

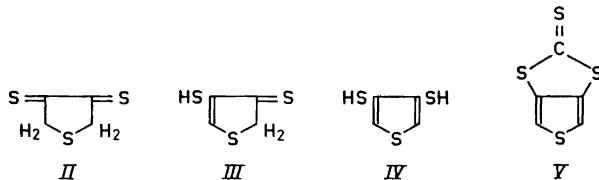
On the Structure of the So-called 3,4-Thiolanedithione

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3,4-Thiophenedithiol (IV) has been prepared through halogen-metal interconversion between the lithium salt of 4-bromo-3-thiophenethiol and *n*-butyllithium at -70° , followed by reaction with sulphur. IR-, NMR- and UV-spectra show that this compound exists in the dithiol form. The compound obtained as a by-product in the commercial thiophene synthesis from butane and sulphur and described in the literature as 3,4-thiolanedithione (II) (*viz.* the tautomeric dithione form of 3,4-thiophenedithiol) is most probably 5-methyl-1,2-dithiole-3-thione (VI)**.

Pyrolysis of the "thiophene tars" obtained in the commercial synthesis of thiophene from butane and sulphur¹ yields as the main product 3-thiophenethiol, the structure of which has been proved by Caesar and Branton² through comparison with an authentic sample, prepared from 3-thiophene-magnesium iodide and sulphur. They² also obtained a subsidiary product (I) which they described as a deep-red oil boiling at $120-125^\circ/2$ mm Hg, and which they claimed to have the empirical formula $C_4H_4S_3$, although the discrepancy between the calculated and found values for carbon and sulphur were large. They suggested this product to be 3,4-thiolanedithione (II) on the following evidence: Boiling of I with alcoholic alkali resulted in the evolution of approximately one mole equivalent of hydrogen sulphide upon acidifi-



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** According to modern nomenclature, *dithiole* means a five-membered ring with two sulphur atoms incorporated in the ring and one double bond. It should not be confounded with *dithiol*, which signifies a compound containing two thiol groups.

cation. Destructive hydrogenation with Raney-nickel yielded *n*-butane. Har-tough³ states as unpublished work by Caesar that I can be reduced to 3-thiophenethiol with zinc dust and hydrochloric acid, though no mention of this occurs in Ref.² The IR-spectrum of I showed absorption characteristics neither for the thiophene ring nor for the thiol group. From the UV-spectrum of the product⁴ and from mechanistic considerations² on the formation of I from butane and sulphur, they chose II as its most probable structure, in preference to the three other isomeric thiolanedithiones. The IR-data eliminate the possibility of I existing as the tautomeric thiolenedithione (III) or as the dithiol (IV). As Caesar and Branton² admit that their structure assignment is rather speculative, it is unfortunate that in a recent handbook on sulphur compounds, I is described as 3,4-thiophenedithiol⁵.

Although it has been found that some 2-hydroxythiophenes exist predominantly as the tautomeric thioen-2-ones⁶, an investigation of the structures of methyl-, methylthio- and bromothiophenethiols^{7,8} showed that in these cases the compounds exist as thiols. It seemed to us therefore rather improbable that 3,4-thiophenedithiol should exist in its dithione form II, in which the aromatic character of the thiophene ring has been entirely lost. In view of this, we decided to investigate the true structure of 3,4-thiophenedithiol in greater detail.

3,4-Thiophenedithiol was prepared by treating 4-bromo-3-thiophenethiol⁷ with two moles of *n*-butyllithium at -70° followed by one mole of sulphur. We obtained the product as a yellow liquid boiling at $88-93^\circ/1.5$ mm Hg, which was soluble in alkali. Though not as unstable as the bromothiophene-

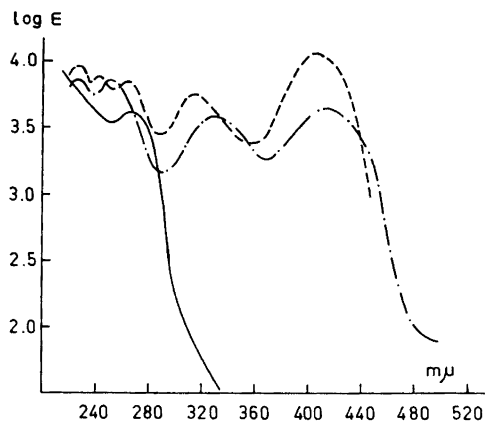
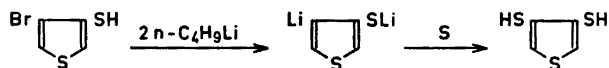


