Unequal S–S Bond Lengths in a Symmetrically-substituted Thiathiophthen

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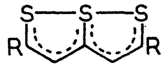
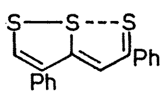
Summary The S–S bond distances in 3,4-diphenylthiathiophthen are much more unequal than those reported for 2,5-diphenylthiathiophthen.

RECENT X-ray examinations of the crystal structures of 2,5-dimethylthiathiophthen (Ia)[1] and of 2,5-diphenylthiathiophthen (Ib)[2] have indicated that in these symmetrically-substituted thiathiophthen derivatives the two S–S distances are more nearly equal than in the unsymmetrically-substituted molecules (II)[3] and (III).[4] We have carried out an X-ray analysis of the symmetrically-substituted 3,4-diphenylthiathiophthen (IV),[5] in which we expected steric interactions to force the planes of the phenyl rings to be almost perpendicular to the thiathiophthen nucleus and thus to eliminate the possibility of conjugation of the phenyl rings to the thiathiophthen nucleus.

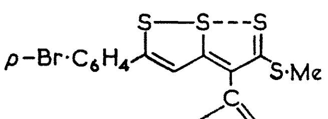
Very thin, dark-red crystals of (IV), obtained by crystallization from cyclohexane, were kindly supplied by Dr. D. H. Reid of St. Andrews University. *Crystal data.* Monoclinic, $C_{17}H_{12}S_3$, $M = 312{\cdot}5$, $a = 13{\cdot}924(13)$, $b = 6{\cdot}842(8)$, $c = 15{\cdot}350(13)$ Å, $\beta = 90°\ 45'(4')$, $Z = 4$, $D_c = 1{\cdot}42$ g. cm.$^{-3}$,‡ systematic absences: $h0l$, when $l = 2n + 1$;



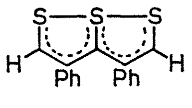
(I) a; R = Me
b; R = Ph



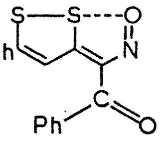
(II)



(III)



(IV)



(V)

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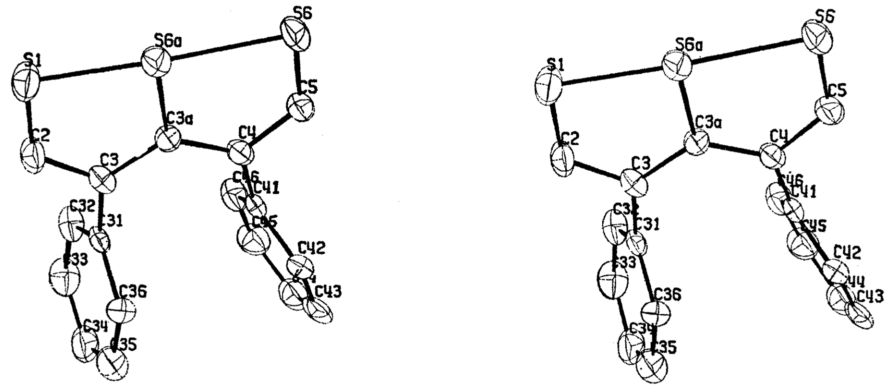

FIGURE 1. *Stereoscopic view of the molecule looking down the* b-*axis.*

$0k0$, when $k = 2n + 1$; space group $P2_1/c$. Cu-K_α(λ = 1·54178 Å, μ = 43·2 cm.$^{-1}$). The cell dimensions and intensity data were collected on a Picker FACS-1 computer-controlled diffractometer with Cu-K_α radiation. The structure was solved by the symbolic addition method[6] and at the present stage of refinement, the R-factor on 1342 reflexions is 0·10. A stereoscopic drawing of the molecule is shown in Figure 1, while Figure 2 shows the bond lengths. The e.s.ds of the S–S, C–S, and C–C distances are 0·004, 0·013, and 0·020 Å, respectively.

The S–S distances (2·233 and 2·433 Å) are much more unequal than those reported in (Ib) [2·297(3) and 2·355(3) Å],[2] and approach the range of distances found in the unsymmetrically-substituted derivatives (II) and (III).[3,4] The shorter S–S distance also compares reasonably with the S–S distance (2·178 Å) found in 3,5-epidithio-2-nitroso-1,5-diphenylpenta-2,4-dien-1-one (V).[7] The thiathiophthen ring is effectively planar (maximum deviation 0·02 Å) with C(3,1) and C(4,1) displaced by 0·06 Å in *opposite* directions from this plane. The bond angles external to the thiathiophthen ring at C(3) and C(4) exhibit substantial deviation from 120°. The angles C(3a)–C(3)–C(3,1) and C(3a)–C(4)–C(4,1) are 128° and 126°, respectively, while C(2)–C(3)–C(3,1) and C(5)–C(4)–C(4,1) are 117° and 116°, respectively. The two phenyl rings make angles of 70° and 74° with the best plane through the thiathiophthen ring, while C(3) and C(4) deviate by 0·10 and 0·11 Å from the phenyl rings to which they are bonded.

The central C–S bond (1·749 Å) is considerably longer than the other two "outer" C–S bonds (1·664 Å). While this effect is noticeable in several other thiathiophthen structures, [1,4] the present example shows the greatest difference in those bonds. The two "outer" C–C bonds [*i.e.*, C(2)–C(3) and C(4)–C(5)] are longer than the two "inner" C–C bonds [C(3)–C(3a) and C(3a)–C(4)]. Indeed, apart from the disposition of the sulphur atoms, (IV) is quite symmetrical about the central C–S bond. This geometry would seem to be more in accord with the theories of Maeda[8] and Hoffmann[9] than with the concept of "single-bond no-bond" resonance originally suggested[10] to describe the thiathiophthen system.

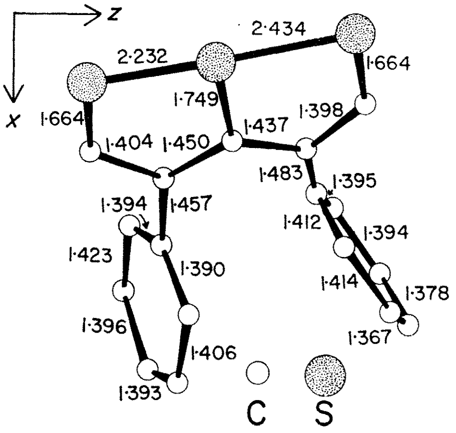

FIGURE 2. *View down the* b-*axis showing bond lengths.*

(*Received, June 9th,* 1969; *Com.* 810.)

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‡ It is very difficult to obtain a precise density measurement for these crystals because they are so thin. A number of experiments on flotation in various salt solutions lead us to believe the density is in the range 1·4—1·5 g. cm^{-3}.

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