

Equal Sulphur-Sulphur Bonds in an Unsymmetrical Thiophiophthene Derivative

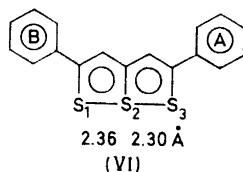
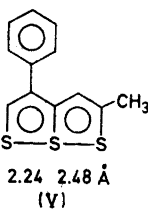
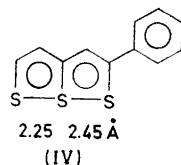
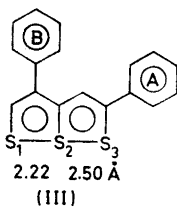
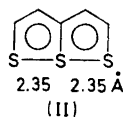
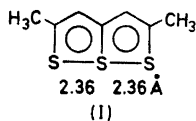
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X-Ray structure studies of 2,5-dimethylthiophiophthene (I)^{1,2} show that the sulphur-sulphur bonds in this symmetric derivative are of equal length, 2.36 Å.

Crystals of thiophiophthene (II) are isomorphous with crystals of 2,5-dimethylthiophiophthene, and the thiophiophthene system is isostructural in the two compounds. From a recent X-ray investigation the S—S bonds in (II) are 2.35 Å.³

The structure study of 2,4-diphenylthiophiophthene (III) shows that the S—S bonds there are 2.22 and 2.50 Å, respectively, and the difference in S—S bond length is assumed to be due to the substituents.⁴



The twist angles of phenyl groups A and B in (III) about the respective connection bonds are 25 and 52°, respectively,

and the conjugation across the former connection bond is therefore somewhat greater than the conjugation across the latter; LCAO MO calculations gave the π -bond orders 0.29 and 0.24,⁴ respectively. Furthermore, as phenyl group A is closer to a terminal sulphur atom than is phenyl group B, one may assume that the electron cloud on the terminal sulphur atoms are perturbed to different degrees. If one assumes that more electrons are pulled away from S(3) than from S(1), thus making S(3) more electronegative than S(1), one may explain the bonding in the linear S—S—S arrangement by reference to the bonding in linear trihalide ions. It has been found for the latter through structure investigations and by theoretical calculations,⁵⁻⁸ that the less electronegative of the terminal halogen atoms forms the strongest bond with the central halogen atom.

A Fourier projection of 2-phenylthiophiophthene (IV) has been reported.⁹ By assuming a distance of 4.70 Å between the terminal sulphur atoms one arrives at 2.25 and 2.45 Å for the two S—S bond lengths by measurements on the Fourier map.

Compound (V), 2-methyl-4-phenylthiophiophthene, has recently been studied.¹⁰ The sulphur-sulphur bonds there are 2.24 and 2.48 Å, respectively, and the phenyl group is twisted 70° about the connection bond.

By comparing the S—S bond lengths in compounds (III), (IV), and (V) one finds that it is the substituent in 2-position which affects the sulphur-sulphur bonding. It is interesting to note that the methyl group in (V) and phenyl group A in (III) have almost the same effect on the bonding in the sulphur sequence of the respective compounds.

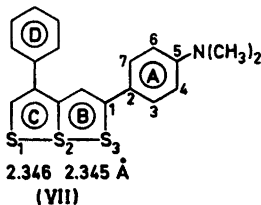
The sulphur-sulphur bonds in 2,5-diphenylthiophiophthene (VI) are slightly unequal; they are 2.30 and 2.36 Å, respectively.¹¹ Phenyl group A is almost coplanar with the thiophiophthene system and phenyl group B is twisted 45° about the connection bond. The conjugation across the connection bond to A is therefore more pronounced than the conjugation across the connection bond to B. According to the above, one should expect that S(2)—S(3) would be a longer bond than S(1)—S(2), but the experimental results show the opposite. There may, however, be an explanation to this as discussed below.

In crystals of 2,5-diphenylthiophiophthene (VI) there is a close contact,

3.25 Å, between S(3) and the plane of the thiothiophthene system of a symmetry related molecule, with the bond C—S(3) forming an angle of 77° with this plane. The close contact is 0.30 Å shorter than the sum of the van der Waals radius for sulphur and the half-thickness of an aromatic molecule, 3.55 Å,¹² and in fact compatible with a corresponding close contact present in crystals of the benzene-chlorine (1:1) charge-transfer complex.¹³ There, the chlorine molecules are arranged perpendicular to the planes of the benzene molecules, and the distance from a chlorine atom to the nearest benzene plane is 3.28 Å as compared with the corresponding van der Waals distance of 3.50 Å. It seems likely, therefore, that in crystals of (VI) there may be a transfer of charge from the π -system of the molecule towards S(3) of a symmetry related molecule. As a result, S(3) becomes less electronegative than S(1) and S(2)—S(3) becomes a shorter bond than S(1)—S(2).

