Chapter 16

Heterocyclic thiazyl and selenazyl radicals; synthesis and applications in solid state architecture

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Abstract

A wide range of heterocyclic sulfur-nitrogen and selenium-nitrogen radicals have been characterized in recent years. Synthetic routes to these materials are summarized, and the modes of association which they exhibit in the solid state are illustrated. The potential use of these radicals as building blocks for low-dimensional molecular conductors is outlined, and some strategies for generating specific solid state architectures are explored. Recent attempts to prepare conductive materials from custom-built bifunctional 1,2,3,5-dithia- and diselenadiazolyls are described.

1. INTRODUCTION

The last decade has seen a tremendous growth in the chemistry of cyclic and heterocyclic compounds containing conjugated -S=N- units [1,2,3]. Preparative routes to all the known binary S,N compounds - rings, chains and cages, some charged and others neutral - are now well established, and a reasonably clear understanding of their electronic structures has emerged. The nuclear and electronic instabilities associated with numerically electron-rich \( \pi \)-systems have been recognized [4,5], as have the spectroscopic [6,7], chemical [8] and electrochemical [9] consequences of low-lying antibonding acceptor levels. Likewise, and in an attempt to bridge the man-made barrier between inorganic and organic chemistry, the applicability [10] of the Hückel \( 4n+2 \) rule has been explored both theoretically [11] and experimentally [12,13]. Finally, and perhaps most gratifyingly to synthetic chemists, the often baffling structural rearrangements that these systems can undergo have yielded some of their mystery to detailed mechanistic analysis [14].
More recently, synthetic research has focused on heterocyclic systems based on inorganic, organic [3,15] and metallosubstituted frameworks [16]. Much of the impetus behind this research can be traced back to the discovery of the conducting [17] and superconducting [18] properties of \((\text{SN})_x\) polymer [19]. Alternative routes to the polymer, other than those involving the generation and polymerization of \(\text{S}_2\text{N}_2\), have been pursued [20], as has the synthesis of heteropolymers containing carbon [21] and phosphorus [22]. The development of these latter materials, however, appears to be limited by the susceptibility of the \(-\text{S}--\text{N}\)-linkage to hydrolysis. One of the most fruitful areas of research, from both basic and applied perspectives, has involved the study of radical species. The generation and characterization of these systems is the subject of the present review.

1.1 Binary sulfur- and selenium-nitrogen radicals

The electronic feature of \(-\text{E}--\text{N}\ (\text{E} = \text{S, Se})\) units which distinguishes them from other inorganic "\(\text{AB}\)" catenate building blocks, e.g., SiO, PN, BN, is their electron count; formally speaking, each unit possesses three \(\pi\)-electrons. In binary sulfur-nitrogen compounds an even \(\pi\)-electronic configuration requires either an even number of \(-\text{E}--\text{N}\) units, e.g., \(\text{S}_2\text{N}_2\), or an overall molecular charge, e.g., \(\text{S}_3\text{N}_3^-\) and \(\text{S}_4\text{N}_4^+\). Thermodynamically stable radical species are scarce. In contrast to nitric oxide, thionitric oxide \([\text{NS}]^+\) polymerizes irreversibly upon condensation, as does \([\text{S}_3\text{N}_3]^+\) (generated by the vaporization of \((\text{SN})_x\) polymer) [23,24]. Several transient radical cations have been characterized, e.g., \([\text{S}_4\text{N}_4]^+\) [25], formed during the reduction of \(\text{S}_4\text{N}_4\), and the dianion \([\text{S}_4\text{N}_5]^{-2}\), obtained by reduction of the bicyclic anion \(\text{S}_2\text{N}_2\) [26]. \(\gamma\)-Radiation of \(\text{S}_4\text{N}_4\) in the solid state produces a broad unresolved ESR signal that has been attributed to the radical cation \([\text{S}_4\text{N}_4]^{+2}\) [27]. The only stable binary radicals are the cations \([\text{S}_x\text{Se}_y\text{N}_z]^+\) (x = 1, 2 and 3), all of which have been characterized by ESR spectroscopy [28,29]. X-ray studies on salts of \([\text{S}_3\text{N}_3]^{+2}\) [23,30], \([\text{Se}_3\text{N}_3]^{+2}\) [29b] and the mixed radical cation \([\text{Se}_2\text{SN}_2]^{+2}\) [31] have shown the same basic structural features. In the solid state the radicals form dimeric units in which two cations associate in a centrosymmetric head-to-head fashion; the structure of the \(\text{AsF}_6^0\) salt of \([\text{S}_3\text{N}_2]^+\), 1, is typical. All the dications are characterized by two long intradimer \(\text{S}--\text{S}\) (or \(\text{Se}--\text{Se}\)) contacts, as well as strong cation-anion interactions. Although the dimeric units are formally diamagnetic, structural defects lead to ESR activity for most of these materials. There is one report of a structure consisting of discrete, unassociated \([\text{S}_3\text{N}_3]^{+2}\) cations [30].

