $P2_12_12_1$. The cell dimensions are $a = 7.8275(5)$ Å, $b = 32.975(1)$ Å, and $c = 5.8320(3)$ Å. There are eight molecules per unit cell; $D_c = 1.697$ g cm^{-3}, $D_m = 1.694$ g cm^{-3}.

The structure was solved by direct methods [3] and refined by full matrix least squares. With anisotropic temperature factor coefficients for all atoms except hydrogen, the present R is 0.028.

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2. Stanford, R. H., Jr. *Acta Cryst.* **16** (1963) 1157.
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The Structure of 2,5-Diphenyl-3,4-trimethylene-6a-thiathiophthene

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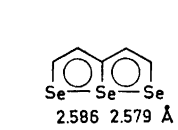
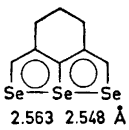
The results from the structure investigations of 6a-selenaselenophthene (I)[1] and 3,4-trimethylene-6a-selenaselenophthene (II)[2] show that the introduction of a 3,4-trimethylene bridge in (I) causes a decrease in the Se–Se distances; the sum of the Se–Se distances in II, 5.111(3) Å, is 0.054 Å smaller than the sum of the Se–Se distances in I, 5.165(3) Å.

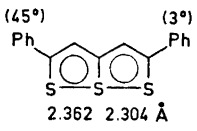
An analysis of the structure of 2,5-diphenyl-3,4-trimethylene-6a-thiathiophthene (IV) has been carried out in order to find to which extent the 3,4-trimethylene bridge affects the sulphur-sulphur bonding there, and the preliminary results from this study are given.



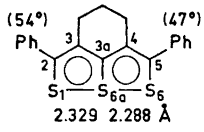
(I)



(II)



(III)



(IV)

The sulphur-sulphur distances in (IV) are S(1) – S(6a) = 2.329(1) Å and S(6a) – S(6) = 2.288(1) Å, and the sum of the S – S distances, 4.617(1) Å, is 0.049 Å smaller than the sum of the S – S distances in 2,5-diphenyl-6a-thiathiophthene (III),[3] 4.666(3) Å. Hence, a 3,4-trimethylene bridge has the same effect on the S – S bonding in 6a-thiathiophthenes as it has on the Se – Se bonding in 6a-selenaselenophthenes.

Other bond lengths in the 6a-thiathiophthene system of IV are: S(1) – C(2) = 1.709(3) Å, S(6a) – C(3) = 1.755(3) Å, S(6) – C(5) = 1.710(3) Å, C(2) – C(3) = 1.378(4) Å, C(3) – C(3a) = 1.425(4) Å, C(3a) – C(4) = 1.426(4) Å, and C(4) – C(5) = 1.381(4) Å.

A sample of 2,5-diphenyl-3,4-trimethylene-6a-thiathiophthene was generously supplied by M. Stavaux.[4] The crystals are dark red and belong to the monoclinic space group $P2_1/c$. The cell dimensions are $a = 6.882(1)$ Å, $b = 12.871(1)$ Å, $c = 19.049(1)$ Å, and $\beta = 94.98(2)°$. There are four molecules per unit cell; $D_c = 1.393$ g cm^{-3}, $D_m = 1.38$ g cm^{-3}.

The structure analysis is based on X-ray data collected on a paper-tape controlled Siemens AED diffractometer using Cu$K\alpha$ radiation. 2546 refractions were observed within $\theta = 71°$.

The structure was solved by the heavy atom method and refined by full matrix least squares. The present R factor is 0.036.

We thank Dr. M. Stavaux, Département de Chimie, Université de Caen, France, for a sample of 2,5-diphenyl-3,4-trimethylene-6a-thiathiophthene.

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Spectrophotometric Studies of Copper(II) Chelates of 1-Nitroso-2-naphthol-6-sulphonic and 2-Nitroso-1-naphthol-6-sulphonic Acids in Aqueous Solution

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The formation of copper(II) chelates by some *o*-nitrosonaphtholsulphonic acids has been discussed in previous papers.[1,2] As rather strong complexes are formed by ligands of this type with copper(II), only spectrophotometric methods can be used in general to study the complex formation reactions.

In the present paper, results for copper(II) chelates of two ligands, 1-nitroso-2-naphthol-6-sulphonic and 2-nitroso-1-naphthol-6-sulphonic acids, are reported. This ligand pair is well suited for a comparison of the chelation abilities of two isomeric *o*-nitrosonaphthols.

1-Nitroso-2-naphthol-6-sulphonic acid forms an orange yellow copper(II) chelate and 2-nitroso-1-naphthol-6-sulphonic acid a less stable chelate, which, however, is bright red in colour.

The absorption spectra of the 1 : 1 copper(II) chelates CuL are reproduced in Figs. 1 and 2. Application of Job's