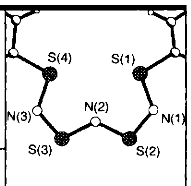
Sulfur–nitrogen chains: rational and irrational behaviour*



CHEMICAL
SOCIETY
REVIEWS

Jeremy M. Rawson and John J. Longridge

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW

* Dedicated to Arthur Banister, on the occasion of his retirement; an inspiring teacher to all who have been fortunate enough to work for him.

Poly(sulfur nitride), $[SN]_x$, was the first example of a polymeric metal, and the discovery of its superconducting properties in 1973 fuelled a generation of research into the areas of sulfur–nitrogen chemistry and molecular conductors. The synthesis, structure and properties of $[SN]_x$ now form part of many undergraduate courses and it is an often cited textbook example. Now, in the 1990s, small fragments of $[SN]_x$ may prove useful as molecular wires in the development of nanoscale technology. Although the preparations of many thiazyl chains can be carried out in a rational high-yielding manner, it is the diverse reaction chemistry, which often involves unexpected changes in the chain size, which provides one of the most rewarding and stimulating aspects of this area.

1 Introduction

Poly(sulfur nitride), $[SN]_x$ is a one-dimensional polymer in which sulfur and nitrogen atoms form an alternating chain (Fig. 1). Its physical properties are exceptional:[1,2] it is a conducting material at room temperature and becomes superconducting below liquid helium temperature. Its one-dimensional structure leads to a large degree of anisotropy. Consequently, its conductivity is greatest along the chain, where π-orbitals on sulfur and nitrogen overlap to form a conduction band. In addition to its conducting properties, the high electronegativity of $[SN]_x$, even greater than that of gold, produces several further unusual physical properties. The high electronegativity of poly(sulfur nitride) leads to several enhancements in device efficiency; for example $[SN]_x$ can act as an efficient barrier electrode in ZnS junctions,[2a] increasing the quantum efficiency of the blue-emission by a factor of 100 over gold; and it can also be used to increase the efficiency of GaAs solar cells (conventionally Au–GaAs) by as much as 35%.[2b] In addition $[SN]_x$ is remarkably inert; it does not react with water or acidic solutions, but slowly decomposes in alkaline solutions. Because of the high electronegativity of $[SN]_x$, metal ions interact more strongly with a poly(sulfur nitride) surface than with other metal electrodes.[2c] In some instances this can lead to enhancement of catalytic properties, *e.g.* $[SN]_x$ surfaces pretreated with metal ions have been used as catalysts and can improve the rates of conversion[2c] of acetylene to ethylene by factors of up to 10^7.

Despite such appealing properties, industrial exploitation[3] of $[SN]_x$ in modern devices has been hampered by synthetic problems; the classical route to $[SN]_x$ involves the 'cracking' of red S_4N_4 over silver wool to give colourless crystals of S_2N_2 which slowly polymerise over a period of weeks to form golden $[SN]_x$ (Fig. 1). The slowness of the polymerisation, coupled with the explosive nature[4] of both the S_4N_4 starting material and intermediate S_2N_2 molecule, has prompted researchers to investigate other synthetic[5] strategies to $[SN]_x$. In addition, other processing techniques[6] have been sought so that $[SN]_x$ can be prepared in thin films on a variety of substrates, such as OTEs (optically transparent electrodes), plastics and other metal surfaces. In particular, vacuum sublimation[6a] of powdered $[SN]_x$ and electroreduction[6b] of $[S_5N_5]^+$ salts have proved valuable routes to the formation of $[SN]_x$ films.

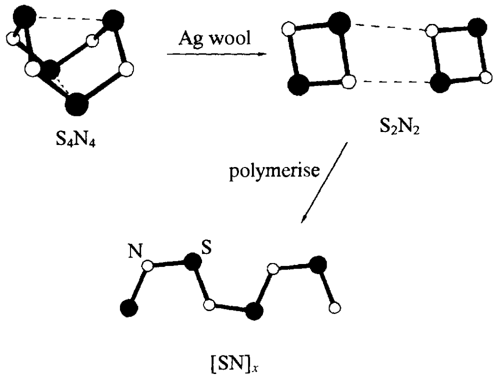
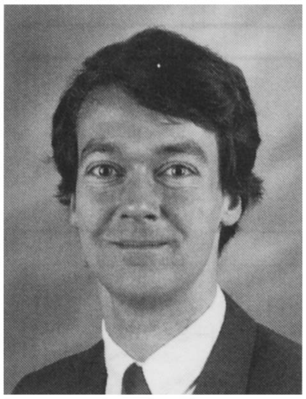
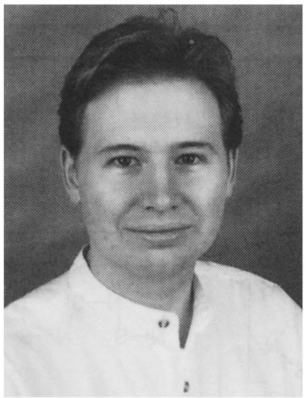


Fig. 1 Synthesis and structure of $[SN]_x$





Jeremy Rawson obtained both his BSc and PhD degrees from the University of Durham. He was a post-doctoral fellow with Dr Arthur Banister (University of Durham, 1990–1992) and Dr. Richard Winpenny (University of Edinburgh, 1993–1994) before returning to Durham to take up a temporary lectureship. He moved to Cambridge in 1995 where he is now a University Lecturer and Fellow of Magdalene College. His current research interests include the magnetic properties of main-group π radicals and polynuclear metal complexes bridged by sulfur–nitrogen rings and chains.

John Longridge graduated from the University of Durham in 1995, and is presently a graduate student at the University of Cambridge.

The physical properties of $[SN]_x$ have led to a great resurgence of interest in group 15/16 chemistry in recent years. In particular the inclusion of carbon-based fragments into the thiazyl backbone would allow the properties of $[SN]_x$ to be modified by changing the electronic properties of the chain substituents. This has led not only to the preparation of C/N/S-based polymers[7] but also to the development of C/N/S-based heterocyclic rings,[8] and sulfur–nitrogen chains (*i.e.* small fragments of conducting $[SN]_x$). These small fragments of conducting $[SN]_x$ could find novel applications in the field of nanoscale technology, particularly molecular wires.[9]

Nanoscale devices function on a molecular rather than macroscopic level and one of the key features required for many nanoscale devices to operate effectively is the molecular wire; a functional group which will conduct electrons between different parts of a molecule, allowing the different components to interact in an effective manner. The molecular wires presently used typically possess delocalised π systems and are frequently small fragments of conducting polymers such as acetylene oligomers or fused aromatics. Fig. 2 illustrates how a molecule of this type can respond to light (so-called photo-induced electron transfer) and is exemplified by a $Ru(bipy)_3$ derivative.