Incorporation of SN and SeN units into heterocyclic frameworks, along with carbon (and/or phosphorus) can, in principle at least, lead to a wide variety of radical species, both charged and neutral [32]. In contrast to most simple binary radicals, many of these heterocyclic species exhibit remarkable thermodynamic stability. The purpose of this chapter is two-fold, (i) to provide a general overview of the synthesis and structural features of these species (sections 2 and 3), and (ii) to offer a contemporary account of our efforts to utilize some of these systems in the development of electrically conducting materials (section 4).
2. HETEROCYCLIC RADICAL ANIONS

2.1. Reduction of sulfur diimides and related compounds

The combined electronegativities of sulfur and nitrogen lead to high electron affinities for compounds containing the -S=N- unit; a value of 2.907 eV (vertical) has been calculated for S\textsubscript{4}N\textsubscript{4} [33]. Consistently, binary sulfur nitrides are easily reduced, either chemically or electrochemically, but the one-electron reduction products degrade rapidly in solution [34]. By contrast, the reduction of simple organic sulfur diimides RNSNR with, for example, alkali metals affords radical anions [RNSNR]\textsuperscript{2-} whose thermodynamic stability resembles that of the iso-electronic thionite anion [SO\textsubscript{2}]\textsuperscript{2-}. ESR parameters for a range of these radicals have been reported [35]; g-values and hyperfine coupling constants indicate substantial spin density on sulfur. However, in contrast to [SO\textsubscript{2}]\textsuperscript{2-}, which associates in the solid state through a long S\ldots S contact [36], the structural fate of simple salts of the type [RNSNR]\textsuperscript{2-} is unknown.

A number of cyclic internal salts, however, have recently been prepared, the solid state structures of which reveal a fascinating insight into the chemistry of these radical anions. The diposphathiatrazinyl radical [Ph\textsubscript{4}P\textsubscript{2}N\textsubscript{3}S]\textsuperscript{2-} 2, as well as its selenium analogue, can be generated by reduction of the corresponding S-chloro (or Se-chloro) derivative with triphenylantimony [37,38]. The ESR hyperfine coupling constants and g-values of both radicals reveal a spin distribution in which the unpaired electron is restricted to a \(\pi\)-orbital spanning the NSN (NSeN) fragment. In the related eight-membered ring radical [Ph\textsubscript{6}P\textsubscript{3}N\textsubscript{4}S]\textsuperscript{2-} 3 hyperfine coupling to phosphorus is more pronounced, presumably the result of increased hyperconjugative interactions [39] arising from the expected ring puckering.
The ESR spectrum of the latter derivative also displays a temperature dependence (an alternating line-width effect) attributable to a torsional motion of the phosphazeny1 backbone [40].

In the solid state the six-membered ring of \([\text{Ph}_4\text{P}_2\text{N}_3\text{S}]^+\) rearranges to the twelve-membered heterocycle 4 [41]; the structure is characterized by a transannular S--S linkage (2.385(1) Å) similar in length to the weak bond found in the dithionite ion [36]. The rearrangement is entirely reversible; dissolution of the dimer regenerates the ESR signal of the radical. The bond interchange exemplified in the association of \([\text{Ph}_4\text{P}_2\text{N}_3\text{S}]^+\) finds an interesting analogy in the chemistry of simple acyclic sulfur diimides. When, for example, a mixture of two different diimides \(\text{RNSNR}^+\) and \(\text{R'NSNR'}^+\) is reduced with potassium, a scrambling of the R and R' groups of the resulting radicals occurs (eqn. 1). The position of the final equilibrium depends on the nature of the R and R' [42]. When these are sufficiently different (e.g. \(\text{R} = \text{Ph}, \text{R'} = \text{Me}_3\text{Si}\)), the equilibrium is shifted well to the right hand side, thus providing an effective route for the preparation of mixed sulfur diimides.

\[
[\text{RNSNR}]^+ + [\text{R'NSNR'}]^+ \rightleftharpoons 2 [\text{RNSNR}]^+ \quad (1)
\]

Conjugation of the sulfur diimide radical anion π-system can stabilize it with respect to rearrangement. For example, replacement of one \(\text{Ph}_3\text{P}\) group of \([\text{Ph}_4\text{P}_2\text{N}_3\text{S}]^+\) with a carbon-based moiety extends spin density to the third nitrogen (C-N-P) of the ring, while still maintaining an overall internal salt charge distribution. Association of these radicals occurs without rearrangement (see section 3.5).

2.2. Reduction of thiadiazoles and thiadiazines

A wide variety of stable radical anions of aromatic heterocyclic derivatives incorporating the sulfur diimide \(-\text{N}=\text{S}=\text{N}-\) linkage have been generated by both chemical and electrochemical means; several have been characterized by ESR spectroscopy [43,44,45]. The parent heterocycles are typically prepared by condensation of a diamino-aromatic compound with sulfur or thionyl chloride; in several cases selenium analogues are also known. In recent years there has been a sustained interest in the use of these materials in charge transfer applications [46,47]. Table 1 summarizes the reduction potentials for these systems. Despite this wealth of ESR and electrochemical data, there are relatively few structural reports on salts of radical anions of this type [48].

3. NEUTRAL HETEROCYCLIC RADICALS

Several families of \(7\pi\)-electron heterocyclic sulfur-nitrogen radicals have been characterized during the last decade. These include the two isomeric forms of the dithiazolyl ring 5 and 6, the two forms of the dithiadiazolyl system 7 and 8,
Table 1
Reduction potentials (V vs. S.C.E.) of aromatic -N=E=N-(E = S, Se) derivatives.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Potential (V)</th>
</tr>
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<tbody>
<tr>
<td><img src="image1" alt="Structure 1" /></td>
<td>-1.51, -2.5 (E = S) [44]</td>
</tr>
<tr>
<td><img src="image2" alt="Structure 2" /></td>
<td>-1.38, -2.3 (E = Se) [44]</td>
</tr>
<tr>
<td><img src="image3" alt="Structure 3" /></td>
<td>-1.64, -2.5 [44]</td>
</tr>
<tr>
<td><img src="image4" alt="Structure 4" /></td>
<td>-0.96, -1.38 [45]</td>
</tr>
<tr>
<td><img src="image5" alt="Structure 5" /></td>
<td>-0.96, -1.8 [44]</td>
</tr>
<tr>
<td><img src="image6" alt="Structure 6" /></td>
<td>+0.10, -0.82 [46]</td>
</tr>
<tr>
<td><img src="image7" alt="Structure 7" /></td>
<td>-0.02 [47]</td>
</tr>
<tr>
<td><img src="image8" alt="Structure 8" /></td>
<td>+0.12 (E = S), +0.04 (E = Se) [47]</td>
</tr>
</tbody>
</table>