Fig. 1. UV-spectrum of ——— 3,4-thiophenedithiol in hexane, of ----- 5-methyl-1,2-dithiole-3-thione according to Ref.^{2,9}, of -.-.-.- 3,4-thiolanedithione in *isooctane* according to Ref.⁴

thiols⁷, it nevertheless decomposes after some time even when stored at -15° . Apart from elementary analyses, the product was further characterized as the trithiocarbonic acid derivative (V) obtained in amber-coloured needles upon reacting IV with carbon disulphide in alkali. We suggest naming V as thieno[3,4-d]-1,3-dithiolane-2-thione. The structure of IV was proved by studying its UV-, IR- and NMR-spectra.

Its UV-spectrum (Fig. 1) in hexane solution is that to be expected for a thiophene derivative⁹, having an absorption peak at $269\text{ m}\mu$ ($\log \epsilon = 3.60$) and being similar to the UV-spectrum of methyl 3-thienyl sulphide⁹.

Its IR-spectrum (Fig. 2) shows a strong peak due to S-H stretching at $3.95\ \mu$ (2530 cm^{-1})¹⁰ with additional characteristic peaks at $6.75\ \mu$ (1480 cm^{-1}), $7.15\ \mu$ (1400 cm^{-1}), $7.52\ \mu$ (1330 cm^{-1}) and $8.30\ \mu$ (1200 cm^{-1}) which fall in the regions, or almost so, given by Katritzky and Boulton¹¹ for the characteristic ring stretching frequencies of thiophenes. The presence of the three peaks at $10.80\ \mu$ (926 cm^{-1}), $11.60\ \mu$ (862 cm^{-1}) and $12.70\ \mu$ (787 cm^{-1}) is characteristic for 3,4-disubstituted thiophenes and has been found by the present authors in many 3,4-disubstituted thiophenes (cf. IR-spectra in Refs.^{7,12}).

Its NMR-spectrum in *cyclohexane* solution showed two peaks with relative intensities of 1:1 at $\tau = 2.91\text{ ppm}$ and $\tau = 6.69\text{ ppm}$. The resonances occur in the region characteristic for thiophenic ring hydrogens^{8, 13} and thiophenic thiol hydrogens⁸ respectively. At higher resolution the bands show some fine-structure due to couplings between the ring and thiol hydrogens⁸. For 3,4-thiolanedithione, only one resonance is expected, while a structure like III contains three types of non-equivalent hydrogens.

The above-mentioned spectroscopic data thus show not only that the compound is a thiophenethiol but also that it is the 3,4-isomer, *i.e.* the rearrangements that are known to occur in some halogen-metal interconversions involving bromothiophenes¹⁴ have not been observed here.

Since the NMR-spectrum of the dithiol in 30% *cyclohexane* solution did not undergo any change during a period of several months, it is evident that in the 3,4-thiophenedithiol system the dithiol form is the most stable tautomer,

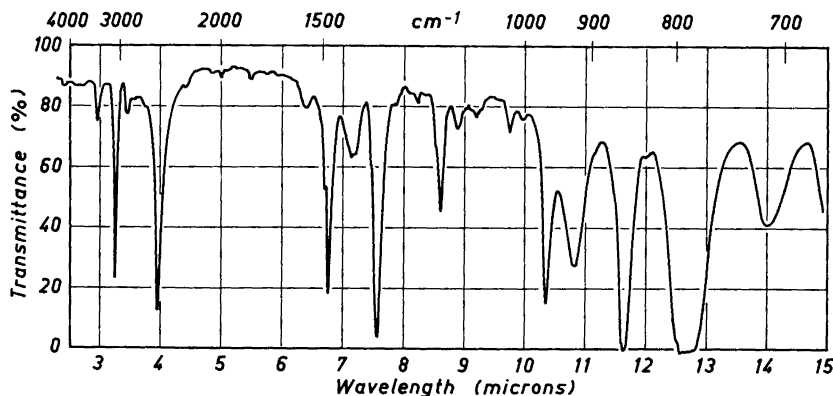
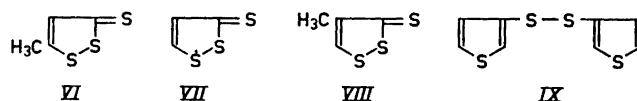


Fig. 2. IR-spectrum of 3,4-thiophenedithiol.

