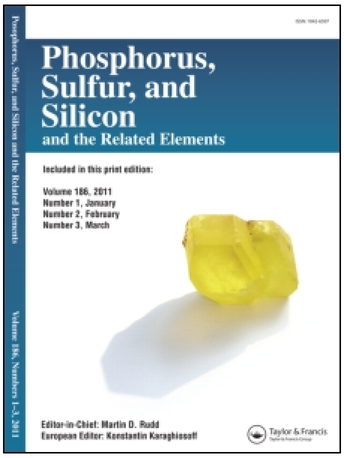

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THE PREPARATION OF PHENYLENE-BRIDGED SULFUR-NITROGEN CHAINS

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The preparation of sulfur-nitrogen chains linked by bridging phenylene units are described.

Keywords: sulfur; nitrogen; thiazyl chains; molecular wires

INTRODUCTION

Poly(sulfur nitride), $[SN]_x$, was the first example of a polymeric metal.[1] The discovery of its superconducting properties below liquid helium temperature in 1973 led to a great deal of research into the area of sulfur-nitrogen chemistry. The structure of $[SN]_x$ is composed of an alternating chain of sulfur and nitrogen atoms forming a one-dimensional polymer (Fig. 1). The π-orbitals on sulfur and nitrogen atoms overlap to form a conduction band and the conductivity is anisotropic with conduction greatest along the chain. Small fragments of conducting $[SN]_x$ (thiazyl chains) might find novel applications in the field of nanoscale technology, particularly as molecular wires.[2]

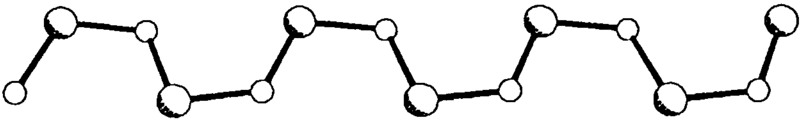


FIGURE 1 One-dimensional structure of $[SN]_x$

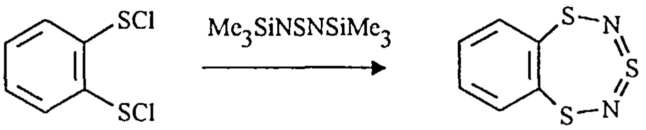
Thiazyl Chains

Synthetic strategies for the preparation of thiazyl chains with up to nine heteroatoms in the chain, e.g. ArS_5N_4Ar, have been developed.[2] However, the syntheses of longer chains have so far been unsuccessful; longer chains exhibit a propensity to decompose[2] to shorter chains through the elimination of S_4N_4, a thermodynamic sink in sulfur-nitrogen chemistry. Alternatively, we have begun to investigate whether current synthetic methodologies can be applied to join shorter chains together; particularly using suitable bridging groups in order to retain the delocalised π-framework. Herein we report the use of phenylene dithiols as precursors for difunctional thiazyl chains.

The dithiols were converted to the sulfenyl chloride by chlorination with SO_2Cl_2. Thiazyl chains were then prepared by condensation with $Me_3SiNSNSiMe_3$.

Reaction of 1,2-$C_6H_4(SCl)_2$ with $Me_3SiNSNSiMe_3$

Rees and co-workers previously reported[3] that reaction of 1,2 $C_6H_4(SCl)_2$ with bis(trimethylsilyl) sulfur diimide ($Me_3SiNSNSiMe_3$) did not yield the difunctional chain, but rather lead to intramolecular cyclisation, forming the ring-closed product C_6H_4SNSNS (Scheme 1).



SCHEME 1

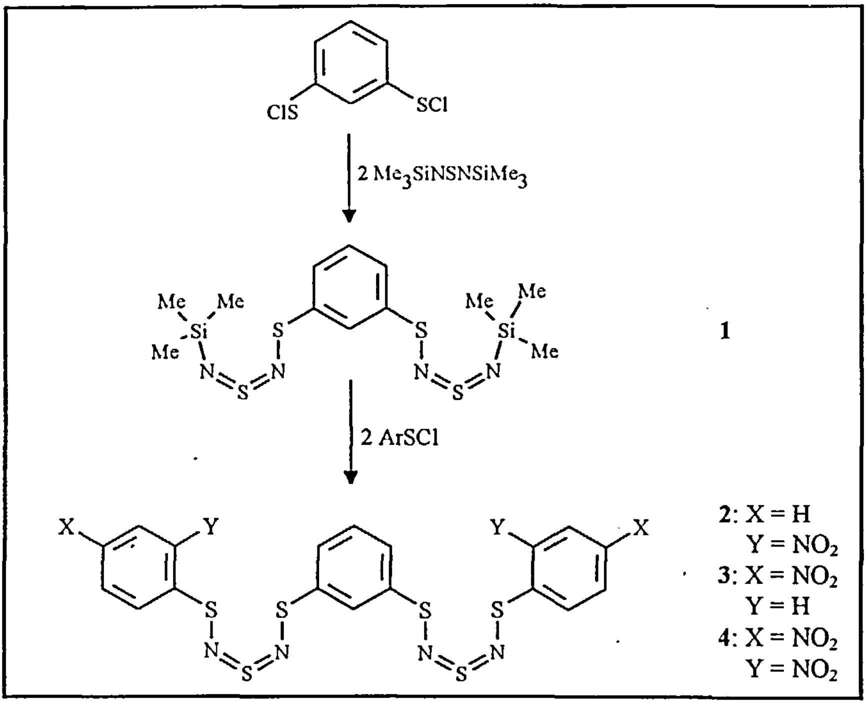
Our preliminary experiments with the 3,4-dimercaptotoluene derivative, indicated a similar intramolecular cyclisation. In order to inhibit the intramolecular process, we utilised *meta*-substituted dithiols, in which the ring closure is sterically inhibited.

Reaction of 1,3-$C_6H_4(SCl)_2$ with $Me_3SiNSNSiMe_3$

Addition of 1,3-$C_6H_4(SCl)_2$ to $Me_3SiNSNSiMe_3$ in a 1:2 mole ratio yielded the bifunctional thiazyl chain, 1,3-$C_6H_4(SNSNSiMe_3)_2$ (**1**) in quantitative yield (^1H and ^{13}C NMR). There was no evidence for either ring closure or polymer formation, indicating $Me_3SiNSNSiMe_3$ to be significantly more reactive than 1,3-$C_6H_4(SNSNSiMe_3)_2$ towards 1,3-$C_6H_4(SCl)_2$.

Reactivity of 1,3-$C_6H_4(SNSNSiMe_3)_2$

The silyl groups attached to the chain make **1** a useful intermediate for the preparation of longer thiazyl chains. Chain-capping has been achieved via condensation with ArSCl to form the new difunctional chains **2-4** (Scheme 2), whereas condensation with a further equivalent of 1,3-$C_6H_4(SCl)_2$ yielded an insoluble polymer.



SCHEME 2

Acknowledgements

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