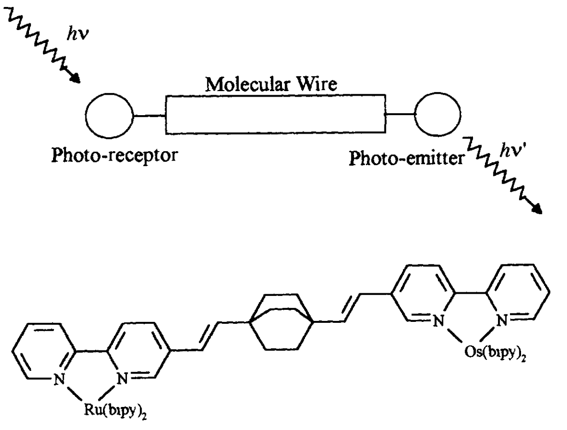


Fig. 2 Schematic representation of a photosensitive molecular device

The conductivity of pure $[SN]_x$ is *ca.* 1×10^3 S cm^{-1} at room temperature (*cf.* polyacetylene 1×10^{-7} and 1×10^{-2} S cm^{-1} for *cis* and *trans* forms respectively[10]) and we might therefore expect that the efficiency of molecular devices with thiazyl linkages might be superior to those of the corresponding acetylene-bridged molecules.

This review article aims to describe the chemistry of some of these sulfur–nitrogen chains; the types of sulfur–nitrogen chain we might expect to form; their relative stabilities; their physical properties; their structures and reactivity. In particular, although some references and comparison will be made to short thiazyl chains, containing two or three heteroatoms, this review will highlight the chemistry of the longer-chain compounds (*i.e.*, containing at least two thiazyl, –S=N–, units).

2 Types of thiazyl chain and electron counting

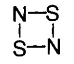
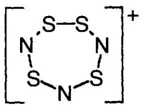
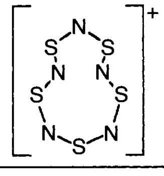
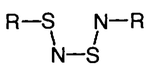
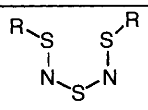
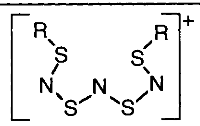
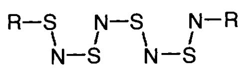
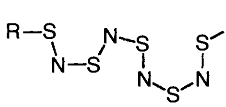
Thiazyl chains can be split conveniently into three categories dependent on composition; sulfur-rich, nitrogen-rich and even-chain compounds. These are highlighted in Table 1. We can utilise the same electron-counting rules[11] used for sulfur–nitrogen rings to π-electron count these compounds. In these systems, each S donates two electrons to the π system and each N is a one-electron donor. Unlike the sulfur–nitrogen rings where $[4n + 2]\pi$ Hückel configurations are preferred,[†] the chain-like structures only favour even numbers of π electrons (Table 2), *i.e.* a full, or 'closed-shell', electronic configuration. Because N provides only one electron, virtually all thiazyl chains reported to date (highlighted in bold in Table 1) contain an even number of N atoms and are neutral. There are a small number of chains with odd numbers of N atoms, but these are charged so as to retain a full π-shell, *e.g.* $RSNSR^+$ (R = Cl, Br) and $RS_4N_3R^+$. Indeed cationic chains should be particularly stabilised *via* the lowering of the filled molecular orbitals induced by the positive charge on the system, and in addition, the ionic contribution to the lattice energy should also assist their stabilisation in the solid state.

Table 1 Sulfur–nitrogen chain compounds as a function of chain length, with known derivatives highlighted

Chain length	S-rich	N-rich	Even-chain
3	**$RSNSR^+$**	**$RNSNR$**	
4			**RS_2N_2R**
5	**RS_3N_2R**	$RN_3S_2R^{+/-}$	
6			$RS_3N_3R^{+/-}$
7	**$RS_4N_3R^+$**	**RN_4S_3R**	
8			**RS_4N_4R**
9	**RS_5N_4R**	$RN_5S_4R^{+/-}$	
10			$RS_5N_5R^{+/-}$
11	$RS_6N_5R^+$	RN_6S_5R	

Intuitively the observation of both $ArS_4N_3Ar^+$ and $XSNSX^+$ cations indicates that sulfur-rich compounds will have a tendency to form cationic systems, and this can readily be understood by the number of electrons filling antibonding molecular orbitals; For an acetylene chain, $(CH)_x$, each C provides one p-orbital for the formation of π molecular orbitals

Table 2 A comparison of sulfur–nitrogen ring compounds and sulfur–nitrogen chain compounds and their respective π electron counts

π-electron count	6	8	10	12	14
Ring					
other examples:	$S_3N_2^{2+}$		$S_3N_3^-$, $S_4N_4^{2+}$		
chain					
other examples			RN_4S_3R		

[†] A number of sulfur–nitrogen systems are also known which are formally $4n\pi$ anti-aromatic molecules, but these do not have planar π-delocalised structures analogous to the thiazyl chains and Huckel $[4n + 2]\pi$ aromatics. Instead they take up cage structures,[8] *e.g.* S_4N_4, S_5N_6, $S_4N_5^+$ and $S_6N_5^+$.

and donates one electron to this π manifold. The result is a set of bonding and antibonding π orbitals of which only the bonding orbitals are filled. In comparison, in thiazyl oligomers, each S donates two electrons and each N one electron for π-bonding and some of the formally antibonding orbitals will also be occupied to accommodate the additional electrons, provided by S. Consequently, if the thiazyl chain contains an odd number of electrons, removal of the unpaired electron from its antibonding orbital not only strengthens the π-bonding character, but also lowers the energy of the bonding orbitals through the introduction of the positive charge. In general the removal of an electron to form a cationic system is preferred over the addition of an electron to generate an anionic system since the latter requires the addition of a further electron into an antibonding orbital. This observation also explains the propensity for sulfur–nitrogen rings to form cationic rather than anionic systems, although anionic rings, such as the 10π Hückel $S_3N_3^-$ are known.

Compounds with the same chain lengths will also have similar sets of molecular orbitals, and it is perhaps not too surprising to find that the isoelectronic $RS_4N_3R^+$ and RN_4S_3R chains take up similar geometries (see section 5).

3 Synthesis of sulfur–nitrogen chains

3.1 Historical background

Prior to the 1970s, sulfur–nitrogen chemistry was plagued by structural mis-assignments and the diverse nature of many reactions which typically yielded multiple and sometimes unexpected products.[12] With the development of modern analytical methods (particularly X-ray crystallography and more recently multinuclear NMR) and theoretical studies, the area of sulfur–nitrogen chemistry has been revolutionised and many unusual mechanistic processes have been rationalised. As a consequence, controlled syntheses of many sulfur–nitrogen compounds can now be achieved. In this section we aim to outline early developments in the area of sulfur–nitrogen chains and illustrate more rational synthetic methodologies.

