

Crystal and Molecular Structure of the Aromatic Sulphur Compound 2,2'-Bi-1,3-dithiole. Evidence for *d*-Orbital Participation in Bonding

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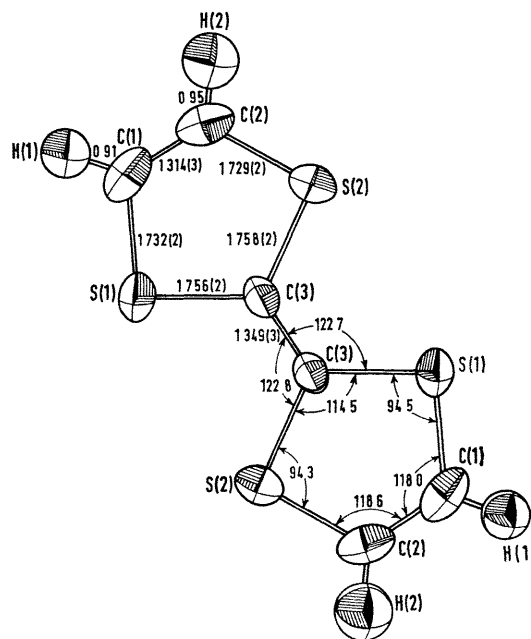
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Summary The structure of a new heteroaromatic sulphur compound has been determined; the results support the inclusion of *d*-orbitals in CNDO molecular orbital calculations.

ALTHOUGH derivatives of 2,2'-bi-1,3-dithiole have been examined, it is only recently that Wudl *et al.*¹ have isolated the parent compound itself which being an odd-membered sulphur-containing heterocycle, is expected to be a planar aromatic system, similar to the sulphur-containing systems examined by Visser *et al.*² We have determined the crystal structure of 2,2'-bi-1,3-dithiole and compared the results with predictions based on CNDO calculations.

2,2'-Bi-1,3-dithiole forms orange, light-sensitive needles; *crystal data*: C₆H₄S₄, monoclinic, $a = 7.364$, $b = 4.023$, $c = 13.922$ Å, $\beta = 101.42^\circ$, $Z = 2$, space-group $P2_1/c$, $\mu = 10.77$ cm⁻¹. 2496 independent hkl intensities were collected on an automated Picker full-circle diffractometer with Mo- K_α ($\lambda = 0.71069$ Å) radiation. The structure was solved by the standard heavy-atom method, and the model, including the hydrogen atoms, was refined by full-matrix least-squares to a final R of 0.048 on the observed data. Bond lengths and bond angles are given in the Figure.

The crystal has a short b axis and consequently all the molecules in the cell are stacked along this axis. Each molecule contains two symmetry-independent C-C double bonds, the bridging bond [1.349(3) Å] being longer than the terminal bond [1.314(3) Å]. This trend mirrors the results obtained for heptafulvalene³ where the bridging double bond (1.373 Å) was shown to be longer than the



FIGURE

Bond lengths and angles in 2,2'-bi-1,3-dithiole. Thermal ellipsoids are 50% probability surfaces. The centre of the molecule is located at a crystallographic centre of symmetry.

ring double bonds (1.332—1.343 Å).† The S-C bond

† Before corrections for thermal motion.

distances agree with the results obtained for the dithienyl systems.² It is noteworthy that the bonds between the S atoms and the bridging carbon are longer than those between these same sulphur atoms and the ring double bonds. Furthermore the C-S bonds reported here are longer than those reported for the dithienyl system, where these bonds ranged from 1.67(2) to 1.71(2) Å.

In contrast to the dithienyl systems, the overall molecule is not planar but is slightly distorted into a chair conformation. The central carbon and sulphur atoms lie in a plane (A), the largest deviation from the best least-squares plane being 0.007 Å. In addition, the two symmetry related planes (B) through the sulphur atom and end carbon atoms lie 0.116 Å apart. The angle between planes (A) and (B) is 2.1°.

CNDO calculations on an idealized dithiole system were carried out using a program written by Dr. J. W. McIver.⁴ The input bond lengths and the results obtained for the population matrix with and without the inclusion of the sulphur *d* orbitals⁵ are shown in the Table. The results indicate that inclusion of sulphur *d* orbitals is necessary to explain the relative lengths of the two C=C bonds. In order not to bias the calculations, standard C-C double bond and C-S single bond lengths were used. Both calculations predict that the S(1)-C(1) [S(2)-C(2)] bonds have a larger electron population than the S(1)-C(3) [S(2)-C(3)] bonds, but only when *d* orbitals are included is

the predicted electron population larger for C(1)-C(2) than for C(3)-C(3). This is in agreement with the experimental bond lengths. A similar correlation between number of electrons and bond length has been observed for a series of hydrocarbon molecules.⁶

Comparison of number of electrons per bond according to Lowdin orthogonalized CNDO results and experimental bond lengths*

	Number of electrons in bond		Experimental bond distances (Å)	Input bond distances (Å)
	without <i>d</i>	with <i>d</i>		
C(3)-C(3)	1.432	1.238	1.349(3)	1.34
C(1)-C(2)	1.374	1.297	1.314(3)	1.34
S(1)-C(3)	0.361	0.450	1.756(2)	1.71
S(2)-C(3)			1.758(2)	
S(1)-C(1)	0.388	0.486	1.732(2)	1.71
S(2)-C(2)			1.729(2)	

* The overlap populations reported here from the CNDO results were obtained by assuming that the CNDO calculation can be represented as an *ab initio* calculation in which the basis set has been Lowdin orthogonalized (J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, 5136). By performing the reverse transformation, the results can be analysed according to the usual Mulliken procedure (J. W. McIver, to be published).

We thank Dr. J. W. McIver for advice on the CNDO results.

(Received, May 12th, 1971; Com. 751.)

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⁵ D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 1967, **47**, 158.

⁶ J. W. McIver, P. Coppens and D. Nowack, *Chem. Phys. Letters*, in the press.