and the thiatriazinyls 2, 9 and 10. In some cases selenium analogues have also been characterized. Typically, the radicals are generated by reduction of the corresponding 6π-cations by any of a number of chemical reducing agents, including zinc, silver, copper, stannous chloride and triphenylantimony. The preparative chemistry leading to the cations, and the structural and electronic characterization of the radicals, is described in subsequent sections. It should be noted that a large number of 1,3,2-dithiazolidinium cations [49] and 1,3,2-dithiazolidinyl radicals [50] have also been reported. Because the latter radicals do not possess a formally unsaturated skeleton (they more nearly resemble open-chain sulfinimidyls [RSNSR]⁺ [51]) their properties are not highlighted here; the generation and ESR features of these radicals have been reviewed elsewhere [32].
3.1. 1,3,2-Dithiazolyls

Of the two possible isomers, those based on the 1,3,2-framework are more common. They are typically accessed by reduction of the appropriate dithiazonium cations, either by triphenylantimony or zinc powder. The cations can be prepared in several ways, the most flexible and efficient being (i) the addition of the SNS! cation to acetylenes (eqn. 2) [52,53] and (ii) the condensation of trimethylsilyl azide with a bis(sulfenyl chloride) (eqn. 3) [54]. The first method is very effective for the generation of monocyclic derivatives, while the second is useful for preparing condensed ring materials. Salts of several cations have been structurally characterized [52,55]. Thermolysis of N-substituted 1,3,2-dithiazoles also provides a useful route to radicals.

\[
\text{SNS}^+ \text{AsF}_5^- + \text{R} \equiv \text{C} \equiv \text{C} \text{R} \rightleftharpoons \text{S} \equiv \text{N} \equiv \text{S} + \text{AsF}_5^- \quad (2)
\]

\[
\text{Ph}_{2} \text{S} \equiv \text{N} \equiv \text{SPh} + \text{Me}_3 \text{SiCl} - \text{Me}_3 \text{SiCl} \rightleftharpoons \text{Ph}_{2} \text{S} \equiv \text{N} \equiv \text{SPh} + \text{Cl}^- \quad (3)
\]

The structures of several radicals have been reported; the 4,5-bis(trifluoromethyl) compound has been studied in the gas phase by electron diffraction [53], while the benzo [53,55] and 4,5-dicyano [57] derivatives have been characterized in the solid state by X-ray crystallography. In the solid state both the 4,5-dicyano and benzo derivatives exist as discrete dimeric units. In the former the two molecular halves adopt a face-to-face orientation 11, while the latter exhibits a centrosymmetric geometry 12. In both cases the two rings are connected by long S--S contacts (mean values 3.175 Å and 3.145 Å). The internal structural parameters of the radicals differ from those of the cations; the S-C and
S-N bonds lengthen on reduction. These changes have been explained in terms of the occupation of the antibonding SOMO (singly occupied molecular orbital) (see Figure 1) following a one-electron reduction. The crystal packing of the dimers reveals no indication of the alignment required for conductive properties (see section 4). By contrast, the crystal structure of \([\text{C}_2\text{S}_3\text{N}_3]^+\) 13 exhibits a head-to-head stacked structure in which the S--S separation (3.697 Å) is equal to the unit cell repeat distance along \(b\) [58]. The electrical and magnetic properties of this compound have not been reported [59].

**Figure 1.** Schematic projections of the \(\pi\)-SOMOs of simple 1,3,2-dithiazolyls, 1,2,3,5-dithiadiazolyls and 1,2,4,6-thiaatriazinyls.

The triad of oxidation states (2+, 1+, 0) available to benzobis(dithiazole) has been examined [60]. In its tetrachloroferrate salt, the radical cation associates to the dimeric dication 14, but no stacking of dimers (see section 4) is observed [61]. The radical cation also forms a 2:1 semiconducting salt with TCNQ, but no structural information has been reported. Structural information is also absent for the neutral diradical; solution ESR evidence indicates negligible exchange interactions between the two radical (\(S = \frac{1}{2}\)) centers. Attempts to generate diselenazolyl radicals have been unsuccessful. While, for example, benzobis(diselenenyl chloride) can be condensed with trimethylsilyl azide to afford benzodiselenazolium chloride, reduction of this salt leads to extrusion of nitrogen from the five-membered ring [62].
3.2. 1,2,3-Dithiazolyls

Reports of this radical system are few. A variety of benzo derivatives have been characterized by ESR spectroscopy [51b,63], but there are no solid state or gas phase structural details available. The radicals can be generated by reduction of the corresponding benzo-1,2,3-dithiazolium salts. These can be easily prepared by the Herz reaction, i.e., the cyclization of an aromatic amine with sulfur monochloride [64], but other methods have been described [65]. The simple benzo derivative has also been generated during the reduction of benzo-1,3,2,4-dithiadiazine [66]. There are no reports of any 1,2,3-diselenazolyl derivatives.