as in this system equilibration can be expected to be rapid and should certainly have been established during this period. It seems therefore very improbable that Caesar and Branton² should have obtained the product entirely in its unstable form and that no equilibration should have occurred during their distillation. It is also rather improbable that the product I is a thiolanedithione corresponding to one of the three remaining isomeric thiophenedithiols, since the latter appear to be very unstable compounds with properties differing from I. Pandya and Tilak¹⁶ tried in vain to obtain the 2,5-isomer from 2,5-dilithiumthiophene and sulphur, and we have tried to prepare the 2,4- and 2,3-isomer from 4-bromo-2-thiophenethiol and 3-bromo-2-thiophenethiol according to the same method as used for the 3,4-isomer. The product obtained in the attempted synthesis of 2,4-thiophenedithiol decomposed as soon as the solvent (ether) was removed at room temperature. In the case of the 2,3-isomer, we did manage to obtain an IR-spectrum of the undistilled residue obtained upon removal of the ether before the product decomposed. In this spectrum, the S-H stretching band was present indicating the presence of at least one SH group. It seems thus quite clear that I is certainly not 3,4-thiolanedithione (which exists entirely, or almost so, in its tautomeric dithiol form) and hardly any of the other isomeric thiolanedithiones.

The conditions under which I is formed¹ together with its chemical and physical properties, point instead rather convincingly to the conclusion that this by-product of the thiophene synthesis is not at all a thiophene, but is impure 5-methyl-1,2-dithiole-3-thione (VI) (a trithione).



It is known that treatment of olefins with sulphur at higher temperatures and pressures leads to the 1,2-dithiole-3-thione system¹⁶⁻¹⁸. Lüttringhaus *et al.*¹⁷ obtained the unsubstituted ring (VII) from propylene and sulphur and Spindt *et al.*¹⁸ obtained 4-methyl-1,2-dithiole-3-thione (VIII) in rather good yield on heating *isobutylene* and sulphur in a bomb. VI is, however, most conveniently prepared through the reaction of ethyl acetoacetate with phosphorus pentasulphide¹⁹ and has also been obtained in the reaction of *n*-butyl sulphide and *n*-butyl disulphide with sulphur²⁰. It is characteristic for the 1,2-dithiole-3-thiones that they split off sulphur as sodium sulphide upon treatment with alkali^{16,18}, as was also observed for I. The boiling-point of I is the same range as that given for VI (which has an m.p. of 33°) and finally, the UV-spectrum of the alleged 3,4-thiolanedithione as given in Ref. 4 is almost identical with that of authentic VI²⁰ (Fig. 1), showing the characteristic absorption at 410 m μ ^{18,20} of this ring system. The minor differences are most probably due to impurities in I. If the 3-thiophenethiol obtained through reduction of I with zinc and hydrochloric acid³ is not due to 3,3'-dithienyl disulphide (IX)²¹ possibly present* as an impurity in I, its formation must involve an

* Caesar and Brantons analytical data fit very well for a mixture of 89 % VI and 11 % IX.

interesting rearrangement from the 1,2-dithiole-3-thione system to the thiophene ring system, with the elimination of one sulphur atom.

It seems probable that the present findings are of relevance in connection with the mechanism of the formation of thiophene from butane and sulphur, and it is obvious that Harthouh's hypothesis²² regarding the constitution of the major constituent of the "thiophene-tars" cannot explain the formation of 5-methyl-1,2-dithiole-3-thione.

EXPERIMENTAL

3,4-Thiophenedithiol. Into the usual nitrogen-swept four-necked apparatus was introduced 228 ml of 1.29 N ethereal *n*-butyllithium and the solution cooled to -70° . 25.4 g (0.128 mole) of 3-bromo-4-thiophenethiol⁷, freshly prepared from 3,4-dibromothiophene, was dissolved in 50 ml of ether and added with stirring to the *n*-butyllithium. After 10 min, 5.2 g (0.16 mole) of sulphur was added in one portion and the mixture stirred at -70° for a further half hour. It was then poured into water, the aqueous phase was separated, the ether phase extracted with two portions of 2 N sodium hydroxide and the combined aqueous phase acidified with 2 N hydrochloric acid under strong cooling. The acidified mixture was immediately extracted with three portions of ether, dried and fractionated *in vacuo* after removal of the solvent. After a forerun consisting of 5.4 g of impure 3-thiophenethiol, boiling at $52-72^{\circ}/2$ mm Hg, 9.3 g (49 %) of crude 3,4-thiophenedithiol distilled at $80-92^{\circ}/2$ mm Hg. Redistillation yielded the pure product as a yellow oil, b.p. $88-93^{\circ}/1.5$ mm Hg. (Found: C 32.87; H 2.87; S 64.19. Calc. for $C_4H_4S_2$ (148.3): C 32.40; H 2.72; S 64.87).

