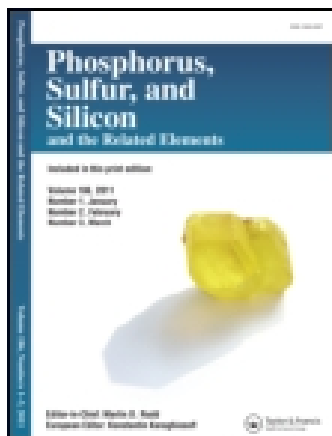


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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gpss20>

The Preparation of Phenylene-Bridged Sulfur-Nitrogen Chains

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Published online: 02 Apr 2008.

To cite this article: John J. Longridge & Jeremy M. Rawson (1997) The Preparation of Phenylene-Bridged Sulfur-Nitrogen Chains, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 124:1, 501-504, DOI:

[10.1080/10426509708545669](https://doi.org/10.1080/10426509708545669)

To link to this article: <http://dx.doi.org/10.1080/10426509708545669>

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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.^[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 $[\text{SN}]_x$ 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 $[\text{SN}]_x$ (thiazyl chains) might find novel applications in the field of nanoscale technology, particularly as molecular wires.^[2]

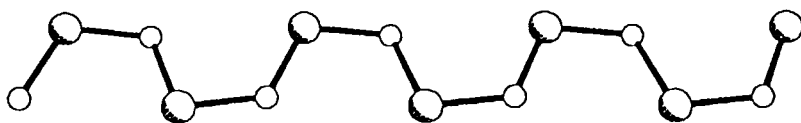


FIGURE 1 One-dimensional structure of $[\text{SN}]_x$

Thiazyl Chains

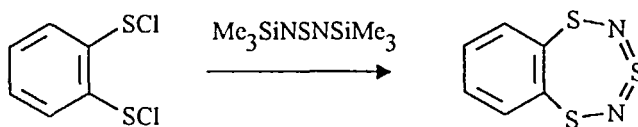
Synthetic strategies for the preparation of thiazyl chains with up to nine heteroatoms in the chain, e.g. $\text{ArS}_5\text{N}_4\text{Ar}$, have been developed.^[2] However, the syntheses of longer chains have so far been unsuccessful; longer chains exhibit a propensity to decompose^[2] to shorter chains 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 $\text{Me}_3\text{SiNSNSiMe}_3$.

Reaction of 1,2-C₆H₄(SCl)₂ with Me₃SiNSNSiMe₃

Rees and co-workers previously reported^[3] 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.

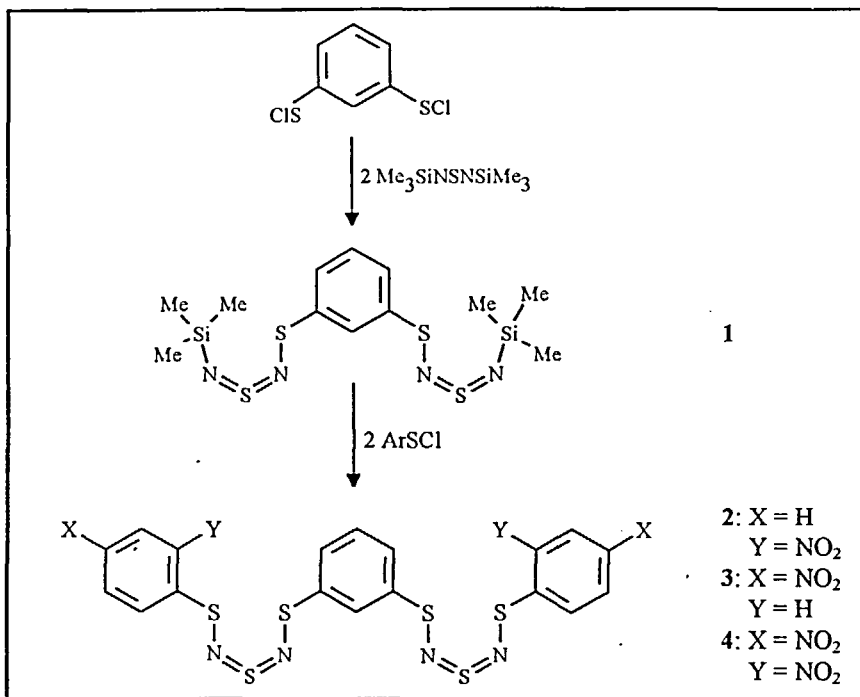
Reaction of 1,3- $C_6H_4(SCl)_2$ with $Me_3SiNSNSiMe_3$

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-C₆H₄(SCl)₂ yielded an insoluble polymer.



SCHEME 2

Acknowledgements

The authors would like to thank the E.P.S.R.C. and the Newton Trust for a studentship (JJL).

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