3.3. 1,2,3,5-Dithia- and diselenadiazolyls

1,2,3,5-Dithiadiazolyl radicals are prepared almost exclusively by reduction of the corresponding dithiadiazolium salts. Early reports on the preparation of the cations employed the condensation of nitriles with S₃N₃Cl₃, or with sulfur chlorides and ammonium chloride [67]. The reaction of nitriles with S₃N₃Cl₃ has recently been examined by ¹⁴N NMR spectroscopy [68]. It was found that the initial addition product is a dichlorodithiatrazine (eqn. 4). The latter material then thermally degrades over varying time periods (depending on the nature of R) to the dithiadiazolium ring. Other, more specific routes to the 1,2,3,5-cations have also been developed. The 5-chloro compound, for example, can be prepared by the condensation of N,N'-bis(trimethylsilyl)carbodiimide with sulfur monochloride [69]. Likewise, the 5-bromomercapto cation has been obtained, as its tribromide salt, from the reaction of S₄N₄ with bromine in carbon disulfide [70]. However, the most effective, and high-yield synthesis of organosubstituted derivatives involves the use of an amidine [71,72], or a persilylated amidine [73,74,75], with excess SCl₂ (eqn. 5). This reaction also generates small amounts (<5%) of the eight-membered dithiatetrazocine [76], but in one case (R = NMe₂), this latter derivative can be made in moderate yields [77].

\[
\begin{align*}
\text{RCN} & \xrightarrow{\text{S₃N₃Cl₃}} R\text{N} & \xrightarrow{\text{Cl⁻}} R\text{N} & \xrightarrow{\text{Cl⁻}} R\text{N} \quad (4) \\
R\text{N}_2 & \xrightarrow{\text{N,N'-bis(trimethylsilyl)carbodiimide}} R\text{N}_2 \xrightarrow{\text{SCl₂}} R\text{N}_2 \quad (5) \\
\end{align*}
\]

Diselenadiazolium salts can be made by an extension of the latter route; for example, the reaction of N,N,N'-tris(trimethylsilyl)benzamidine with a mixture of
SeCl$_4$ and Ph$_3$Sb (a selenium dichloride synthon) affords the 5-phenyl derivative in high yield [73]. There are no reports of tellurium analogues, although the reaction of N,N,N'-tris(trimethylsilyl)benzamidine with TeCl$_4$ has been investigated [78].

Reduction of 1,2,3,5-dithia- and diselenadiazolium salts can be effected under relatively mild conditions in organic media; reported reductants include triphenylantimony, zinc and copper. Cyclic voltammetry on the phenyl derivatives indicates that the sulfur compound is reduced slightly more readily (at 0.68 vs 0.61 V, relative to Ag/Ag$^+$), as expected from simple electronegativity arguments [73]. In many cases the radicals can be separated and purified by sublimation. ESR studies on dithiadiazolyls with a wide range of 4-substituents (R = CF$_3$, F, Cl, Br [69], Me [79], CCl$_3$ [80], Ph [80,79,81], t-Bu [82], NMe$_2$ [72]) indicate that hyperfine coupling to nitrogen is remarkably insensitive to substituent effects, far less, for example, than in the corresponding 1,2,4,6-thiatetrazinyls (see section 3.5). UV-photoelectron studies on a series of dithiadiazolyls and thiatetrazinyls have revealed similar trends in the first ionization potentials [83,72]. Theoretical studies [69,72,83] have confirmed the simple HMO picture of the electronic structures of these radicals, and provided a simple rationale for the insensitivity of dithiadiazolyls to substituent effects. The SOMO (Figure 1) is of $a_2g$ symmetry, and the presence of the vertical nodal plane prevents, at least to first order, conjugative interactions between the ligand R and the unpaired electron.

The gas phase molecular structure of the CF$_3$ derivative has been determined by electron diffraction [69]. Association of the radicals occurs in solution; quantitative ESR measurements have indicated association enthalpies near -9 kcal mol$^{-1}$ (for R = Ph, t-Bu, CF$_3$) [79,84]. In the solid state association into discrete dimers is observed for simple dithiadiazolyls. For R = CF$_3$ [69], Me [85] and NMe$_2$ [72] the dimers adopt a twisted conformation in which one ring within a cofacial pair is rotated approximately 90° about an axis through the ring centroids (e.g., 15), while for R = Ph, an eclipsed conformation 16 has been found [86]. MNDO calculations suggest a small (<5 kJ mol$^{-1}$) energetic difference between these two modes of association [69]. The intradimer S--S contacts in all these compounds fall in the range 3.1-3.2 Å. There are a variety of close interdimer contacts, but no unusual stacking features (see section 4) are observed. The mixed radical/radical cation combination [PhCN$_2$S$_2$][S$_2$N$_2$]$^+$ Cl$^-$ has recently been reported; its structure 17 consists of pairs of cofacially aligned [PhCN$_2$S$_2$][S$_2$N$_2$]$^+$ units distributed about inversion centers [24]. The mean S--S contact between the CN$_2$S$_2$ and S$_2$N$_2$ rings is 2.838 Å, with longer S--S contacts of 3.522 Å between the two S$_2$N$_2$ rings. A mixed radical dimer/closed shell cation has been characterized as its chloride salt [CF$_3$CN$_2$S$_2$][Cl], but no unusual stacking features are present [69]. Two compounds, formally [PhCN$_2$S$_2$][S$_2$N$_2$] and [PhCN$_2$S$_2$][S$_2$N$_2$][Cl], have recently been reported, both of which contain stacks of alternating CN$_2$S$_2$ and S$_2$N$_2$ rings [24]. These latter materials appear to best formulated as ionic (A$^+$ B$^-$ A$^+$ B) rather than covalent (A-B-A-B) structures.

The replacement of sulfur by selenium leads to stronger inter-radical interactions. In the dimer of the phenyl derivative, [PhCN$_2$Se$_2$]$^+$, a cofacial arrangement of radicals is observed, as in the corresponding sulfur compound [73].
The dimers, however, are stacked in the unit cell in a herring-bone fashion along a two-fold screw axis, with short interdimer Se-Se contacts. Internal structural comparisons, employing both computed and experimental geometries [24,72,73], of rings (CN₂S₂ and CN₂Se₂) with different oxidation states (+1/0), find a simple MO interpretation based on the occupancy of the a₂ orbital shown in Figure 1. As in dithiazolium/dithiazolyl pairs (section 3.1), there is a general lengthening of the endocyclic bonds, most notably the S-S (or Se-Se) linkages, occasioned by reduction. The extent of these structural changes has been used as an indication of the formal degree of charge transfer [24].

