

- istry*, Vol. 1, Pergamon, London 1960, p. 117.
- Ehrenberg, A. *Acta Chem. Scand.* **11** (1957) 1257.
  - Manganiello, V. C. and Phillips, A. H. *J. Biol. Chem.* **240** (1965) 3951.
  - Margoliash, E., Smith, E. L., Kreil, G. and Tuppy, H. *Nature* **192** (1960) 1125.

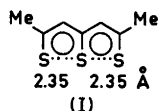
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## The Sulphur-Sulphur Bonds in an Unsymmetrical Thiothiophthene Derivative

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Bezzi *et al.*<sup>1,2</sup> in 1958 discovered the thiothiophthene "no-bond resonance" system through an X-ray crystallographic study of the dimethyl derivative (I).



They found the sulphur atoms to be co-linear and equally spaced with sulphur-sulphur distances of 2.36 Å (later,<sup>3</sup> 2.35 Å was reported), as compared with the value 2.10 Å for a sulphur-sulphur single bond in a *cis*-planar disulphide group.<sup>4</sup>

The electronic structure of the thiothiophthene ring system has been calculated by Giacometti and Rigatti,<sup>5</sup> in terms of sulphur-sulphur bonds made up from both fractional  $\sigma$  and  $\pi$  bonds.

Klingsberg<sup>6</sup> has shown that (II) and (III) react with phosphorus pentasulphide to yield the same compound (IV), and preliminary results of a crystal structure

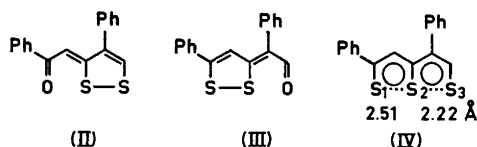


Table I. Atomic coordinates, in fractions of corresponding cell edges.

	<i>x</i>	<i>y</i>	<i>z</i>
S <sub>1</sub>	0.3248	0.1634	0.2569
S <sub>2</sub>	0.1275	-0.1060	0.0763
S <sub>3</sub>	-0.0450	-0.3437	0.0870
C <sub>1</sub>	0.3757	0.1877	0.1142
C <sub>2</sub>	0.3016	0.0679	-0.0337
C <sub>3</sub>	0.1887	-0.0778	-0.0649
C <sub>4</sub>	0.1129	-0.2054	-0.2209
C <sub>5</sub>	-0.0027	-0.3362	-0.2363
C <sub>6</sub>	0.4988	0.3425	0.1444
C <sub>7</sub>	0.5706	0.3233	0.0336
C <sub>8</sub>	0.6827	0.4677	0.0565
C <sub>9</sub>	0.7216	0.6275	0.1997
C <sub>10</sub>	0.6530	0.6460	0.3098
C <sub>11</sub>	0.5405	0.5020	0.2865
C <sub>12</sub>	0.1560	-0.1951	-0.3481
C <sub>13</sub>	0.0667	-0.1818	-0.4511
C <sub>14</sub>	0.1088	-0.1762	-0.5736
C <sub>15</sub>	0.2367	-0.1812	-0.5990
C <sub>16</sub>	0.3265	-0.1945	-0.4985
C <sub>17</sub>	0.2869	-0.2016	-0.3751

analysis of this unsymmetrical thiothiophthene derivative are given here.

The crystals are triclinic, and belong to the space group  $P\bar{1}$  with  $a = 10.18$  Å,  $b = 8.52$  Å,  $c = 10.29$  Å,  $\alpha = 118.8^\circ$ ,  $\beta = 94.3^\circ$ ,  $\gamma = 101.1^\circ$ .<sup>7</sup> There are two mole-