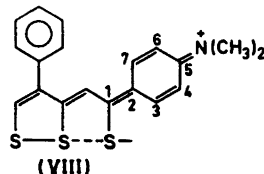
From the above, it seems likely that intramolecular environment (substituents) as well as intermolecular environment (donating or accepting groups) may perturb the bonding in the S—S—S sequence of the thiothiophthene system.

An X-ray study of 2-*p*-dimethylanilino-4-phenyl-thiothiophthene (VII) has been carried out in order to obtain better understanding of the bonding in thiothiophthene derivatives, and the preliminary results from this study are given here.

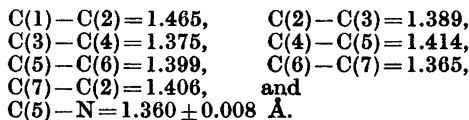


The sulphur-sulphur bonds in (VII) are 2.346 and 2.345 ± 0.003 Å, respectively, and thus equal within one standard deviation. The angle between the plane of ring B and that of ring C is 5°, the phenyl groups A and D are twisted 14 and 81°, respectively, about respective connection bonds, and the planar dimethylamino group is twisted 5° about the C(5)—N bond.

The sulphur-sulphur bonds in (VII) may now be compared with those in compound



(III). It is seen that the introduction of a *p*-dimethylamino group in phenyl group A in (III) causes a pronounced change in the sulphur-sulphur bonding. Thus S(1)—S(2) increases from 2.22 to 2.35 Å and S(2)—S(3) decreases from 2.50 to 2.35 Å. In accordance with the above explanation one may expect that the presence of the *p*-dimethylamino group in (VII) causes a decrease in the electronegativity of S(3) in this compound relative to that of S(3) in compound (III), for example through a transfer of charge from the *p*-dimethylanilino group towards S(3). The fact that the polar form (VIII), from bond length data, clearly contributes to the structure of (VII) supports this idea. The bond lengths of interest in this connection are,



A sample of 2-*p*-dimethylanilino-4-phenyl-thiothiophthene was generously supplied by Klingsberg.¹⁴ The crystals are deep red and belong to the monoclinic space group $P2_1/c$. The cell dimensions are $a = 7.158$ Å, $b = 7.413$ Å, $c = 33.237$ Å, and $\beta = 90.14^\circ$. There are four molecules per unit cell; density, calc. 1.338, found 1.332 g/cm³.

The structure analysis is based on X-ray data collected on a paper-tape controlled Siemens AED diffractometer using $\text{CuK}\alpha$ radiation. 2378 reflections were observed within $\theta = 71^\circ$.

Approximate coordinates for the sulphur atoms were found from a three-dimensional Patterson synthesis, and the remaining C and N atoms were found from a subsequent Fourier synthesis. The atomic parameters were refined by least squares methods, and the present *R* factor is 0.059.

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thiothiophthene. One of us (A. H.) wishes to thank *The Norwegian Research Council for Science and the Humanities* for economic aid.

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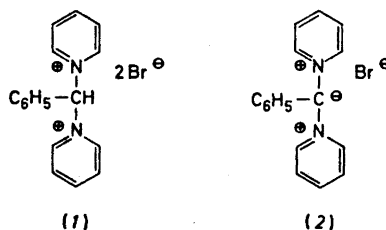
An Improved Method for the Preparation of 1-Deuterated Aldehydes

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Several methods exist for the preparation of 1-deuterated aldehydes.¹ However, these methods are usually inexpedient due to any of the following limitations: low

synthetic yields, low deuterium incorporation, costly reagents, inaccessibility of starting materials or limited applicability. Recently, a convenient method for the conversion of *gem*-dihalides into 1-deuterated aldehydes was described.² In this case, benzylidene dibromide was converted into the bisiminium salt (1) which was isolated and allowed to exchange a deuterium (from deuterium oxide) *via* the ylide (2). Warming of the reaction mixture then furnished benzaldehyde-*d* and pyridine in high yield and with high deuterium incorporation.



It has now been found that the *gem*-dibromides required can be generated *in situ* from the corresponding aldehydes and that the bisiminium salts need not be isolated. The preparation and purification of frequently unstable *gem*-dibromides is therefore unnecessary.

The procedure consists (method A) of the addition of 4 mmoles of the aldehyde to a stirred pre-prepared solution of triphenylphosphine dibromide in pyridine (from 8 mmoles of bromine and triphenylphosphine and 15 ml of dry pyridine). The resulting thick slurry is warmed for 2 h at 70°C, cooled to 0°C, and 10 ml of deuterium oxide is added. After standing overnight at room temperature, the clear solution is warmed for 30 min at 70°C, extracted with petroleum ether, washed repeatedly with water, and the aldehyde from the dried solution purified by column chromatography.

In this way, anisaldehyde is converted in 85 % yield into anisaldehyde-*d* of 90 % isotopical purity (by PMR). By repeating the procedure an isotopical purity of 99 % can be attained.

The bisiminium salt can be isolated by the addition of dry ether, filtration under nitrogen and washing with ether. The reaction (method B) of isolated anisaldehyde-derived bisiminium salt with buffered deuterium oxide according to the