Apart from their basic redox behaviour, and the generation of mixed radical species, the chemistry of these radicals has not yet been explored to any great extent. Perhaps their most intriguing reaction is with molecular oxygen, which leads to eight-membered dithiatetrazocene derivatives [87]. The oxidative addition of [PhCN₂S₂]⁺ to low valent transition metals has also been reported recently [88], and it is likely that further work in this area will lead to a wide variety of metallodithiadiazolyl complexes.

3.4. 1,3,2,4-Dithiadiazolyls

The preparative method for this class of radicals again involves the reduction of the corresponding cations, which can be made in good yield by the addition of the salts of the SNS⁺ cation to nitriles [52,51c,84]. Reduction can then be achieved, under mild conditions, e.g., with zinc powder or triphenylnitromine [89]. Several radicals have been studied by ESR spectroscopy and, consistently with theoretical calculations [52], spin density is distributed primarily over the SNS moiety. There are no solid state structural reports on monofunctional radicals of this type. These 1,3,2,4-systems are the thermodynamically less stable of the two isomeric forms, and can be converted into the 1,2,3,5-modification [89]. The
isomerization, which is second order in radical, can be activated photochemically; a mechanism involving a centrosymmetric association and bond switching process (eqn. 6) has been proposed [84].

\[
\begin{align*}
\text{R} & \quad \text{N} & \quad \text{S} & \quad \text{N} \\
\text{S} & \quad \text{N} & \quad \text{S} & \quad \text{N} \\
\text{S} & \quad \text{N} & \quad \text{S} & \quad \text{N} \\
\end{align*}
\xrightarrow{hv}
\begin{align*}
\text{N} & \quad \text{S} & \quad \text{N} & \quad \text{S} \\
\text{N} & \quad \text{S} & \quad \text{N} & \quad \text{S} \\
\text{N} & \quad \text{S} & \quad \text{N} & \quad \text{S} \\
\end{align*}
\]

(eqn. 6)

The propensity of the 1,3,2,4-radicals to isomerise has hindered their isolation and solid state characterization. The crystal structure of the 1,4-phenylene bridged biradical system, however, has recently been reported [90]. The radicals are dimerized in a trans fashion, producing the steplike connectivity shown in 18. The internal structural features of the molecule show little indication of any quinoidal involvement in the ground state electronic structure. The intradimer S-S separation of 3.214 Å is comparable to those found in the dimers of 1,2,3,5-derivatives. The redox chemistry of the [(SNSNC)-(CNSNS)]^{2+} dication, prepared by the double addition of SNS\(^+\) to cyanogen, has recently been explored [91]. One-electron reduction affords a radical cation, which has been characterized by ESR spectroscopy. Two-electron reduction leads to a product with the formal composition of the neutral biradical. No structural data, however, are available for either of these reduced materials.

3.5. 1,2,4,6-Thia- and selenatriazinyls

The 1,2,4,6-thiatriazine framework is pseudo-odd-alternant; consistently there exists a triad of stable oxidation states - cation, neutral radical and anion. Access to these derivatives is easiest via the +1 oxidation state. The preparative method of choice is the condensation of an imidoylamidine with sulfur dichloride (eqn. 7); aryl [92], CCl\(_3\) [93] and CF\(_3\) [83] substituted derivatives have been generated. The procedure has been extended to afford a 1,2,4,6-selenatriazine, although more forcing conditions are required to effect HCl elimination [92]. Heterocycles with one phosphorus have been made by a similar condensation sequence (eqn. 8) [38,94]. Diphosphathiatriazines can be prepared in a variety of ways [95], but the only method which is also suitable for the corresponding selenium derivative involves the use of N,N'-bis(trimethylsilyl) sulfur (or selenium) diimide (eqn. 9) [38]. A more unusual route to 1-chloro-thiatriazines involves the reaction of sodium dicyanamide with thionyl chloride, which produces the 1,3,5-
trichloro compound [96]. The latter undergoes a range of substitution reactions, and extension of this chemistry should, in principle, allow access to a wide range of 3,5-substituted compounds.

Reduction of 1-chloro thia- and selenatriazines affords the corresponding 7π-electron radicals, several examples of which have been studied by ESR spectroscopy [83, 97, 98]. The spin distribution in thiatriazinyls, as manifested in the hyperfine coupling constants $a_N$, is far more sensitive to substituent effects than it is in dithiadiazolyls. Further reduction of the 3,5-diphenyl radical affords the corresponding 8π-electron anion, which has been structurally characterized as its imide [99]. In solution thia- and selenatriazinyl radicals associate; quantitative ESR measurements on the 3,5-phenyl substituted derivatives indicate more extensive association for the selenium compound [92]. The radical dimer [Ph$_2$C$_2$N$_3$S)$_2$] 19 has been characterized in the solid state by X-ray crystallography [92, 97]. The same mode of dimerization is also observed for the corresponding selenium compound. Analysis of the internal structural parameters of derivatives representing each of the three oxidation states (+1/0/-1) available to the C$_2$N$_3$E framework has been interpreted in terms of the progressive effects of occupation of the $b_1$ SOMO shown in Figure 1 [99].