3.2 Initial syntheses of thiazyl chains

The first reported syntheses of sulfur–nitrogen chains appeared in the mid-1960s and early 1970s, and described[13,14] the preparation of RS_3N_2R (trithiadiazenes) and the shorter chains, RNSNR (known as sulfur diimides). The chemistry of sulfur diimides is particularly extensive and beyond the scope of this review, except as reagents for the synthesis of other sulfur–nitrogen chains. As with many other areas of sulfur–nitrogen chemistry, early syntheses of S/N chains involved the ubiquitous S_4N_4 molecule;[13] the reaction of S_4N_4 with aromatic Grignard reagents or diazomethanes yielded RS_3N_2R in low yield. The more traditional 'boil-and-bake' approach (involving the condensation of HCl between S–Cl and N–H bonds, and concurrently forming S–N bonds) was also utilised with some success.[14]

3.3 Rational syntheses

For many years the standard synthetic route to inorganic rings and chains has involved condensation reactions, typically with loss of HCl.[12,14] Such reactions occur at elevated temperatures, so as to remove the HCl from the reaction mixture. Recently, condensation reactions, particularly involving the loss of Me_3SiCl, $Me_3SiOSiMe_3$ or metal halides,[8] have been used successfully in the synthesis of inorganic rings and chains. These condensation reactions occur smoothly at low temperatures and lead to clean products in high yield. This technique has been extensively employed[15] in the syntheses of sulfur–nitrogen chains; one of the most common reagents being bis(trimethylsilyl)sulfur diimide, $Me_3SiNSNSiMe_3$. The synthesis of this reagent itself (see Scheme 1) provides a useful example of the use of both LiCl and $Me_3SiOSiMe_3$ as thermodynamic sinks, the sulfur diimide being formed in excellent yields under mild conditions.[15]

$$\begin{tikzcd}
ArN_4S_3Ar & & \\
ArNSNSiMe_3 \arrow[u, "SCl_2"'] \arrow[r, "ArSCl"] & ArS_2N_2Ar & \\
Li[N(SiMe_3)_2] \arrow[u, "ArNSO"'] \arrow[d, "SOCl_2"] & & \\
Me_3SiNSNSiMe_3 \arrow[r, "ArSCl"] \arrow[d, "SCl_2"] & ArS_2N_2SiMe_3 \arrow[r, "ArSCl"] & ArS_3N_2Ar \\
Me_3SiN_4S_3SiMe_3 \arrow[r, "ArSCl"] & ArS_4N_4SiMe_3 \arrow[r, "ArSCl"] & ArS_5N_5Ar
\end{tikzcd}$$

Scheme 1 Rational syntheses of some sulfur–nitrogen chains

The stoichiometric condensation of $Me_3SiNSNSiMe_3$ with ArSCl in 1 : 1 or 1 : 2 mole ratios gives the anticipated $ArS_2N_2SiMe_3$ and ArS_3N_2Ar chains[16] (although an excess of ArSCl yields the $ArS_4N_3Ar^+$ cationic chain!).

The syntheses of other sulfur–nitrogen chains can be designed in an analogous manner[17] and are illustrated in Scheme 1. SCl_2 plays a particularly important role in the syntheses of longer-chain thiazyl oligomers; coupling of two small thiazyl chains containing the trimethylsilyl functional group provides a convenient route to long-chain molecules. It should be noted that for some long chain compounds, the choice of aryl substituent plays a key role in determining the stability and this is discussed further in section 5.2. Using these simple condensation reactions, chain lengths up to ArS_5N_4Ar have been prepared.

4 Structures of sulfur–nitrogen chains

4.1 Structure of $[SN]_x$

Despite several structure determinations,[1] the precise structure of $[SN]_x$ is still open to some debate. The structure determinations have been persistently hampered by crystal defects which arise during the polymerisation of S_2N_2. Although the way in which the atoms are linked together in the alternating *cis–trans* configuration is not disputed, the bond lengths are not precise. The X-ray diffraction study tends to indicate an alternating set of long and short bonds [1.593(5) and 1.628(7) Å], intermediate between S–N (*ca.* 1.69 Å) and S=N (*ca.* 1.54 Å) bonds,[16] although the errors on these bond lengths are so large that they are the same (within three esds). The nature of these bonds, intermediate between S–N and S=N, is consistent with the extensive π delocalisation required for conduction. The '*cis–trans*' alternating polymeric chain facilitates a set of secondary S···N interactions between atoms in the same chain, composed of electrostatic $S^{\delta+}\cdots N^{\delta-}$ interactions, coupled with pπ–pπ interactions. The bond angles at N and S are about 120° and 106°, respectively. Each $[SN]_x$ chain deviates only slightly (0.17 Å) from planarity, and there is a series of weak interactions between chains.

4.2 Thiazyl chains

The structural features described in section 4.1 for $[SN]_x$ are also observed in many of the sulfur–nitrogen chains, which can be considered as small fragments of $[SN]_x$. The structures[17,18] of $O_2NC_6H_4S_2N_2C_6H_4OMe$, PhN_4S_3Ph and $O_2NC_6H_4S_4N_4SiMe_3$ chains are shown in Fig. 3. In each of these cases the chains take up similar conformations to $[SN]_x$ with an alternating '*cis–trans*' configuration. In comparison to $[SN]_x$, these oligomers definitely exhibit alternating long and short S–N bonds, consistent with a more localised structure of the form [–S–N=S=N–], although these too are intermediate between S–N and S=N bond lengths. Secondary interactions between non-bonded atoms within the chains are still significant. However, the '*cis–trans*' conformation observed in $[SN]_x$ is not exclusive, and other conformations are observed[16,19] in which a

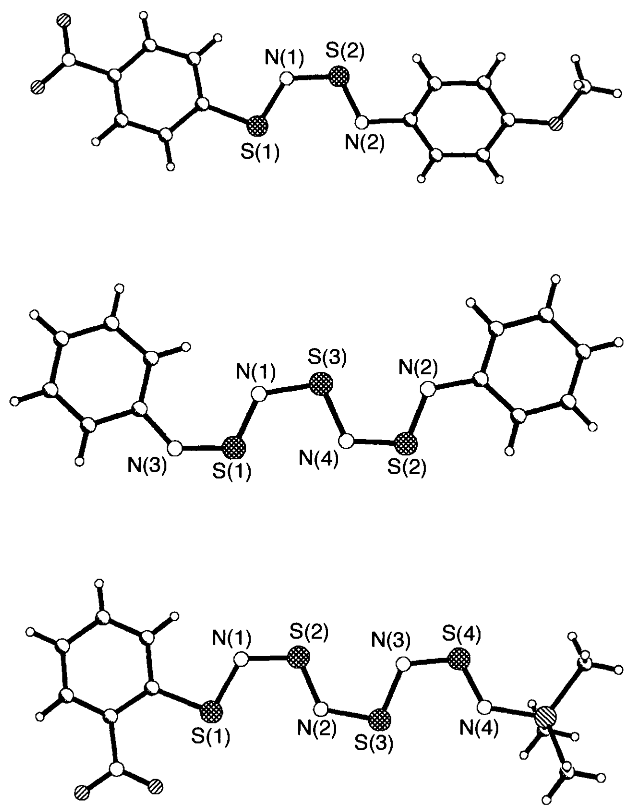


Fig. 3 Molecular structures of $O_2NC_6H_4S_2N_2C_6H_4OMe$, PhN_4S_3Ph and $O_2NC_6H_4S_4N_4SiMe_3$