Thieno [3,4-d] 1,3-dithiolane-2-thione. 5.2 g (0.035 mole) of 3,4-thiophenedithiol was treated with 20 ml of carbon disulphide and 60 ml of 2 N sodium hydroxide and the mixture refluxed for 4 h under nitrogen. The excess carbon disulphide was then allowed to evaporate off. The resulting dark-coloured product was filtered off, washed and dried, giving 3.2 g (48 %) of crude product, m.p. $139-141^{\circ}$. After decolorizing with Norit and recrystallization from 50 ml of acetic acid, 2.3 g of pure product was obtained in amber-coloured needles, m.p. $141-141.5^{\circ}$. (Found: C 31.78; H 1.28; S 67.34. Calc. for $C_5H_2S_4$ (190.3): C 31.55; H 1.06; S 67.38.)

The UV-measurements were carried out with a Beckman model DU-spectrophotometer. The IR-spectra were recorded on a Perkin-Elmer Infracord spectrophotometer. The NMR-spectra were obtained with a Varian Associates model V-4 300-B high resolution spectrometer, operating at 40.00 Mc/s and a flux-stabilized 12 in. magnet equipped with shim-coils from the same company. The magnet sweep was calibrated with the conventional side-band technique using a General Radio 617-C interpolation oscillator and a Hewlett-Packard 524-D frequency counter. The chemical shifts were obtained from cyclohexane solutions containing 2 % of tetramethyl silane and are given as τ -values²³.

Acknowledgements. The authors wish to express their thanks to Prof. Arne Fredga for his interest in this work and for all facilities put at their disposal. Thanks are also due to Mr Bo Gestblom and Mr S. Johansson for recording the NMR- and UV-spectra respectively. The elementary analyses were carried out at the Analytical Department of the Chemical Institute. A grant from the *Swedish Natural Science Research Council* to S. G. is gratefully acknowledged.

REFERENCES

1. Rasmussen, H. E., Hansford, R. C. and Sachanen, A. N. *Ind. Eng. Chem.* **38** (1946) 376.
2. Caesar, P. D. and Branton, P. D. *Ind. Eng. Chem.* **44** (1952) 122.
3. Hartouh, H. D. Thiophene and its derivatives, New York 1952, p. 432.
4. Ref.³, p. 105.
5. Reid, E. E. Organic Chemistry of bivalent sulfur. Volume I. New York 1958, p. 71.
6. Gronowitz, S. and Hoffman, R. A. *Arkiv Kemi* **15** (1960) 499.
7. Gronowitz, S., Moses, P. and Hörnfeldt, A.-B. *Arkiv Kemi* **17** (1961) 273.

8. Hoffman, R. A. and Gronowitz, S. *Arkiv Kemi* **16** (1960) 563.
9. Gronowitz, S. *Arkiv Kemi* **13** (1958) 239.
10. Bellamy, L. J. *The infra-red spectra of complex molecules*, London 1958, p. 350.
11. Katritzky, A. R. and Boulton, A. J. *J. Chem. Soc.* **1959** 3500.
12. Gronowitz, S., Moses, P. and Håkansson, R. *Arkiv Kemi* **16** (1960) 267.
13. Hoffman, R. A. and Gronowitz, S. *Arkiv Kemi* **16** (1960) 515.
14. Moses, P. and Gronowitz, S. *Arkiv Kemi*, **18** (1961) 119.
15. Pandya, L. J. and Tilak, B. D. *Chem. & Ind. London* **1958** 981.
16. Böttcher, B. and Lüttringhaus, A. *Ann.* **557** (1947) 89.
17. Lüttringhaus, A., König, H. B. and Böttcher, B. *Ann.* **560** (1948) 201.
18. Spindt, R. S., Stevens, D. R. and Baldwin, W. E. *J. Am. Chem. Soc.* **73** (1951) 3693.
19. Legrand, L., Mollier, Y. and Lozac'h, N. *Bull. soc. chim. France* **1953** 327.
20. Wessely, F. and Siegel, A. *Monatsh.* **82** (1951) 607.
21. Gronowitz, S. and Håkansson, R. *Arkiv Kemi* **16** (1960) 309.
22. Ref.³, p. 433.
23. Tiers, G. V. D. *J. Phys. Chem.* **62** (1958) 1151.

Received June 26, 1961.