ELSEVIER

Coordination Chemistry Reviews
189 (1999) 135–168

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Benzo-fused dithiazolyl radicals: from chemical curiosities to materials chemistry

Jeremy M. Rawson *, Gordon D. McManus

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

Received 19 November 1998; accepted 1 March 1999

Contents

* Corresponding author. Tel: +44-1223-762010; fax: +44-1223-336362.

PII: S0010-8545(99)00118-6

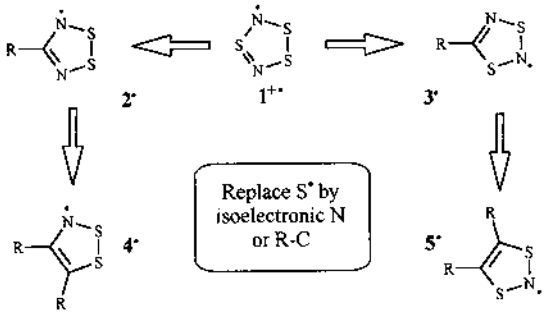
Abstract

Synthetic routes to benzo-fused 1,2,3- and 1,3,2-dithiazolylium salts are described. Their chemical stabilities and physical properties, especially their redox behaviour, are discussed. One electron reduction yields the corresponding benzo fused 1,2,3- and 1,3,2-dithiazolyl radicals. The electronic properties of the dithiazolyl ring are compared with a series of isoelectronic sulphur–nitrogen rings including dithiadiazolyl and trithiadiazolylium radicals. The ability to tune the redox behaviour of the dithiazolyl ring by changing the substituents, coupled with the lower dimerisation energy afforded by delocalisation of the unpaired electron makes these molecules attractive building blocks for the construction of molecular conductors and magnets. Recent results in this area are summarised.

Keywords: Dithiazolyl radicals; Molecular conductors; Molecular magnets

1. Introduction

Our research interests [1] have straddled a number of particularly stable inorganic ring systems derived from the $S_3N_2^{+\bullet}$ radical which was first reported by Demarçay in 1880 [2]. These rings are derived [1] by the simple isoelectronic substitution of R–C for S^+ or N in $S_3N_2^{+\bullet}$, $\mathbf{1}^{+\bullet}$ (Scheme 1).



Scheme 1.

In recent years, the 7π dithiadiazolyl radicals $\mathbf{2}^{\bullet}$ and $\mathbf{3}^{\bullet}$ and the corresponding 6π dithiadiazolylium rings $\mathbf{2}^{+}$ and $\mathbf{3}^{+}$ have been extensively investigated. Derivatives of $\mathbf{2}^{\bullet}$ are of particular interest for materials chemistry; Oakley and co-workers have used dithiadiazolyl and the related diselenadiazolyl radicals as molecular building blocks for the construction of organic conductors [3], whilst our own interests have

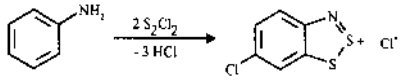
focused on similar materials for the preparation of organic magnets [4]. In addition to their solid state properties, they also exhibit an unusual and varied coordination chemistry which has been recently reviewed [5]. A number of the isomeric 1,3,2,4-dithiadiazolyl radicals, **3**$^{\bullet}$, have been prepared [1]; Primarily this work has arisen through the development of the cycloaddition chemistry of the SNS^+ cation, particularly as its AsF_6^- salt by Passmore [6]. This isomeric dithiadiazolyl radical, **3**$^{\bullet}$, is thermodynamically unstable and undergoes rearrangement to the 1,2,3,5-radical, **2**$^{\bullet}$, either in solution or in the solid state [1,6,7].

The area of heterocyclic sulphur–nitrogen chemistry has often fallen between the traditional disciplines of organic and inorganic chemistry and, the dithiazolylium cations, $\mathbf{4}^+$ and $\mathbf{5}^+$, are typical in this respect. Indeed the literature on these ring systems is extensive and includes entries in Comprehensive Heterocyclic Chemistry [8]. Broadly speaking, the chemistry of the corresponding 6π dithiazolylium cations ($\mathbf{4}^+$ and $\mathbf{5}^+$) has been much more extensively investigated than the characterisation and properties of the related 7π dithiazolyl free radicals (**4**$^{\bullet}$ and **5**$^{\bullet}$). As a consequence, the dithiazolylium *cations* will be discussed, in this review, primarily as precursors to the 7π radicals. Descriptions of the chemistry of these closed-shell cations will be provided only where it enhances a broader understanding of the corresponding dithiazolyl radical chemistry, or where there are curious chemical transformations where we feel an alternative interpretation is possible. For more comprehensive literature pertaining to electrophilic or nucleophilic reactions of the dithiazolylium cations, readers should refer to Ref. [8]. In this review we will concentrate on fused derivatives of the 1,2,3 and 1,3,2-dithiazolyl *radicals*, in which the fused nature of the structures facilitates a greater π-delocalisation of the unpaired spin density. This greater delocalisation allows the electronic properties of the dithiadiazolyl radical to be tuned for materials applications, by modification of the electronic and steric properties of the substituents on the fused ring. At the end of this review we outline some of the properties of dithiazolyl radicals which might favour their application in materials chemistry. Unless otherwise specified, all the dithiazolyl ring systems are fused.