'*cis*' configuration is replaced by a '*trans*' arrangement. This 'defect' to the $[SN]_x$-type structure can arise either at an N atom [such as N(2) in $ClC_6H_4S_3N_2C_6H_4Cl$] or at an S atom [*e.g.* S(3) in the cation $MeC_6H_4S_4N_3C_6H_4Me^+$] (Fig. 4). The energy required to introduce such a 'defect' primarily arises through the breaking of one of the transannular interactions and theoretical calculations[20] have estimated this to be of the order of 25–30 kJ mol^{-1}. This small energy contribution can be overcome by molecular packing forces, or particularly in the case of the cationic $ArS_4N_3Ar^+$ salts, through significant ionic lattice contributions. This is highlighted by two different conformations to the RN_4S_3R chain, depending on substituent; for the PhN_4S_3Ph derivative[17] the 'ideal' $[SN]_x$ type configuration is observed (Fig. 3), whereas for $Bu^tN_4S_3Bu^t$ a 'defect' is found[21] at N(3) (Fig. 4). The longest known thiazyl chain to be crystallographically characterised,[22] $MeC_6H_4S_5N_4C_6H_4Me$ is also shown in Fig. 4 and shows a 'defect' at N(4); this structure can be envisaged as a pair of ArS_2N_2 and Ar fragments on an S_3N_2 chain (which has a characteristic 'open-ring' structure).

The thiazyl chain compounds exhibit similar bond lengths to $[SN]_x$ although there is considerable variation in the bond angles depending on the length of the sulfur–nitrogen chain and the terminal groups; bond angles are typically in the region 102–124° and 118–129° at S and N respectively. Without exception, diaryl-substituted thiazyl chains are approximately planar, facilitating the π-delocalisation along both the thiazyl chain and over the aryl substituents. However, other substituents can produce a more pronounced deviation from planarity, and for example, *o*-$O_2NC_6H_4S_4N_4SiMe_3$ sits[17] on the curve of a circle with an appproximate radius of 50 Å.

Intermolecular interactions are very important in stabilising the metallic state of $[SN]_x$. In $[SN]_x$, the secondary interactions between S atoms in neighbouring chains is 3.48 Å.[1] Strong secondary interactions between heteroatoms are also prevalent in many of the thiazyl chain structures, *e.g.* in $O_2NC_6H_4S_2N_2$-C_6H_4OMe the interplane distance between molecules is only 3.42 Å.[18] However, in many instances, particularly when a chain is terminated with a bulky substituent such as $SiMe_3$, then many of these secondary contacts are often appreciably longer,[17] although still less than the sum of the van der Waal's radii [3.63 (S···N) to 4.06 Å (S···S)], *e.g.* S···S in $O_2NC_6H_4S_4N_4$-$SiMe_3$ at 3.73 Å. In addition the presence of a positive charge on the thiazyl chain leads to electrostatic repulsion between cations and the closest approaches are close to the sum of the van der Waal's radii, *e.g.* $[O_2NC_6H_4S_4N_3C_6H_4NO_2][AsF_6]$ has close contacts at 3.64 Å for S···N and S···S contacts in the region 3.9 to 4.0 Å.[23]

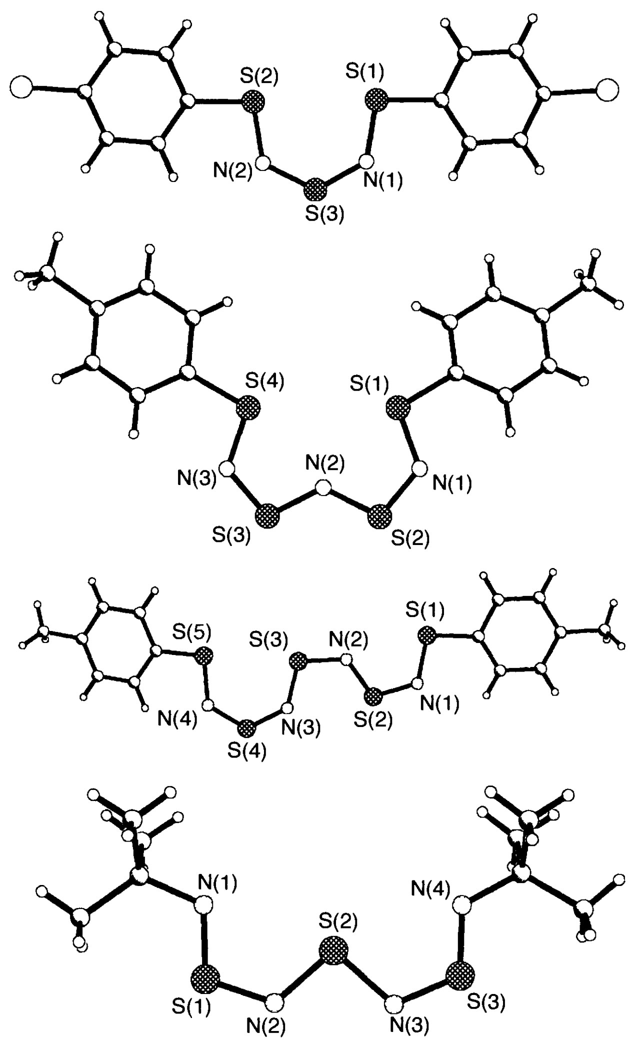


Fig. 4 Molecular structures of $ClC_6H_4S_3N_2C_6H_4Cl$, $MeC_6H_4S_4N_3$-$C_6H_4Me^+$, $MeC_6H_4S_5N_4C_6H_4Me$ and $Bu^tN_4S_3Bu^t$

5 Correlation of sulfur–nitrogen chain lengths and their physical properties

5.1 π-Delocalisation

Each sulfur and nitrogen atom in the thiazyl chain contributes one p-orbital towards the formation of a set of π molecular orbitals. The energies of the π molecular orbitals for two thiazyl chains, HS_3N_2H and HS_5N_4H, are shown in Fig. 5. As the chain-length increases, the number of p-orbitals also increases and the energy gap between π-orbitals becomes smaller, consistent with simple band theory.[10] The distribution of the energies of these π molecular orbitals is an important feature of such thiazyl chains, and plays an important role in determining some of their physical properties, particularly their optical properties, both in solution and in the solid state.

