in order to make the method quantitative. The uronic acid content of the present xylan sample was 10.3 %, but only about 5 % was found after gas chromatography.

The mass spectra of the sample peak and that of the reference substance were identical and thus definitely verified the presence of 4-*O*-methyl-D-glucitol pentaacetate (Fig. 1).

Experimental. Materials. The xylan sample and the methyl 4-*O*-methyl-*β*-D-glucopyranoside, used as reference substance, were obtained from Doc. O. Theander, Swedish Forest Products Research Laboratory, Stockholm, Sweden. The alditol acetates were prepared as described earlier.[3]

Procedure. The cations present in the xylan sample were first removed by acid-treatment in order to liberate all the carboxyl groups.[4] The esterification was then carried out by adding 10 ml 37 % (w/w) propylene oxide solution to *ca.* 100 mg of xylan sample and the mixture was allowed to stand at room temperature for 7 days. The ester was reduced overnight in the presence of 100 mg sodium borohydride. The treated sample as well as the reference substance were then hydrolysed in 4.0 % (w/w) sulphuric acid solution at 120°C for 1 h. The monosaccharides formed were finally reduced, acetylated, and subjected to gas chromatography according to the procedure described elsewhere.[3]

Apparatus. A Perkin-Elmer gas chromatograph, Model 900, equipped with a differential flame detector was used. The peak areas were measured by an Infotronics electronic integrator, Model CRS-1, connected to the gas chromatograph. The mass spectra were recorded by a Perkin-Elmer mass spectrometer, Model 270 B.

Acknowledgements. The financial support of the *National Research Council for Technical Sciences* is gratefully acknowledged. We also wish to express our best thanks to Doc. O. Theander, Swedish Forest Products Research Laboratory, Stockholm, Sweden, for the xylan and reference substance samples and Mr. P. Karvonen for recording the mass spectra.

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Received November 26, 1969.

The Sulphur-Sulphur Bonds in 2-Methyl-4-phenyl-thiothiophthene

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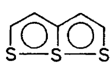
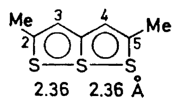
Gleiter and Hoffmann[1] have calculated potentional energy curves for the three-centre four-electron bond in thiothiophthene (I) with and without the utilization of sulphur 3*d* orbitals. The molecular dimensions found for the thiothiophthene system in (II)[2] is used as a model structure, and the potential energy is calculated as a function of a displacement of the central sulphur atom towards one of the terminal sulphur atoms.

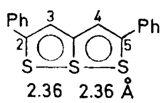
From the energy curves a symmetric structure is preferred when 3*d* orbitals are utilized and an asymmetric structure is preferred when 3*d* orbitals are not utilized. The energy minimum in the former case is flat and broad, about 0.3 Å.



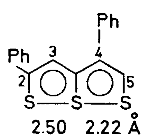
(I)



(II)



(III)



(IV)

X-Ray studies of thiothiophthene derivatives show that the S—S bonds in the sulphur sequence may be of equal or of different lengths, *e.g.* compounds II, III, and IV.[2-4] From additional structure data available on thiothiophthene derivatives[5-9] the differences in S—S bond lengths vary within a range of 0.3 Å. This indicates that the three-centre bond in thiothiophthene has a rather flat and broad energy minimum about the symmetric structure in agreement with the results from Gleiter and Hoffmann's calculations.

The difference in S—S bond lengths is 0.06 Å in compound (III) and 0.28 Å in compound (IV). Thus the effect of a phenyl substituent on the three-centre bond depends on the position of the phenyl group. A better understanding of the bonding in the thiothiophthene system might perhaps be obtained from investigations of the relative effects of different substituents on the three-centre bond. We have therefore carried out an X-ray study of 2-methyl-4-phenyl-thiothiophthene, and the preliminary results are given here.

The sulphur-sulphur distances in 2-methyl-4-phenylthiothiophthene, given in Fig. 1, are $S_1-S_2 = 2.475 \pm 0.002$ Å and $S_2-S_3 = 2.237 \pm 0.002$ Å. They agree with the corresponding S—S distances in (IV) which are 2.499 ± 0.003 Å and 2.218 ± 0.003 Å, respectively. Thus, the exchange of the 2-phenyl group in (IV) with a methyl group leaves the bonding in the sulphur sequence almost unchanged.

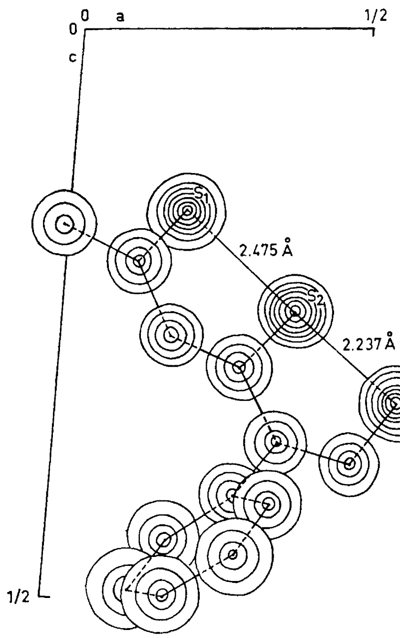


Fig. 1. Electron density map for 2-methyl-4-phenyl-thiothiophthene, showing the electron density in planes perpendicular to *b* and passing through respective atomic positions. Contour intervals, 2 e·Å^{-3} for carbon and 4 e·Å^{-3} for sulphur. Lowest contour 1 e·Å^{-3}.

A sample of 2-methyl-4-phenyl-thiothiophthene was generously supplied by Klingsberg.[10] The crystals are deep red and belong to the monoclinic space group $P2_1/c$. The cell dimensions are $a = 9.566$ Å, $b = 6.683$ Å, $c = 18.603$ Å, and $\beta = 94.9°$. There are four molecules per unit cell; density, calc. 1.404 g/cm^3, found 1.404 g/cm^3.

The structure analysis is based on photographic data collected by the equi-inclination Weissenberg technique (Cu*K*α radiation). The intensities of the 1933 observed $h0l-h6l$ and $0kl$ reflections were estimated visually.

Approximate coordinates for the sulphur atoms and the carbon atoms of the thiothiophthene system were found from a three-dimensional Patterson synthesis, and the remaining carbon atoms were found from a subsequent Fourier synthesis. The atomic parameters were refined by least squares methods, and the final *R* factor is 0.074.

An electron density map, showing the eletron density in planes passing through the respective atomic positions, is given in Fig. 1.

The authors are indebted to Dr. E. Klingsberg, American Cyanamid Co., for providing a sample of 2-methyl-4-phenyl-thiothiophthene. One of us (A.H.) wishes to thank *The Norwegian Research Council for Science and the Humanities* for economic aid.

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Received November 25, 1969.