\[
\begin{align*}
\text{(7)} & & \begin{array}{c}
\text{R} \quad \text{N} = \text{N} \quad \text{R} \\
\text{H}_2\text{N}^+ \quad \text{NH}_2 \\
\text{Cl}^{-}
\end{array} & \xrightleftharpoons{xs \text{SCl} \quad \text{SeCl}_4} & \begin{array}{c}
\text{R} \quad \text{N} = \text{N} \quad \text{R} \\
\text{E} \\
\text{Cl}^{-}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{(8)} & & \begin{array}{c}
\text{R} \quad \text{P} \quad \text{N} = \text{N} \quad \text{R} \\
\text{Me}_3\text{SiN} \\
\text{N(SiMe}_3)_{12}
\end{array} & \xrightleftharpoons{xs \text{SCl} \quad \text{SeCl}_4} & \begin{array}{c}
\text{R} \quad \text{P} \quad \text{N} = \text{N} \quad \text{R} \\
\text{E} \\
\text{Cl}^{-}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{(9)} & & \begin{array}{c}
\text{R} \quad \text{P} + \text{P} \quad \text{R} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl}^{-}
\end{array} & \xrightleftharpoons{} & \begin{array}{c}
\text{R} \quad \text{P} + \text{P} \quad \text{R} \\
\text{E} \\
\text{N} \\
\text{SiMe}_3
\end{array}
\end{align*}
\]

The spectroscopic and structural effects of sequential replacement of carbon by phosphorus in both thia- and selenatriazinyls have been explored [38]. The highly delocalized charge distribution of the parent C$_2$N$_3$E (E = S, Se) heterocycle evolves into an internal salt distribution in the P$_2$N$_3$E system (i.e. 2). The solid
state structures of the intermediate CPN₃E radicals reveal an interesting dichotomy. For E = S the radical dimer 20 resembles that found for the C₃N₃S system 19, i.e., the two rings are fused through a single long S--S contact. For E = Se, the dimer structure 21 more nearly resembles a charge transfer adduct; there is an interannular Se-N bond, and the endocyclic structural parameters within the two rings resemble those expected for -1 (N-bonded) and +1 (Se-bonded) oxidation states.

4. NEUTRAL π-RADICALS AS MOLECULAR CONDUCTORS

4.1. Background

The vast majority of synthetic organic conductors [100] utilize charged radicals, either in the form of charge transfer salts such as TTF TCNQ [101] or radical ion (Bechgaard) salts such as those based on the TMTSF and BEDT·TTF [102] donors. Conductivity in these materials requires efficient overlap between the π-systems of the molecular building blocks, which are often stacked in uniform one-dimensional columns. The susceptibility of these columns to undergo a Peierls distortion [103] with consequent loss of conductivity requires designing structures in which intercolumnar interactions are optimised. In the case of Bechgaard salts much effort has been directed towards modifying both the size and shape of the counterion.

Another approach to molecular conductors, one which obviates the need for counterions, involves the use of neutral rather than charged π-radicals. One early proposal [104] was focused on odd-alternant hydrocarbons, the phenalenyl radical (ply⁺) in particular, and was premised on the idea that charge transfer between the non-bonding SOMOs of two such radicals, i.e., the disproportionation reaction shown in eqn. 10, would be energetically more favorable than, for
example, between two TTF** radicals. Several variations [105] on the phenalenyl framework have been pursued experimentally, but a paucity of structural data has hindered progress.

As alternatives to hydrocarbon-based radicals, the heterocyclic thiazyl radicals described in previous sections offer both advantages and disadvantages as molecular building blocks. Replacement of carbon by nitrogen leads to a localization of spin density within the heterocyclic ring. The unpaired spin distribution in 1,2,4,6-thiatriazinyls, for example, is almost completely confined to the heterocyclic ring, while the corresponding 2,4,6-triphenyl-thiopyranyl radical exhibits substantial spin leakage onto the exocyclic phenyl groups [106]. The introduction of nitrogen also inhibits dimerization, i.e., N-N bond formation is less favorable than C-C bond formation. Accordingly, while thiopyranyl radicals associate at the 4-position, thia- and selenatriazinyls dimerize through the chalcogen [107]. However, while the nitrogen content of thiazyl radicals inhibits association, the high effective potential of nitrogen (and sulfur) leads to some potentially detrimental features. Thus, although the triad of oxidation states for the thiatriazine ring can be generated (see Section 3.5), the relatively high IP of the radical leads to a large disproportionation energy [99]. Likewise, as a result of the electron-richness of these rings, the SOMO is not non-bonding. Accordingly electron transfer is accompanied by significant structural reorganization.

Based on current solid state evidence, the six-membered thiatriazinyl framework seems a less attractive candidate for the construction of ordered stacks of molecular "plates". Although the spin distribution can be easily modified by the 3,5-substituents, dimerization occurs through a single atom, producing a rather short S--S bond. By contrast dithiazolyls and dithiadiazolyls, in which the spin density is partitioned between two sulfurs, associate through much longer S--S contacts. Even in those structures where there is only one S--S link (e.g., 15), the interannular separation remains well beyond 3Å.

4.2. Cyano-functionalized 1,2,3,5-dithia- and diselenadiazolyls

Of the various five-membered heterocyclic radicals described above, the 1,2,3,5-dithiadiazolyl system 7 holds the most potential as a building block for the elaboration of molecular materials. It is the thermodynamically more stable of the two isomeric forms (7 and 8), and there exists a simple and flexible preparative method, the condensation of a persilylated amidine with SCl₂ (eqn. 5), that can be extended to the generation of the corresponding selenium-based derivatives. While the structural evidence (section 3.3) on simple sulfur-based dimers provides no indication that the desired mode of packing, i.e., vertical arrays of cofacially aligned "plates", the structure of [PhCN₉Se₂]₂ indicates that selenium derivatives are more susceptible to molecular stacking.