2. 1,2,3-Dithiazolylium salts and 1,2,3-dithiazolyls

2.1. The Herz reaction

1,2,3-Dithiazolylium salts were first prepared [9] by Herz in 1922 from the reaction of aniline hydrochloride, and its derivatives, with an excess (4–5 molar equivalents) of S_2Cl_2. Almost invariably the aromatic ring becomes substituted by chlorine *para* to the amine N atom (Eq. 1).



(1)

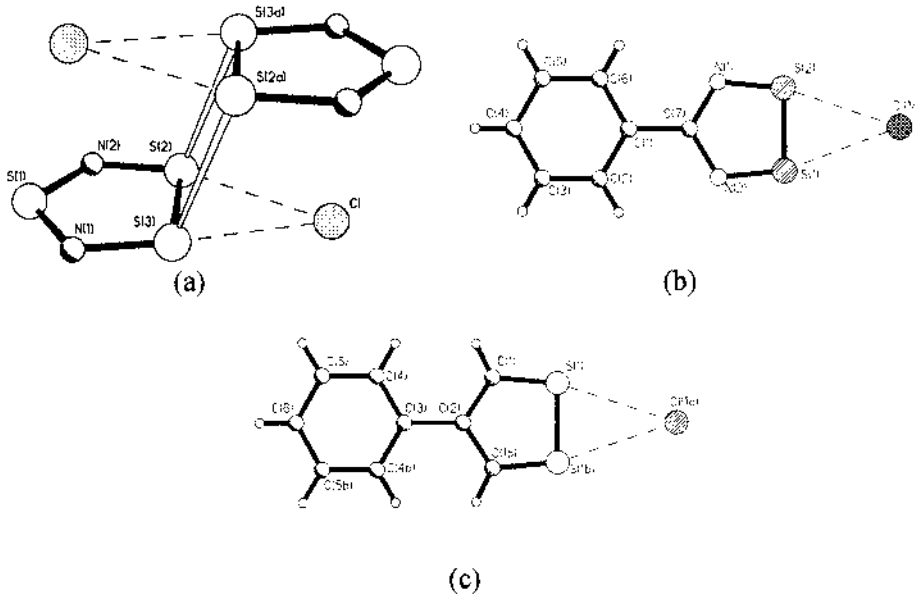


Fig. 1. Crystal structures of $([S_3N_2]Cl)_2$, [PhCNSSN]Cl and PhC(CH)SS(CH)]Cl which all exhibit close S···Cl contacts.

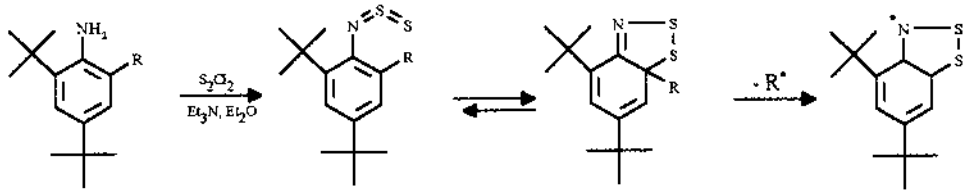
Whilst the stoichiometry of the reaction appears simple, the reaction mechanism is not well-understood, despite numerous studies [10], and the reaction typically gives rise to a number of by-products. A number of the impurities have been characterised and these include mixtures of chlorinated and non-chlorinated dithiazolylium derivatives [11], sulphur-diimides, **6** [12], as well as the acyclic and cyclic products, **7** and **8** [12–15], azo-benzene derivatives [15] and benzothiazoles [16]. The reaction would appear to have two key features; ring-closure and chlorination of the aromatic ring and these are described briefly in Sections 2.1.1 and 2.1.2.