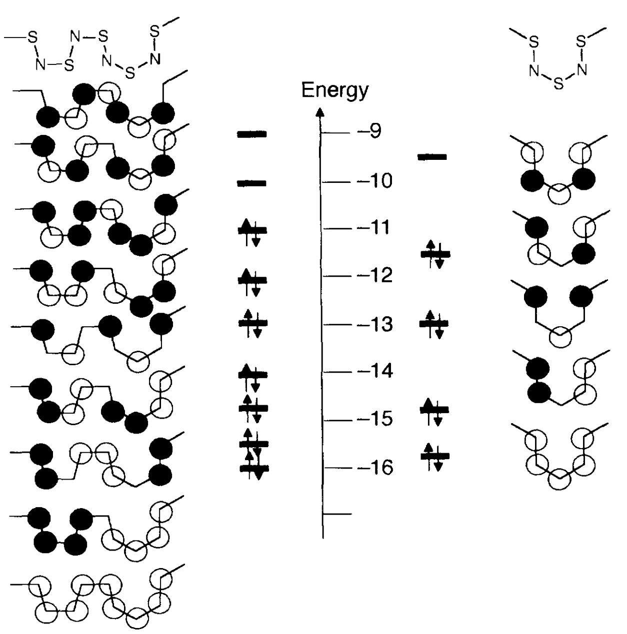


Fig. 5 The energies of the π-molecular orbitals of HS_5N_4H and HS_3N_2H

5.2 Optical properties and delocalisation

As the chain length increases, the energies between different π-molecular orbitals decreases and the energy, *hν*, to excite electrons between different π-orbitals becomes smaller. This leads to the observation[16,17] of a 'red-shift' as the chain-length becomes longer and is indicative of a 'tight' π-manifold and more extended π-delocalisation. Electron-withdrawing substituents on the thiazyl chains can also lead to a slightly increased red-shift,[16] as can the introduction of a positive charge which produces a lowering of the orbital energies.[16] The UV–VIS absorption maxima for a series of thiazyl chains are given in Table 3, and illustrate the effect of chain length, electron-withdrawing substituents and charge on the absorption maxima. In general short sulfur–nitrogen chains (less than six heteroatoms) tend to be brightly coloured; yellow or orange whereas the longer chains (greater than six heteroatoms) tend to produce very intense deep-coloured solutions; typically deep green, royal blue or purple.

In the solid state, a similar set of colours is observed; short thiazyl chains tend to be brightly coloured, whereas the longer chains tend to have a metallic lustre, similar to that observed for 'golden' $[SN]_x$ or 'silver' polyacetylene, $[CH]_x$.

5.3 Stability

The stability of thiazyl oligomers, particularly long-chain ($n > 7$) derivatives, is particularly dependent on the terminal functional groups. Zibarev and coworkers have noted[17] that electron-withdrawing substituents on aromatic terminal groups are particularly good at stabilising longer chain lengths. For example, reaction of $Me_3SiN_4S_3SiMe_3$ with ArSCl (Ar = Ph, *o*-$NO_2C_6H_4$) in a 1 : 2 mol ratio yielded ArS_5N_4Ar when Ar = *o*-$NO_2C_6H_4$. However, when Ar = Ph, the only recovered products were PhS_3N_2Ph and S_4N_4. The stability of very long thiazyl chains is questionable and, for example, reaction of $ArS_4N_4SiMe_3$ [Ar = *o*-$NO_2C_6H_4$ or 2,4-$(NO_2)_2C_6H_3$] with SCl_2 does not lead to the 17-heteroatom chain, ArS_9N_8Ar, but rather to the isolation[17] of the decomposition products, ArS_5N_4Ar. The disproportionation of these thiazyl chains is described in section 6.4. For short chain oligomers there appear to be no such problems with disproportionation.

6 Reactivity

In comparison to the development of synthetic routes to thiazyl chains, their chemistries are poorly understood. Indeed those reactions which have been carried out appear diverse and, like other areas of sulfur–nitrogen chemistry, somewhat unexpected at first glance. A series of reported reactions are described below which initially seem both unusual and varied. However, a common theme appears in many of them and this is discussed in more detail in section 6.5.

6.1 Scrambling of terminal groups and preparation of ArS_2N_2Ar'

In the presence of a catalytic quantity (5–25 mol%) of alkali metal (Na, K) mixtures of RNSNR and R′NSNR′ undergo rapid scrambling[18] of the terminal groups to yield mixtures of starting materials and the mixed product, RNSNR′. The position of the equilibrium is dependent on the nature of the R groups. If they are similar (*e.g.* Ph and MeC_6H_4 or $MeOC_6H_4$) then there is an approximately statistical distribution of products whereas for dissimilar groups the equilibrium favours the cross-product. An extension of this reaction is the reaction of PhNSNPh with PhS_3N_2Ph in the presence of alkali metal to yield PhS_2N_2Ph.

In this reaction, the radical anion $RNSNR^{\cdot-}$, formed by reduction of the neutral thiazyl chain with alkali metal, possesses 5π electrons and three π molecular orbitals. Oakley and coworkers proposed that two of these molecules could associate in solution to form a dimer[18] (dimerisation processes are well known in other areas of sulfur–nitrogen chemistry[8]) in which the two molecules are weakly associated *via* overlap of the two singly occupied molecular orbitals, with the S···S bridge contributing the greatest extent. This dimeric intermediate can then rearrange to form the mixed thiazyl chain (Scheme 2).

6.2 Reduction of $ArS_4N_3Ar^+$

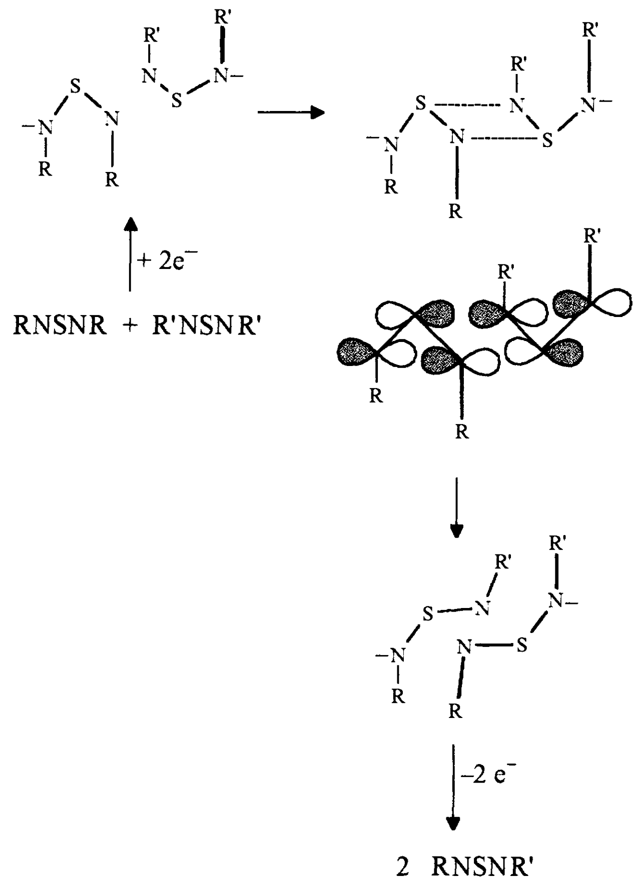
Wolmershauser and coworkers recently investigated[22] the redox behaviour of the $ArS_4N_3Ar^+$ cation and observed that reduction led to the unstable $ArS_4N_3Ar^{\cdot}$ radical which disproportionated to ArS_5N_4Ar and ArS_3N_2Ar. The disproportionation reaction was postulated to proceed through a four-centred S_2N_2 ring intermediate; this reaction can be considered to occur in a similar manner to that described in section 6.1 for the scrambling of terminal groups in short-chain thiazyl compounds. An analysis of the frontier molecular orbitals[23a] indicates that one electron reduction of the $ArS_4N_3Ar^+$ cation yields a neutral radical with the unpaired electron occupying a π-type orbital of the same symmetry to that of the sulfur diimides discussed in section 6.1.