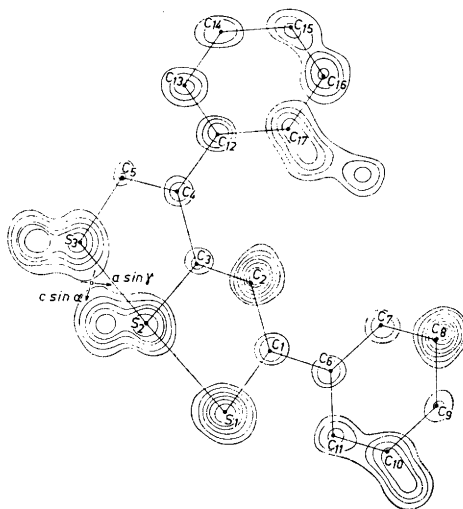


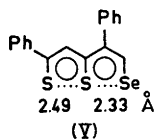
Fig. 1. Electron density projection of (IV) along the *b* axis. Contour intervals, 1 e·Å<sup>-3</sup> for carbon and 3 e·Å<sup>-3</sup> for sulphur. Lowest contour 5 e·Å<sup>-3</sup>.

cules per unit cell; density, calc. 1.38, found, 1.39 g/cm<sup>3</sup>. The experimental error is estimated to be within 0.5 %.

Approximate coordinates for the sulphur and carbon atoms were found from a three-dimensional Patterson synthesis, and the atomic parameters were refined by least squares methods. The coordinates in Table I correspond to the last isotropic refinement cycle. At this stage  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  was 0.17 for 2087 observed reflections. An electron density projection along the *b* axis is reproduced in Fig. 1.

The results show that the sulphur-sulphur distances in (IV) are different,  $S_1-S_2 = 2.510 \pm 0.008$  Å and  $S_2-S_3 = 2.216 \pm 0.008$  Å. One may therefore conclude that the thiothiophene system in (IV) is perturbed by the presence of phenyl groups in unsymmetrical positions.

A preliminary note on the structure of (V), isosteric with (IV), has recently been published by van den Henden and Klingsberg.<sup>8</sup> They find the sulphur-sulphur dis-



tance in (V) to be  $2.492 \pm 0.003$  Å, which is very nearly the same as the equivalent  $S_1-S_2$  distance in (IV). Furthermore, if one subtracts the difference in covalent radii of selenium and sulphur, 0.12 Å, from the selenium-sulphur distance in (V), one arrives at the value 2.21 Å which is close to that found for the  $S_2-S_3$  distance in (IV).

The authors are indebted to Dr. E. Klingsberg, American Cyanamid Co., for providing a sample of (IV).

1. Bezzi, S., Mammi, M. and Garbuglio, C. *Nature* **182** (1958) 247.
2. Bezzi, S., Garbuglio, C., Mammi, M. and Traverso, G. *Gazz. Chim. Ital.* **88** (1958) 1226.
3. Mammi, M., Bardi, R., Garbuglio, C. and Bezzi, S. *Acta Cryst.* **13** (1960) 1048.
4. Hordvik, A. *Acta Chem. Scand.* **20** (1966) 1885.
5. Giacometti, G. and Rigatti, G. *J. Chem. Phys.* **30** (1959) 1633.

6. Klingsberg, E. *J. Am. Chem. Soc.* **85** (1963) 3244.
7. Hordvik, A., Sletten, E. and Sletten, J. *Acta Chem. Scand.* **20** (1966) 1172.
8. van den Henden, J. H. and Klingsberg, E. *Private communication* (1966).

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## The Identification of Organic Compounds

### VII.\* Improved Methods for the Preparation of 3,5-Dinitrobenzoyl Derivatives and Picrates of Aliphatic Amines

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**N**-Substituted benzamides are often low-melting compounds, and Vecera, Volakova, Kazakova, and Jurecek<sup>1</sup> and Volakova<sup>2</sup> have therefore proposed to use the *N*-substituted 3,5-dinitrobenzamides for the identification of amines. We are able to recommend these derivatives as they are highly crystalline compounds with melting points distributed over a range of temperature sufficiently wide to differentiate between isomeric compounds.

Unfortunately, the procedure proposed by Vecera *et al.*<sup>1</sup> and Volakova<sup>2</sup> for the preparation of the derivatives is very troublesome as a standing period of about 12 h is required. We have succeeded in working out a method, described below, by which the preparation of the derivative can be carried out within 10–15 min.

*Picrates* are also widely used for the characterisation of aliphatic amines. The procedures given in various text-books of organic analysis do not always lead to a precipitation of the picrates although they should be only slightly soluble in the medium used. We have found that the reason is, that the reaction mixture contains an

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