Purification of Herz salts is best achieved via metathesis to one of a number of more soluble salts ($AlCl_4^-$, BF_4^-, ClO_4^-, AsF_6^- and $SbCl_6^-$) which can be recrystallised to a high degree of purity [17–19]. The low solubility of the chloride salt is reminiscent of a number of other chloride salts of compounds containing disulphur links [1]. Invariably these compounds are characterised by strong S···Cl interactions in the solid state in which the Cl atom sits approximately equidistant from the two sulphur atoms, forming close contacts to both chalcogen centres (Fig. 1). It is likely that a similar structural motif is observed for these Herz salts, although, to our knowledge no chloride salts of the Herz cation have been crystallographically characterised.

2.1.1. Ring closure in the Herz reaction

Elegant work by Inamoto and co-workers [12], studied the condensation reaction of 2,4,6-tri(*tert*-butyl)aniline (**9**) with S_2Cl_2 (Scheme 2). They observed condensa-

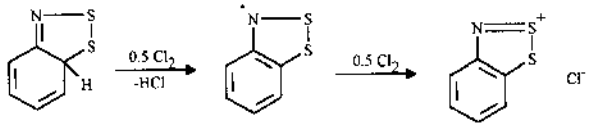
tion to form a thiosulphinylamino group (**7**), isoelectronic with the sulphinylamine group, RNSO. The *cis*,*cis*-structure associated with the thiosulphinylamine group [12] places the terminal S atom in an ideal position for ring closure and an equilibrium was observed in solution between acyclic (**7**) and cyclic (**8**) forms. The acyclic and cyclic derivatives **7a** and **8b** have been characterised by X-ray crystallography [14]. The cyclisation energy (ΔH_{cycl}) was estimated at -4.9 kcal mol^{-1} from variable temperature NMR studies [13].



a: R = Me; b: R= ^{t}Bu; c: R=H

Scheme 2.

Mild thermolysis of **8** leads to formation of the 4,6-di-*tert*-butyl-benzodithiazolyl radical, **10•**, via dealkylation of **8b** (or dehydrogenation of **8c**) [11]. Dealkylation of **8b** has also been achieved by addition of PCl_5, eliminating *tert*-butyl chloride and forming the corresponding di-(*tert*-butyl)benzodithiazolylium cation, characterised as its $SbCl_6^-$ salt by X-ray diffraction [17]. Formation of the intermediate dithiazolyl radical, **10•**, was confirmed through EPR spectra of solutions of S_2Cl_2 in CCl_4 with three equivalents of the parent amine [11,20,21]. Molecular chlorine or S_2Cl_2 have been reported [11] to oxidise these radicals to dithiazolylium salts (Scheme 3) which precipitate quantitatively in appropriate solvents (but see Ref. [22][1]).



Scheme 3.

[1] Reduction of benzo-1,2,3-dthiazolylium chloride with Zn/Cu couple yielded the benzo-1,2,3-dithiazolyl radical (EPR). Subsequent oxidation with S_2Cl_2 yielded a salt-like precipitate which, on attempted reduction with further Zn/Cu couple was EPR silent, indicating that neither benzo-1,2,3-dithiazolylium chloride nor a chlorinated derivative had been formed.