One approach to inducing a more favorable packing pattern involves the use of cyano-functionalized radicals [108]. The idea behind the approach can be traced back to the structure of p-iodobenzonitrile, and indeed to that of the cyanogen halides XCN (X = Cl, Br, I) [109]. In the solid state all these systems adopt a packing pattern in which the molecules align themselves into ribbon-like chains, with close CN--X contacts (i.e., weak N(lone pair)/X-C(σ*) interactions)
acting as molecular ties. The same concepts appear to apply in SN and SeN chemistry. For example, the solid state structures of both the dithia- and diselenadiazoyl radicals bearing a 4-cyanophenyl substituent consist of anti-parallel ribbons of dimers connected by short CN--S/Se contacts. Dimer units in adjacent ribbons are in relatively close proximity, but the stacking of the ribbons (Figure 2) is such that dimers in neighboring layers are offset. As a consequence there are no E--E (E = S/Se) contacts between the layers.

![Figure 2. Anti-parallel ribbons of [(4-NC-C₆H₄)CN₂Se₂]₂ dimers.](image)

The 3- and 2-cyanophenyl derivatives show more interesting structural features. Firstly, the sulfur compound is polymorphic. In the block-like crystals of the β-phase (space group P2₁/n) short CN--S contacts are again found, but the molecular dimers are centrosymmetric, i.e., adopt the geometry shown in Figure 3 (cf. structures 1 and 17). In the α-phase of the sulfur compound (space group P2₁/n), and the isomorphous selenium compound, the radicals dimerize in the more conventional cofacial fashion. As in the 4-cyano structures, the dimers form ribbons connected by CN--S(Se) contacts. The ribbons, however, are now packed in a manner which brings the radical dimers approximately on top of one another (Figure 4). As a result there are a series of close E--E (E = S/Se) contacts within the nearly vertical array of stacked dimers. Similar stacking of dimers is observed in the 2-cyanophenyl selenium derivative (Figure 4).
Figure 4. Stacking of [(3-NC-C₆H₄)CN₂Se₂]₂ (left) and [(2-NC-C₆H₄)CN₂Se₂]₂ (right). Interdimer Se--Se contacts are shown with dotted lines.

Figure 5. Qualitative band energy diagrams for idealized stacked-radical systems.

In summary, the use of the cyanoaryl substituent can induce a favorable orientation of radical dimers. In terms of a simple HMO band model of the electronic structure of these materials, the alignment of discrete dimers in a fashion which produces relatively close interdimer E--E contacts leads to an
evolution of the localized band diagram (Figure 5) for the in-phase (bonding) and out-of-phase (antibonding) interactions of radical SOMOs to one which is spatially more delocalized and energetically more dispersed. The interdimer resonance integral, which is vanishingly small in the non-aligned system, takes on a non-zero value in the stacked structure. Insofar as intradimer interactions dominate, with interdimer contacts being beyond 4.0 Å, there is still a significant gap between the valence and conduction bands of these structures. As a consequence, room temperature conductivities for both E = S and Se fall below 10⁻⁸ S cm⁻¹.

Decreasing the size of the band gap in the above derivatives represents a major challenge. The problem can be addressed in several ways, most notably, within a chemical context, by the design of modified materials in which interactions between columns of radical dimers are enhanced. The introduction of such interactions leads to dispersion of both the valence and conduction bands, and a consequent "stitching together" of the band gap (Figure 5).

4.3. Bifunctional phenylene-bridged 1,2,3,5-dithia- and diselenadiazolyls

An increase in the degree of interdimer interactions can be achieved through the use of polyfunctional radicals. As a starting point for this approach we have constructed biradicals based on the 1,3- and 1,4-phenylene-bridged framework \([E_2N_2O]C_6H_4(CN_2E_2)]\) (E = S, Se); these can be prepared using the standard methods employed for monofunctional systems. Crystals of the 1,4-compounds (E = S, Se) grown by high vacuum sublimation are isomorphous, and belong to the monoclinic space group \(P2_1/n\). The crystal structures consist of diradical dimers packed in a herring-bone fashion (Figure 6). The intradimer E--E separations (mean values 3.121/3.275 Å for E = S/Se) are similar to those observed in monofunctional systems, but there are now a variety of close interdimer contacts to neighboring radical rings. The interlocking nature of the dimers within the herring-bone sheets produces the "perpendicular" interdimer E--E contacts \(r_1\) and \(r_2\) (mean values 3.500/3.578 Å for E = S/Se). Also shown in Figure 6 is a view illustrating the dominant interactions \(r_3 \cdot r_6\) between the herring-bone sheets. For E = Se these contacts are similar to the intercolumnar contacts in TMTSF salts [102], while for E = S they lie outside the van der Waals range.

Crystals of the 1,3-phenylene bridged systems can also be grown by vacuum sublimation but, as in the case of the monofunctional 3-cyanophenyl derivative (E = S), polymorphism is encountered. Needles of the tetragonal \(a\)-phase, space group \(I4_1/a\), can be grown for both E = S and Se [110]. Within the unit cell there are four pinwheel-like clusters (Figure 7) of vertically stacked arrays of diradicals parallel to the y axis. The stacks (Figure 7) consist of molecular "plates" slightly offset from the ideal regular spacing sequence, i.e., the system has suffered a Peierls distortion. The plates, however, do not couple as discrete dimers, as do the 1,4-diradicals. Instead there is a subtle rocking of opposite ends of each molecule so as to produce a zig-zag arrangement of (mean of \(d_1 - d_4 = 3.140/3.284\) Å for E = S/Se) and long (mean of \(d_3 - d_8 = 3.966/4.104\) Å) E--E contacts. The lattice symmetry affords two symmetrically distinct groups, located around the \(4_1\) and \(4\) axes, of intercolumnar contacts. The arrangements of these contacts in both the E = S and Se compounds are similar about the \(4_1\) axes, but there are subtle but
important differences in the clusters about the 4 axes. For the E = S derivative the close contacts are generated between symmetry unrelated atoms, while for E = Se the symmetry related positions are in close proximity.

Figure 6. Two views of the packing in 1,4-{([E₂N₂C]C₆H₄(CN₂E₂)₂) (E = S, Se), showing close interdimer Se--Se contacts.