6.3 Hydrolysis of $[ArS_4N_3Ar]Cl$ and chain lengthening reactions with $(NSCl)_3$

In 1977 Street and coworkers reported[16] the first synthesis of an $[ArS_4N_3Ar]^+$ chain as its chloride salt, and noted that it slowly

Table 3 UV–VIS absorption maxima (nm) for a series of thiazyl chain complexes

Thiazyl chain	$ArNSNSiMe_3$	ArNSNAr	ArS_3N_2Ar	ArN_4S_3Ar	$ArS_4N_3Ar^+$	$ArS_4N_4SiMe_3$	ArS_5N_4Ar
Ar = *o*,*p*-$(NO_2)_2C_6H_3$	413		476			538	587
o-$NO_2C_6H_4$	409		476			521	585
p-$NO_2C_6H_4$	394		458				580
p-ClC_6H_4	383		449		565		
p-MeC_6H_4	355		448	530	582		
C_6H_5	332	415	450	522			



Scheme 2 Skeletal scrambling in sulfur diimides

decomposed on the open bench to give the shorter, ArS_3N_2Ar chain. Although a hydrolysis mechanism evidently takes place, the reaction can be conveniently thought of as loss of thiazyl chloride, NSCl, from the starting material.

Recently, work has shown that the reverse reaction, *i.e.* reaction of NSCl with ArS_3N_2Ar, occurs under ambient conditions and in high yield.[23b] The mechanism is proposed to involve a four-centred intermediate which facilitates a π-orbital interaction between S and N (Scheme 3). This use of thiazyl chloride as a chain-building reagent has previously been exploited in the synthesis of shorter chains. For example, reaction of NSCl with SCl_2 and $AgAsF_6$ leads to insertion[24] of an SN unit into the S–Cl bond, and condensation of NSCl with ArSNHSAr provides a convenient route[14] to ArS_3N_2Ar *via* loss of HCl.

6.4 Disproportionation of long chain sulfur–nitrogen compounds

In section 5.3, the instability of long-chain thiazyls was described. Two types of reaction appear to occur: either a competing reaction may take place during the formation of the thiazyl chain or the resultant chain itself can decompose, usually accompanied by the loss of S_4N_4.

6.4.1 Competing reactions

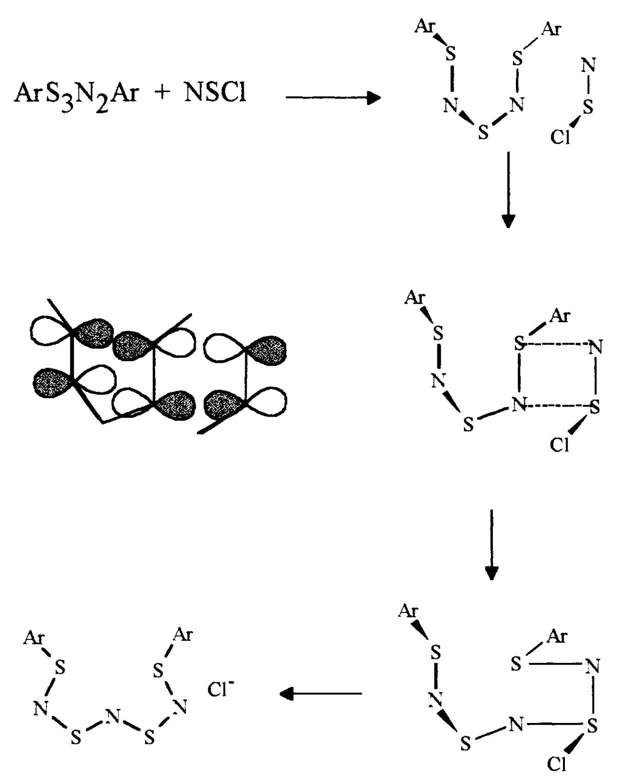
Condensation of $PhNSNSiMe_3$ with SCl_2 did not yield the expected product, PhN_4S_3Ph, but instead yielded the benzodithiadiazine[25] (Scheme 4). This reaction is proposed to occur *via* an intramolecular loss of HCl (with the abstracted *ortho*-hydrogen) from the intermediate PhNSNSCl accompanied by ring closure at the *ortho*-position.

6.4.2 Decomposition reactions

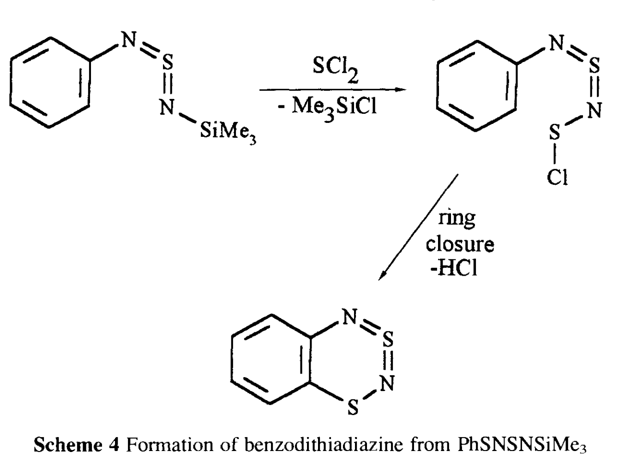
To date, there have been no systematic studies of the decomposition of thiazyl chains. However there are several possible mechanisms (Scheme 5); the first mechanism, postulated[17] by Zibarev and coworkers, involves either trimethylsilyl or aryl group migration (A), with concomitant extrusion of thiazyl units, as S_2N_2, from the thiazyl chain; alternatively, the reaction can be considered to involve the breaking and reformation of S–N bonds and a similar loss of S_2N_2 (B). The ease with which thiazyl chains can undergo rearrangement processes, in comparison to the strength of the C–S bond, indicates that the latter mechanism would appear more favourable.

