The Molecular Structure of an Unsymmetrical 6a-Thiathiophthen

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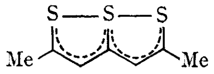
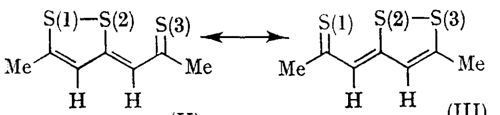
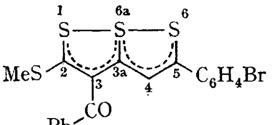
BEZZI *et al.*,[1] in reporting the results of a two-dimensional *X*-ray structure analysis on 2,5-dimethylthiathiophthen (I), found that (I) crystallizes in the space group *Pnma* with four molecules per unit cell, and that the molecule occupies a position with C_s site symmetry. It was then claimed[1] that the equivalence of the two S–S distances is *prima facie* evidence for one-bond no-bond S–S resonance in (I), involving canonical structures (II) and (III). While there is certainly additional evidence[2,3] for resonance of this type involving sulphur in related systems, we consider the conclusion that the two S–S distances in (I) are equal (2·35 Å) is open to some question. If the true *molecular* structure of 2,5-dimethylthiathiophthen were represented by (II), with the S–S distances unequal, but indicative of some degree of S–S bonding between S(2) and S(3), then in view of the overall symmetrical shape of (I), one might anticipate the molecule to occupy a site of symmetry C_s in the crystal with a 2-fold disordered arrangement.[4] In order to resolve the question of equivalence or non-equivalence of the S–S distances in the thiathiophthen system, we have undertaken a single crystal *X*-ray analysis of an unsymmetrical molecule of this class (IV). During the later stages of this study a preliminary account of an X-ray study on another unsymmetrical thiathiophthen derivative (V) has appeared.[5]



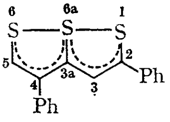
(I)



(II) (III)



(IV)



(V)

3-Benzoyl-5-p-bromophenyl-2-methylthio-6a-thiathiophthen (IV), m.p. 158—159°, was prepared from 5-p-bromophenyl-1,2-dithiol-3-thione[6] by conversion into 5-p-bromophenyl-3-methylthio-1,2-dithiolium methosulphate and condensation[7] with methyl benzoyl dithioacetate. The product had the expected n.m.r. spectrum and its electronic absorption spectrum (λ_{max} 269, 320, 350; 505 mμ; ϵ_{max} 69,600, 27,700, 8500, 17,000 in methylene chloride) resembles that of other 6a-thiathiophthens.[3]

3-Benzoyl-5-p-bromophenyl-2-methylthio-6a-thiathiophthen (IV), $C_{19}H_{13}OS_4Br$, crystallizes as fine red needles belonging to the monoclinic system. The cell parameters, as determined on a precession camera (Mo-K_α, $\lambda = 0{\cdot}7107$ Å), are $a = 13{\cdot}65 \pm 0{\cdot}03$, $b = 10{\cdot}42 \pm 0{\cdot}02$, $c = 27{\cdot}28 \pm 0{\cdot}03$ Å, with $\beta = 98° 30' \pm 20'$, while systematic absences indicate that the space group is $P2_1/c$. The measured density of 1·55 g.cm.$^{-3}$ requires that there be eight molecules of $C_{19}H_{13}OS_4Br$ in the unit cell and hence two crystallographically independent molecules in the crystal asymmetric unit. A total of 3850 independent non-zero structure amplitudes was measured from photographic data collected by the equi-inclination Weissenberg technique (Cu-K_α radiation), and the structure was determined by the symbolic addition procedure.[8] Full-matrix least-squares refinement on the data has given a present R factor of 0·13, with S–S distances $\pm 0{\cdot}007$, S–C $\pm 0{\cdot}015$, and C–C $\pm 0{\cdot}02$ Å.

The average bond distances and angles in the thiathiophthen nucleus are shown in the Figure. The two S–S distances within each molecule are clearly unequal, and are both much less than the sum of the van der Waals radii (3·70 Å).[9] The lengths are similar to the values found in (V) (2·22 and 2·51 Å), although if one considers the 2-phenyl in (V), and the p-bromophenyl in (IV) as common reference points in the two ring systems, the "short" and "long" bonds are reversed in the two compounds. In (IV), there is little conjugation between the thiathiophthen system and either the p-bromophenyl group (average angle of twist 32°) or the carbonyl group (average angle of twist 79°). In one of the two crystallographically independent molecules, the exocyclic S–CH_3 group is coplanar with the thiathiophthen ring system and the "longer" S–S distance is 2·47 Å; in the other molecule the exocyclic sulphur and carbon atoms are 0·14 and 0·39 Å respectively from the plane of the ring and the "long" S–S distance is 2·57 Å.

Comparison of the "short" S–S distances with the values (~2·00—2·10 Å) found in normal disulphide compounds,[10] provides evidence for significant one-bond no-bond resonance in (IV) and (V). Whether such resonance contributions can ever result in equal S–S distances remains an open question until X-ray studies are completed on a thiathiophthen derivative which has C_s molecular symmetry but does not use this symmetry in the crystal.

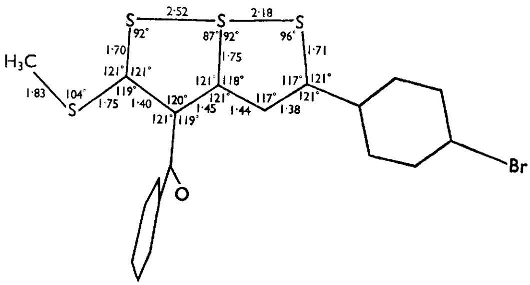


FIGURE. *Average bond distances and angles in the thiathiophthen ring system. There is good agreement between the two molecules with the exception of the "long" S–S distance as noted in the text.*

Examples of the single oxygen (S–S–O) and selenium (S–S–Se) analogues of the thiathiophthen ring system have also been studied crystallographically.[11,12] The S–S distance in the oxygen analogue is 2·12 Å, reasonably consistent with our "short" S–S distance, while the S–S distance in the selenium compound is 2·49 Å, agreeing well with our "long" S–S distance. A review of these various distances persuades us that there may be a typical "short" S–S distance in the thiathiophthen system (*i.e.*, in the 2·12—2·22 Å range) and a typical "long" S–S distance (2·47—2·57 Å), and seems to cast additional doubt on the interpretation of the *X*-ray results on (I)[1,13] where a distance of 2·35 Å was obtained.

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[3] H. Behringer, M. Ruff, and R. Wiedenmann, *Chem. Ber.*, 1964, **97**, 1732.

[4] A classic example of such 2-fold disorder is azulene (J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Cryst.*, 1962, **15**, 1) where the molecule occupies a position of site symmetry C_i in the crystal, although the molecule itself does not have this symmetry.

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[8] Full details will be published later, S. M. Johnson, M. G. Newton, and I. C. Paul, in preparation.

[9] L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1960, 3rd edn., p. 260.

[10] A comprehensive compilation of S–S distances is to be found in A. Hordvik, *Acta Chem. Scand.*, 1966, **20**, 1885.

[11] M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, *Nature*, 1961, **192**, 1282.

[12] J. H. van den Hende and E. Klingsberg, *J. Amer. Chem. Soc.*, 1966, **88**, 5045.

[13] A personal communication cited in reference 12, adds further evidence for statistical disorder in the crystal of (I).