# The Molecular Structure of Thiothiophthene

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So far the structures of a series of thio-thiophthene derivatives have been studied by X-ray crystallographic methods.[1-11] Three of these derivatives, compounds (I)—(III), are symmetric with respect to substituents.

Me $\diagdown$ Me   Ph $\diagdown$ Ph

(I)   (II)

S—S—S   S—S—S

2.36 2.36 Å   2.36 2.30 Å

Ph Ph

(III)

S—S—S

2.23 2.43 Å
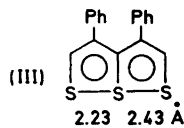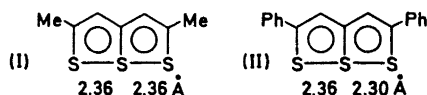
In crystals of (I) [1,2] the molecules lie across crystallographic mirror planes passing through the central sulphur and carbon atoms. Thus the sulphur-sulphur bonds are of exactly equal length, 2.36 Å, and the terminal sulphur atoms have identical environment.

The terminal sulphur atoms in (II) have different environment in the crystals.[6] One of them forms close contact with the thiothiophthene system of a neighbouring molecule while the other does not interact with neighbouring groups or atoms. Furthermore, the phenyl groups in (II) are twisted differently about the respective connecting bonds; the twist angles are 3 and 45°, respectively. It may be assumed that the difference in sulphur-sulphur bond lengths in (II), 0.06 Å, is due to the mentioned close contact and the different twist of the phenyl groups.

The difference between the sulphur-sulphur bond lengths in compound (III) [9] is 0.20 Å. The bonding in the sulphur sequence of this molecule is probably affected by the intramolecular strain caused by the phenyl groups in 3- and 4-positions.

The sum of the S—S bond lengths in compound (I) is 4.72 Å and in compounds (II) and (III) it is 4.66 Å. The difference between these values, 0.06 Å, is significant according to the reported standard deviations.[2,6,9] From the structures of (I) and (II), one gets the idea that methyl groups and phenyl groups affect the bonding in the three-sulphur sequence to different degrees. A structure study of the unsubstituted thiothiophthene would therefore be of interest. This study has been carried out, and the preliminary results are given here.

A sample of thiothiophthene was generously supplied by Reid.[12] The first synthesis of the compound was reported by Traverso.[13] Recrystallization from ethanol yielded orange red crystals belonging to the orthorhombic space group *Pnma*. The cell dimensions are, $a = 7.770 \pm 0.006$ Å, $b = 15.794 \pm 0.018$ Å, and $c = 5.390 \pm 0.012$ Å. There are four molecules per unit cell; density, calc. 1.610 g/cm^3, found 1.610 g/cm^3.
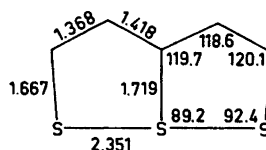

Fig. 1. Bond lengths (Å) and angles (°) in the thiothiophthene molecule.

The structure analysis is based on photographic data collected by the equi-inclination Weissenberg technique (CuKα radiation). The intensities of the 473 observed 0*kl*-5*kl* and *hk*0 reflections were estimated visually.

Approximate coordinates for the sulphur atoms were found from a three-dimensional Patterson synthesis. The atomic parameters were refined by least squares methods, and the final R factor is 0.088.

The crystals of thiothiophthene are isomorphous with those of 2,5-dimethyl-thiothiophthene, and the thiothiophthene systems of the two compounds are isostructural. Thus also in the crystals of thiothiophthene the molecules lie across crystallographic mirror planes passing through the central sulphur and carbon atoms.

The dimensions of the thiothiophthene molecule are shown in Fig. 1. The sulphur-sulphur bond lengths are 2.351 ± 0.002 Å.

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It should be noted that the sum of the S−S bond lengths, 4.70 Å, lies between the sum of the S−S bond lengths in compound (I), 4.72 Å, and the sum of those in compound (II), 4.66 Å.

Furthermore, cf. Fig. 1, the terminal and the central C−S bonds are 1.667 and 1.719 ± 0.009 Å, respectively, as compared with the values, 1.701 and 1.745 ± 0.004 Å, for the corresponding bonds in 2,5-dimethyl-thiothiophthene (I).[2] In 2,5-diphenyl-thiothiophthene (II) the lengths of the terminal C−S bonds are 1.702 and 1.694 ± 0.006 Å, respectively, and the length of the central C−S bond is 1.743 ± 0.006 Å.[5] The terminal C−S bonds in 3,4-diphenyl-thiothiophthene (III) are 1.664 ± 0.013 Å and the central C−S bond there is 1.749 ± 0.013 Å.[9]

The lengths of the terminal and central carbon-carbon bonds in thiothiophthene are 1.368 and 1.418 ± 0.010 Å, respectively. Corresponding bond lengths in compound (I) are 1.363 and 1.402 ± 0.004 Å, corresponding average bond lengths in (II) are 1.381 and 1.399 ± 0.008 Å, and corresponding average bond lengths in (III) are 1.402 and 1.443 ± 0.020 Å, respectively.

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2,4-Dinitroso-1,3-dihydroxynaphthalene as a Metal-Chelating Ligand

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In connection with investigations of the metal chelation properties of nitrosonaphthols, some studies with 2,4-dinitroso-1,3-dihydroxynaphthalene were carried out.

2,4-Dinitroso-1,3-dihydroxynaphthalene is believed to exist in two tautomeric forms (nitrosonaphthol $\rightleftharpoons$ quinonemonoxime). It is more soluble in water than nitrosonaphthols, and in aqueous solution it behaves as a diprotic acid. The constants of the two dissociation equilibria can be evaluated from absorbances at wavelengths in the region $300-360$ nm where the last peaks of the dissociated species are located.
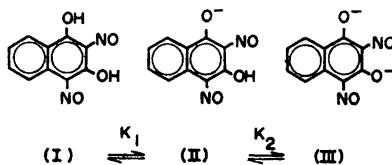
The values of the constants $K_1 = [H^+][HL^-]/[H_2L]$ and $K_2 = [H^+][L^{2-}]/[HL^-]$ were determined in aqueous solutions of varying ionic strength (Table 1). The logarithmic values $pK_1(I=0.1) = 4.53$ and $pK_2(I=0.1) = 9.10$ at 25°C were calculated

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