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## The Preparation of Phenylene-Bridged Sulfur-Nitrogen Chains

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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),  $[\text{SN}]_x$ , was the first example of a polymeric metal.<sup>[1]</sup> 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  $[\text{SN}]_x$  is composed of an alternating chain of sulfur and nitrogen atoms forming a one-dimensional polymer (Fig. 1). The  $\pi$ -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  $[\text{SN}]_x$  (thiazyl chains) might find novel applications in the field of nanoscale technology, particularly as molecular wires.<sup>[2]</sup>

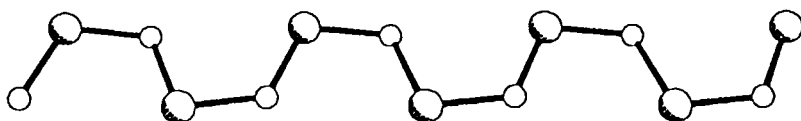


FIGURE 1 One-dimensional structure of  $[\text{SN}]_x$

## Thiazyl Chains

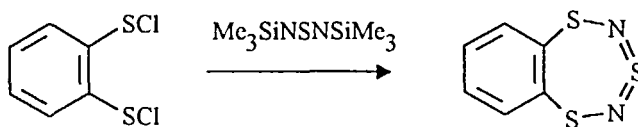
Synthetic strategies for the preparation of thiazyl chains with up to nine heteroatoms in the chain, e.g.  $\text{ArS}_5\text{N}_4\text{Ar}$ , have been developed.<sup>[2]</sup> However, the syntheses of longer chains have so far been unsuccessful; longer chains exhibit a propensity to decompose<sup>[2]</sup> to shorter chains through the elimination of  $\text{S}_4\text{N}_4$ , 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  $\pi$ -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  $\text{SO}_2\text{Cl}_2$ . Thiazyl chains were then prepared by condensation with  $\text{Me}_3\text{SiNSNSiMe}_3$ .

### Reaction of 1,2-C<sub>6</sub>H<sub>4</sub>(SCl)<sub>2</sub> with Me<sub>3</sub>SiNSNSiMe<sub>3</sub>

Rees and co-workers previously reported<sup>[3]</sup> that reaction of 1,2- $\text{C}_6\text{H}_4(\text{SCl})_2$  with bis(trimethylsilyl) sulfur diimide ( $\text{Me}_3\text{SiNSNSiMe}_3$ ) 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.

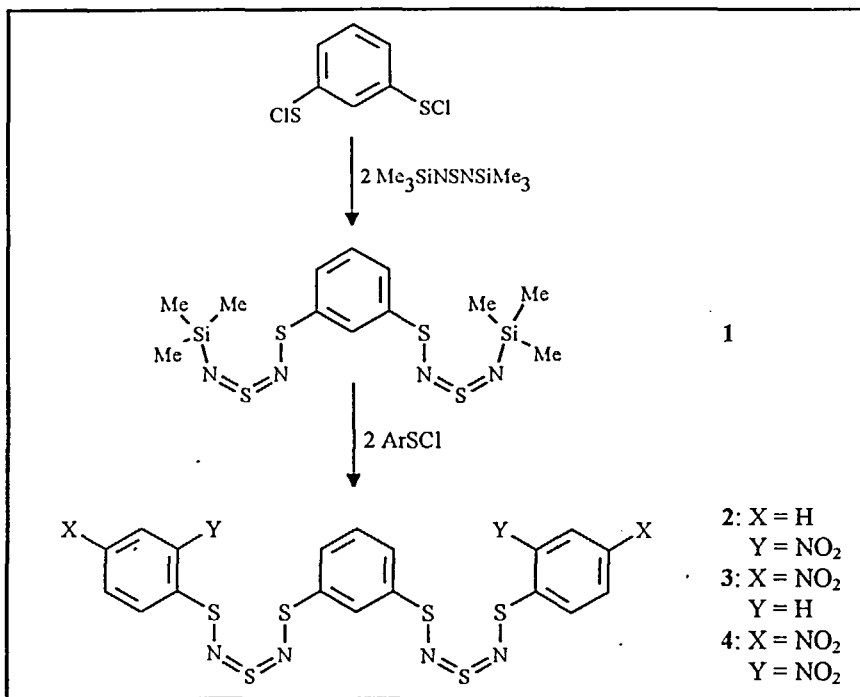
#### Reaction of 1,3- $C_6H_4(SCl)_2$ with $Me_3SiSNSiMe_3$

Addition of 1,3- $C_6H_4(SCl)_2$  to  $Me_3SiSNSiMe_3$  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  $Me_3SiSNSiMe_3$  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<sub>6</sub>H<sub>4</sub>(SCl)<sub>2</sub> yielded an insoluble polymer.



SCHEME 2

### Acknowledgements

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