Resonance Interaction in Thiophen Derivatives. The Crystal Structure of 2-Formylthiophen Thiosemicarbazone

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Summary The crystal structure determination of 2-formylthiophen thiosemicarbazone has revealed the first example of an interaction between a thiophen ring and a group substituted on the ring.

A RECENT survey[1] of the bond distances in thiophen derivatives included only one example of a simple asymmetrically substituted compound, α-thiophencarboxylic acid. However, the thiophen ring still maintained *mm* symmetry. The crystal structure determination of 2-formylthiophen thiosemicarbazone, 2FTTSC, has revealed the first example of a thiophen ring which is distorted from the ideal *mm* symmetry because of an interaction with the attached group.

The pale yellow crystals obtained from ethanol were studied by *X*-ray diffraction techniques using Cu-K_α radiation: $C_6H_7S_2N_3$, *M* 185·3; monoclinic, space group $P2_1/c$ (No. 14), $a = 13{\cdot}580(6)$, $b = 5{\cdot}839(4)$, $c = 24{\cdot}024(9)$ Å, $\beta = 117{\cdot}69(4)°$, $D_m = 1{\cdot}450$ g./cm.^{3}, $Z = 8$, $D_c = 1{\cdot}459$ g./cm.^{3}.

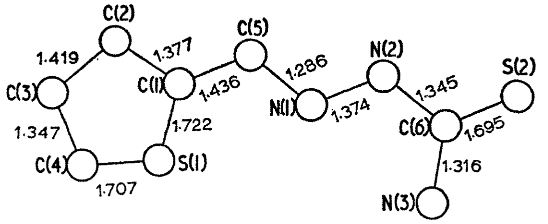

FIGURE. *The 2-formylthiophen thiosemicarbazone molecule, illustrating the atomic numbering, the conformation and the average bond distances of the two molecules.*

The intensities of 2848 non-zero reflections with $2\theta \leqslant 135{\cdot}0°$ (measured with a G.E. diffractometer) were used in the analysis. The sulphur atoms were located in an *E*-map calculated with signs determined by the symbolic addition method.[2] The light atoms were located in Fourier syntheses. The structure, including the hydrogen atoms, was refined by least-squares methods to an *R* (usual residual) of 0·052.

The presence of two molecules of 2FTTSC per asymmetric unit permits two measurements to be made of each bond distance. The average values are given in the Figure; only the C(1)–C(2) bonds with distances of 1·367 ± 0·005 and 1·387 ± 0·004 Å and the C(6)–N(3) bonds with distances of 1·306 ± 0·004 and 1·327 ± 0·004 Å are significantly different in the two molecules. The S(1)–C(1) bond length of 1·722 ± 0·003 Å is significantly different from the S(1)–C(4) bond distance of 1·707 ± 0·004 Å. The asymmetry in the thiophen ring is a result of the interaction between the planar ring and the approximately coplanar thiosemicarbazone side-chain. The C(1)–C(5) distance of 1·436 ± 0·004 Å is significantly less than the 1·48 Å expected for a single bond involving trigonal (sp^2) carbon atoms.[3] The double-bond character in the C(1)–C(5) bond indicates a strong interaction between the ring and the side-chain. The increase in the C(1)–C(2) and C(1)–S(1) bonds relative to the C(4)–C(3) and C(4)–S(1) bonds is in agreement with some double-bond character in the C(1)–C(5) bond. Therefore, the 2FTTSC molecule is best described as a highly delocalized system including both the ring and side-chain.

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[2] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[3] R. A. Alden, J. Kraut, and T. G. Taylor, *J. Amer. Chem. Soc.*, 1968, **90**, 74, and references therein.