6.5 On the prevalence of four-centred S_2N_2 intermediates

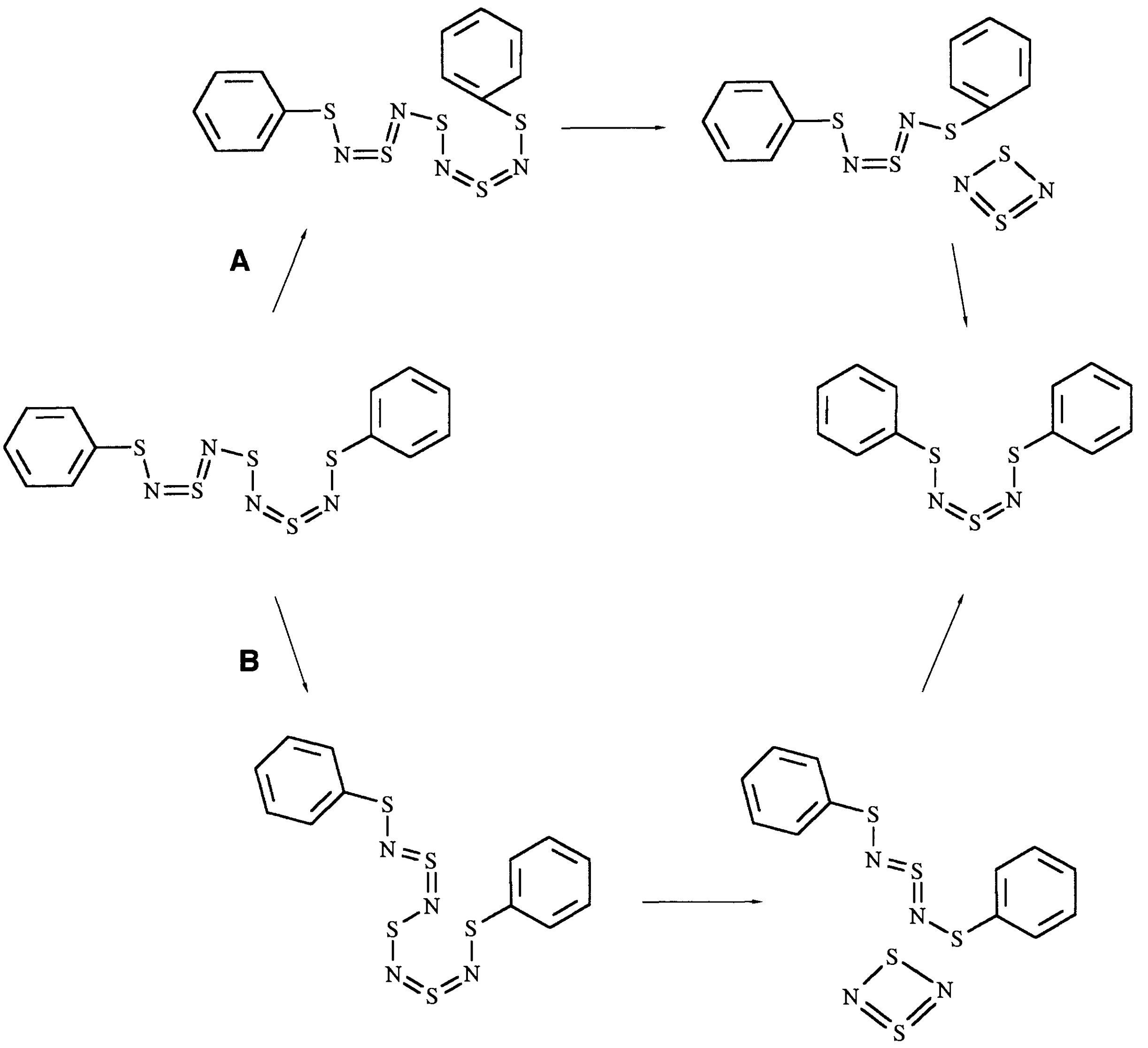
Although these few reactions constitute the greater part of the known reactivity of long-chain thiazyl compounds, a key mechanistic feature proposed by three different groups (and described in sections 6.1 to 6.3) is the four-centred cyclic S_2N_2 intermediate formed by the association of two S/N-containing molecules. In organic chemistry the four-centred intermediate, typically formed by a [2 + 2] cycloaddition of two alkene functional groups, is formally symmetry forbidden and tends to occur, for example, upon photolysis or at elevated temperatures where access to excited states alters the orbital symmetry.[26] In



Scheme 3 Mechanism for the reaction of ArS_3N_2Ar with NSCl



Scheme 4 Formation of benzodithiadiazine from $PhSNSNSiMe_3$



Scheme 5 Proposed chain-shortening mechanisms, for the conversion of ArS_5N_4Ar to ArS_3N_2Ar: (A) *via* aryl group migration; (B) *via* S_2N_2 extrusion

comparison, such four-centred intermediates are favoured in sulfur–nitrogen chemistry since each thiazyl group possesses 3π electrons (2 from S and 1 from N) and the resulting [3 + 3]π interaction yields a favourable 6π electronic interaction. This occurs because the frontier orbitals occupied by thiazyl compounds are different to those occupied by C-based compounds. For example, cyclobutadiene possesses 4π electrons, leading to two partially occupied frontier orbitals whereas cyclic-S_2N_2 possesses 6π electrons and the two partially occupied orbitals of butadiene become completely occupied in S_2N_2.

The reactions described in sections 6.1 and 6.2 both involve a radical mechanism involving association *via* a SOMO–SOMO interaction. The mechanism in 6.3, although involving a four-centred intermediate does not proceed in the same manner but occurs through a HOMO–LUMO interaction in which a pair of electrons from an antibonding ArS_3N_2Ar π orbital are donated into the LUMO of NSCl; the orbital interaction in this case would therefore appear to be identical but in sections 6.1 and 6.2 the interaction is SOMO–SOMO whereas in 6.3 it is a HOMO–LUMO interaction.

6.6 Other reactions

In comparison to sulfur diimides whose chemistries have been examined extensively, the chemistries of the longer S/N chains, as outlined above, have been poorly studied. For example, the sulfur diimides possess a diverse coordination chemistry, but little coordination chemistry of the longer thiazyl chains has been reported. Woollins and coworkers reported[27] that reaction of $ArSNSNSiMe_3$ with $PtCl_2(dppe)$ gives $(ArSNSN)_2Pt(dppe)$ (dppe = 1,2-bisdiphenylphosphinoethane) whereas reaction of ArS_3N_2Ar with $Pt(PPh_3)_4$ led to reduction of the thiazyl chain and formation[28] of $(ArS)_2Pt(PPh_3)_2$. The decomposition of thiazyl chains on metal centres is not unexpected and Vrieze and coworkers have shown that simple sulfur diimides undergo unusual rearrangements when coordinated to metals.[29]

7. Sulfur–nitrogen chains as molecular wires: making the contact

7.1 Thiazyl chains as molecular wires

Theoretical calculations show that the majority of frontier orbitals of aryl-substituted S/N chains (irrespective of chain-length) are of π-character, and the majority of these also exhibit some degree of π-delocalisation onto the aryl substituents. Such delocalisation onto the terminal groups is important if these materials are to function as molecular wires; if the aryl groups were nodal in this respect (*i.e.* did not contribute to the π-framework) then they would insulate the sulfur–nitrogen chain from its surroundings. Instead, this extended π-delocalisation means that such aryl-substituted thiazyl chains can form an effective means of communication between the two terminal groups. The extent to which the π-orbitals are delocalised over the whole molecule and the energy gap between bonding and antibonding orbitals enables us to assess the effectiveness of the intramolecular interactions.[17] We have already seen (section 5.2) that the longer thiazyl chains produce a more delocalised π-framework with relatively small energy gaps between π-orbitals. If the aryl substituent is provided with metal-binding sites then the sulfur–nitrogen chains can be utilised to facilitate communication between the metal ions.

