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A Re-examination of the 2,5-Dimethylthiathiophthen Structure

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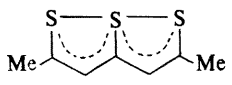
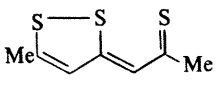
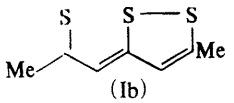
In the two-dimensional *X*-ray crystal structure analysis of 2,5-dimethylthiathiophthen [(I), also (Ia) or (Ib)], Bezzi



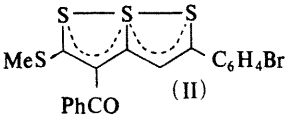
(I)



(Ia)



(Ib)



(II)

et al.[1] assigned the crystal to the orthorhombic centric space group *Pnma* rather than the alternative noncentric $Pn2_1a$ having the same systematic absences. The former space group requires the molecule to have a plane of symmetry in the central C–S bond and hence requires the S · · · S distances to be identical. However, in their *X*-ray crystal structure analysis of 3-benzoyl-5-*p*-bromophenyl-2-methylthio-6a-thiathiophthen (II), Johnson *et al.*[2] found unequal S · · · S distances of 2·52 and 2·18 Å and they suggested therefore that (I) might really be a statistically disordered combination of (Ia) and (Ib). In such a disordered crystal, if the differences between the two molecules were sufficiently large, one should find a doubling of the peaks on the electron-density distribution. For a smaller difference between molecules, the disordering could only show up as an apparently enhanced thermal vibration of the atoms concerned.

We have carried out a full three-dimensional refinement of (I) using diffractometer data (Cu-K_α radiation). Adsorption corrections[3] were applied. The revised orthorhombic cell parameters are: $a = 7{\cdot}846(1)$, $b = 10{\cdot}173(2)$, $c = 5{\cdot}385(2)$ Å. We refined the structure (*Pnma*) by a full-matrix least-squares procedure. With hydrogen atoms included, refinement converged to a conventional R of 0·063 and gave the bond lengths shown in Figure 1. No doubling of peaks was found on the electron density distribution and the anisotropic thermal parameters of all atoms had quite normal magnitudes (Table). Therefore, there is no *prima facie* evidence for statistical disordering in this structure or, if there is disordering, the difference in the two molecular geometries is too small to be detected by *X*-ray structure analysis.

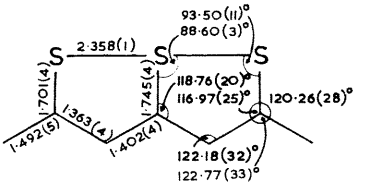


FIGURE. *Bond lengths and angles as obtained from refined analysis of* Pnma. (*E.s.d.'s in parentheses*)

Anisotropic thermal parameters in Å² *for sulphur atoms in space group* Pnma

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S_1	0·010583	0·003086	0·017605	(0)	−0·002766	(0)
S_2	0·14739	0·002973	0·027229	0·000865	−0·02725	0·000808

Although there is no reason to suspect that the true space-group of these crystals is the noncentric $Pn2_1a$, we have refined the data in this space group. If experimental *X*-ray data are free from serious systematic errors, refinement in which one or more space-group symmetries is ignored (by using the correct Laue symmetry) should result in a structure in which, to within a standard deviation or so, the neglected symmetry is preserved. In addition, the agreement between experimental and calculated intensities should be slightly better because more variables are used in the refinement. By using the final parameters from the

Pnma refinement the structure was refined further to give an R of 0·059. However, the new parameters resulted in a quite excessive asymmetry of the molecule and unacceptable bond lengths. It seems therefore that despite the low R value, the data must contain important systematic errors. We do not yet know what these are but are currently examining the role of anomalous dispersion and the weighting scheme used for refinement. The recently reported discrepancy between the atomic parameters obtained for potassium hydrogen malonate[4] refined in $C2/m$ and in $C2$ apparently arises from some other cause.[5]

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