2.1.2. Chlorination of the aromatic ring

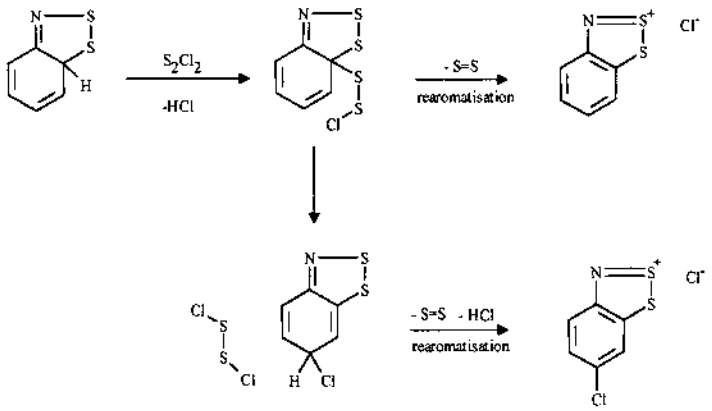
Whilst the ring-closure reaction (Section 2.1.1) would appear well-characterised, chlorination of the aromatic ring which occurs during the reaction is less well-understood, despite numerous studies. Chlorine substitution at the *para* position to the amine N occurs for a variety of deactivating groups (NO_2, COOH, SO_3H) as well as H, although a number of substituents (Br, Me_2N, RO and R groups [10]) have been found to withstand substitution. Chlorination is unlikely to occur prior to cyclisation since experiments using reactive aromatics have indicated that S_2Cl_2 is not an effective chlorinating agent [10]. This is in agreement with the observation of considerable quantities of the unsubstituted radicals (**10**$^{\bullet}$) by EPR spectroscopy (Section 2.1.1) when the reaction is carried out under mild conditions with a deficit of S_2Cl_2. Chlorination of the aromatic ring does not occur after formation of the Herz salt, since attempted chlorination of benzodithiazolylium chloride by S_2Cl_2, by a Cl_2/HCl mixture or by S_2Cl_2/HCl yields only the unchlorinated benzodithiazolylium chloride salt [10,11]. Chlorination of the aromatic ring must, therefore, occur after cyclisation but prior to oxidation to the dithiazolylium chloride salt. Two mechanisms would appear possible, either reaction with the parent radical, **10**$^{\bullet}$, or with the ring-closed product **8**.

Theoretical calculations (Section 2.5) indicate that the majority of the unpaired spin density resides on the heterocyclic ring, although there is considerable delocalisation onto the fused-aromatic substituent. An examination of the hyperfine coupling constants for the benzo-1,2,3-dithiazolyl radical (Section 2.4.3) indicate that the largest H-hyperfine coupling occurs to the H atom *para* to the heterocyclic N. On the basis of the McConnell equation (relating the magnitude of the H-hyperfine coupling constant to the unpaired spin density on C via spin-polarisation [23]), the unpaired spin density at the C atom *para* to the heterocyclic N is greatest and radical chlorination by S_2Cl_2 at the aromatic ring is most likely to occur at this position. However, Mayer indicated [11] that both the Herz radicals and salts are stable with respect to aromatic chlorination. As a consequence, this pathway would not appear to be involved in the substitution process and we must presume that chlorination occurs via reaction of **8** with S_2Cl_2.

After condensation of S_2Cl_2 with the primary amine, followed by ring-closure, H or alkyl group abstraction may be achieved from the *ortho*-position through condensation with S_2Cl_2; Bats et al. [17] have shown that this alkyl abstraction can be achieved with the stronger chlorinating agent, PCl_5. The intermediate disulphide can then undergo rearomatisation with loss of S_2 to form the non-chlorinated Herz salt or chlorination at the *para*-position to yield a quinoidal intermediate (Scheme 4). In the latter case, a further equivalent of S_2Cl_2 facilitates the rearomatisation to form the chlorinated derivative. The composition mixture of final products then depends on the relative rates of the two processes.

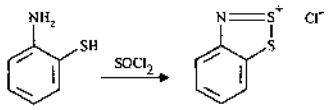
2.1.3. Other synthetic approaches to Herz salts and Herz radicals

Whilst the Herz reaction provides a convenient route to many dithiazolylium salts, the prevalence for chlorination of the aromatic substituent has led to the development of several other approaches to 1,2,3-dithiazolylium salts and 1,2,3-



Scheme 4.

dithiazolyl radicals. A particularly convenient route involves the mild condensation reaction between thionyl chloride and *ortho*-amino-thiophenols, **11** (Eq. 2) [10c].

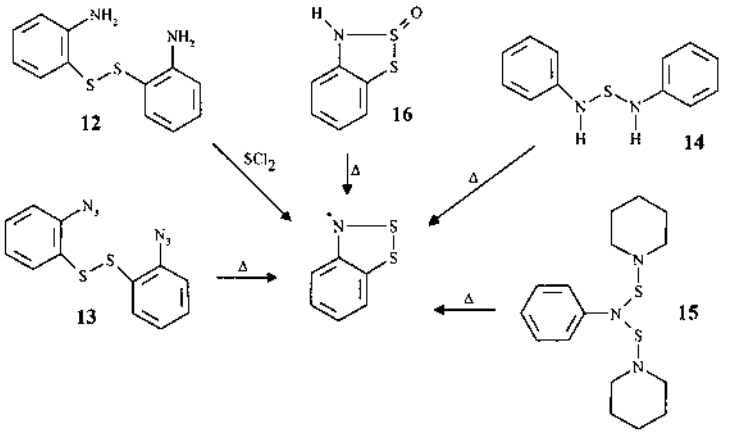


(2)

11

Under these conditions, chlorination of the aromatic ring was not observed and yields of the Herz salts were in excess of 70%. Recently, Oakley and co-workers reported [19] a variant on this reaction in which condensation of diaminobenzenedithiol with S_2Cl_2 led to ring closure at both sites to form a benzo-bis(1,2,3-dithiazolylium)salt. Although, under these conditions, with S_2Cl_2 rather than $SOCl_2$, chlorination of the benzene ring was observed.