7.2 Making contacts

In order for such thiazyl chains to act as molecular wires betwen metal ions, not only must the π-orbitals extend over both the S/N chain and its substituents, but the substituents must be capable of binding metal centres and also be of the correct symmetry to interact strongly with the metal orbitals. In order for the metals to be able to communicate effectively through the thiazyl linkage, the metal orbitals must interact with the π-cloud. This can be achieved by binding the metals in the plane, facilitating dπ–pπ orbital interaction, *e.g.* in pyridine or bipyridine complexes, or *via* an out-of-plane interaction commonly observed for sandwich and half-sandwich complexes such as ferrocenes, in which the d and p- orbitals on the metal interact directly with the π-framework of the sulfur–nitrogen chain (Fig. 6).

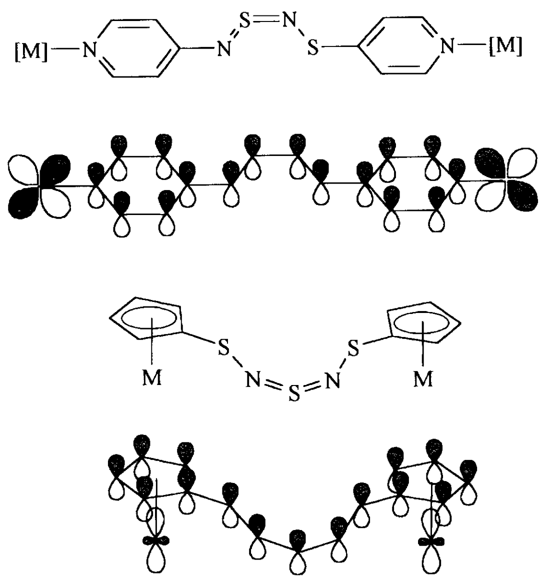


Fig. 6 Two possible modes of communication between aromatic substituents and metal centres; (*a*) in-plane interactions and (*b*) out-of-plane interactions

The key to success in this field remains the preparation of thiazyl chains with suitable substituents for binding active metal sites. To date, only a very few short acyclic sulfur–nitrogen chains have been prepared containing metal-binding sites, *e.g.* the sulfur diimide containing just one coordinating group (perfluoropyridyl) $PhNSNC_5F_4N$ has been reported,[17] but its complexation chemistry has not been explored. Nevertheless, the synthetic methodologies required to prepare such derivatives are established and promise to provide some novel properties.

8 Future prospects

There are many aspects of the chemistry of thiazyl oligomers which remain unexplored. In section 2 we indicated that the compounds prepared to date constitute just a few examples of a potentially large class of heterocyclic chains. The syntheses of ionic chains are yet to be fully exploited, and we anticipate that the lowering of the energies of the π-molecular orbitals (associated with the presence of a positive charge) will produce a series of new stable chains. In addition we have seen that the reactions of thiazyl chains are sometimes unexpected (section 6) and diverse products can appear from seemingly simple reactions. Further work is required to fully establish these reaction mechanisms and subsequently these can be utilised to assist in the design of new molecules. The coordination chemistry of these chains has scarcely been touched and should provide a wealth of valuable information which can be utilised in the design of molecular devices incorporating sulfur–nitrogen chains as the molecular wire.

Oakley and coworkers[18] have already proposed that thiazyl chains with combinations of electron-withdrawing and -donating substituents may prove to be active for non-linear optical applications. Futhermore, it seems apparent that these chains can also fulfil a number of other criteria which provide them with properties desirable for a range of other applications; difunctional materials such as that illustrated in Fig. 7(*a*) have a rod-like nature and may be suitable for development as liquid crystalline materials; the compound illustrated in Fig. 7(*b*), in its coordinated form, would facilitate communication between multiple metal ions; and the molecule shown in Fig. 7(*c*) illustrates one of a family of novel macrocyclic systems in which thiazyl chains link the coordinating bipyridyl functional groups.

The incorporation of other heteroatoms, such as R–P, into the backbone of the chain will allow the electronic properties of the

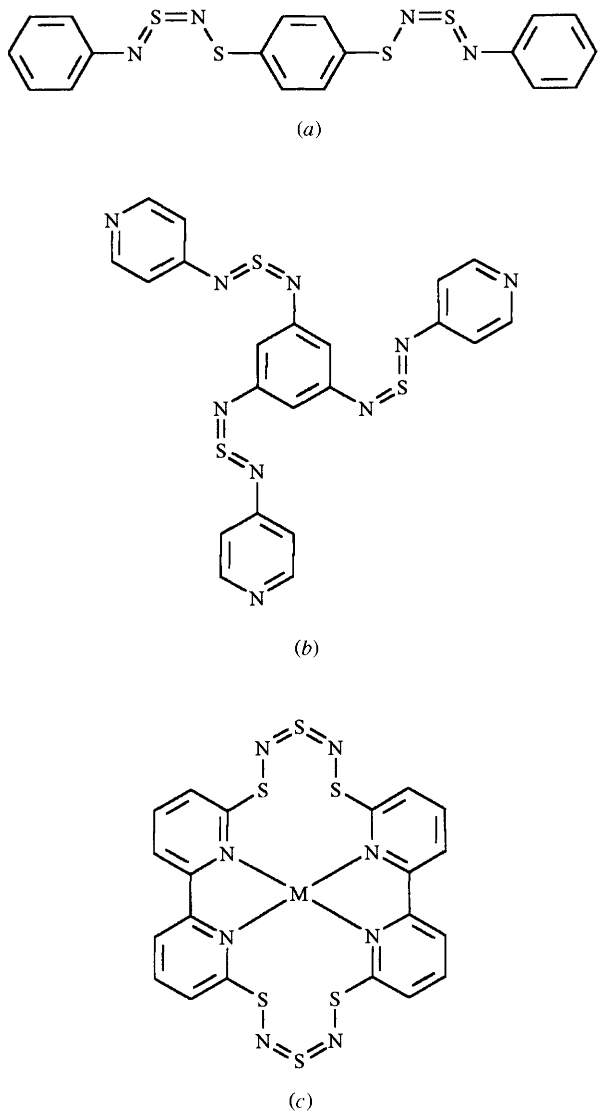


Fig. 7 Structures of some molecules ontaining thiazyl linkages

chain to be modified by fine-tuning the R-group on the chain The potential of these thiazyl-substituted derivatives has yet to be explored but opens-up fascinating new areas of chemistry coupled with the opportunity to develop new molecular materials with unusual properties.

Added in proof: Herberhold and coworkers have recently reported the synthesis of a bis(ferrocene) derivative in which a sulfur diimide (NSN) functional group bridges between the two metallocene units.[30]

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