Figure 7. A projection of the packing in α-1,3-{([E₂N₂C]C₆H₄(CN₂E₂)₂) (E = S, Se) in the xy plane (left) and the zig-zag stacking of diradicals along z (right).
The 1,3-selenium diradical also crystallizes in a second, or β-phase, when the material is sublimed at higher pressures (and temperatures) [111]. This second phase belongs to the monoclinic space group P2₁/n and, in contrast to the α-phase, consists of discrete dimers. The dimers, however, do not form one-dimensional stacks, but generate chain-like arrays parallel to z (Figure 8). A series of interdimer contacts (d₁-d₅, range 3.779 - 3.979 Å) provides links along the chains and between adjacent chains both to the side and also above and below. Overall the structure possesses a much more 3-dimensional network of interactions than is found in the α-phase.

Figure 8. Crystal structure of β-1,3-{(Se₂N₂C)C₆H₄(CN₂Se₂)}. The drawing on the right illustrates the chain-like packing of dimers. Close interdimer Se--Se contacts are shown as dotted lines.

4.4. Magnetic and electrical properties

Two different patterns of association are evident in the phenylene-based bifunctional dithia- and diselenadiazoyle radicals which have been characterized to date. The first of these is the association exemplified by 1,4- and β-1,3-structures in which pairs of molecules form discrete dimers, just as invariably occurs with simple monofunctional radicals. The other structural motif involves the infinite head-to-tail or zig-zag association exhibited by the α-1,3-derivatives. The electrical and magnetic behavior is not, however, straightforward, even within these categories. The 1,4-selenium derivative and β-phase of the 1,3-selenium compound, while molecular solids, both exhibit semiconducting behavior, in contrast to the majority of simply dimerized monofunctional radicals which are insulators. Extended Hückel band structure calculations on the 1,4-compounds show three-dimensional electronic structure with a small but significant degree of dispersion (Figure 9) of the valence and conduction bands in all three directions.
The pseudo-one-dimensional \( \alpha \)-phase of the 1,3-derivatives \((E = S \text{ and Se})\) represents a new structural type for neutral radical solids and provides an important link to the prevailing class of molecular charge transfer conductors. Figure 11 shows a log plot of the single crystal conductivity versus inverse temperature for \( \alpha \)-1,3-[Se\(_2\)N\(_2\)C\(_6\)H\(_4\)(CNSe)]\(_2\)], from which it is clear that the conductivity is activated, and perhaps intrinsic, between about 200 and 300K. Above this temperature other processes intervene and the conductivity shows hysteresis, even at temperatures well below the decomposition point of the sample. It is interesting note that the phenomena which begin to intervene above room temperature in this solid do not have a large influence on the conductivity, and if anything the conductivity is lowered by their intervention. It is also noteworthy that the conductivity of the \( \alpha \)-phase of the selenium compound exhibits a marked pressure dependence; the application of a pressure of 50 tons p.s.i. results in a 1000-fold increase in conductivity.

![Figure 9. Dispersion relations of the highest occupied and lowest unoccupied bands of 1,4-([E\(_2\)N\(_2\)C]C\(_6\)H\(_4\)(CN\(_2\)E))\(_2\) (E = S, Se) along the principal directions in reciprocal space, where \( \Gamma = (0,0,0), B = (a*/2,0,0), Y = (0,b*/2,0), Z = (0,0,c*/2)\).](image)

It is tempting to ascribe the phenomena which occur on a small scale in the \( \alpha \)-1,3-selenium compound above room temperature to the effects which occur on a giant scale in the corresponding sulfur compound. The latter is a poor semiconductor but, as may be seen from Figure 11, exhibits a giant hysteretic enhancement in the paramagnetism at high temperatures. We have previously assigned this behavior to the occurrence of phase kinks in the lattice, which serve to trap isolated spin-bearing dithiadiazolyl units, and it seems this process may occur on a small scale in the selenium compound. It is interesting to note that this phenomenon does not serve as a source of carriers, as would be usual in most semiconductors. It is best explained within our model by noting that the band width of the solid is effectively going to zero as the spin concentration rises, and there is therefore no direct contribution to the conductivity by this process.
Figure 10. Plot of log single crystal conductivity versus reciprocal temperature for α-1,3-[(Se₂N₂C)C₆H₄(CN₂Se₂)].

Figure 11. Spin concentration per molecule as a function of temperature (K) for α-1,3-[(E₂N₂C)C₆H₄(CN₂E₂)] (E = S, Se) from magnetic susceptibility (---) and ESR (--) measurements.
5. SUMMARY

Molecular systems based on 1,2,3,5-dithia- and 1,2,3,5-diselenadiazolyl radicals can be designed so as to afford solid state structures exhibiting one-dimensional stacks of neutral radicals. However, dimerization of these radicals opens up an energy gap at the Fermi level, and the materials are, at best, semiconductors. In order to stabilize highly conducting states in the neutral radical-based materials it will be necessary to overcome the charge density wave or Peierls distortion present in these systems. Just such a problem prevailed in the early charge-transfer conductors, and the remedies for it are well documented, although it should be noted that the half-filled band case (inherent in neutral radicals), is the energetically most favorable case for a charge density wave-driven structural instability, and has never been suppressed in the case of the charge-transfer conductors. The dimensionality of the electronic structure is the key to stabilization of the metallic state. This may be increased by the application of pressure and by the synthesis of compounds designed to foster increased anisotropic interactions.

6. REFERENCES


59. In principle this material should possess a half-filled conduction band, and exhibit metallic properties. The reported unit cell dimensions may, however, represent a sublattice of the actual unit cell, in which case semiconducting or insulating behavior will be observed.


62. G. Wolmershäuser, personal communication.