Other variants on this condensation reaction are the condensation of bis(*ortho*-aminoaryl)disulphides, **12**, with SCl_2 to form the 1,2,3-dithiazolyl radicals in good yield, and the thermolysis of bis(*ortho*-azidoaryl)disulphides, **13**, Scheme 5 [24]. Surprisingly, thermolyses of thiobisamines, **14**, bis(aminothio)amines, **15**, and the hydrolysis product of Herz salts, **16** (see Section 2.2.1) all produce the 1,2,3-dithiazolyl radicals directly [25]. Notably these dithiazolyl radicals were initially incorrectly assigned as thiazetyl radicals [25], but their identity was confirmed by comparison of their (identical) EPR parameters with the corresponding 1,2,3-dithiazolyl radical. (Section 2.4.3). Herz salts can also be prepared by dehydration of the corresponding 2H-1,2,3-dithiazolyl-2-oxides [18]. This reaction is described in more detail in Section 2.2.1 (below).

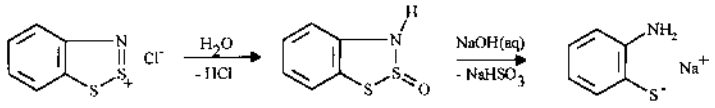


Scheme 5.

2.2. Reactions of Herz salts

2.2.1. Hydrolysis

In neutral aqueous solution, Herz salts hydrolyse to form the 3H-1,2,3-sulfoxide, **16**, which, on treatment with alkali, is further hydrolysed to the corresponding salt of aminothiophenol, **11** (Eq. 3) [10].

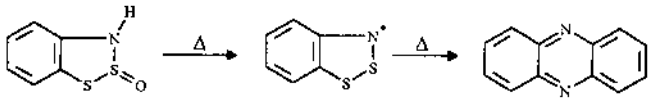


16 **11′** (3)

Derivatives of **11** are important reagents for the synthesis of benzothiazoles, thionapthenes, phenothiazines and benzothiadiazoles [10,26]. The characterisation of derivatives of **16** or **11** has frequently been used to determine the course of the Herz reaction and position of halogenation. Both hydrolysis steps are essentially reversible; the condensation of the free thiol derived from **11′** with $SOCl_2$ has already been described as a convenient route to Herz salts (Section 2.1.3) [10c]; whereas dissolution of **16** in strong acid reforms the Herz salt via dehydration [18]. The latter is particularly useful since this provides good yields of Herz salts with non-interacting anions which can be recrystallised to analytical purity [18].

2.2.2. Thermolysis

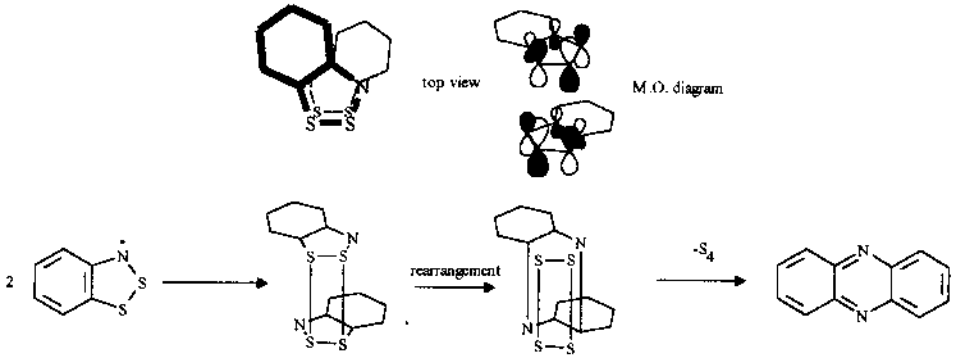
Thermolysis of the S-oxide, **16**, at 80°C was initially reported to yield a thiazete radical (see Section 2.1.2)[25], now reassigned as the 1,2,3-dithiazolyl radical on the basis of EPR data. Further heating of these radicals above ca. 120°C leads to high yields of phenazines (e.g. 80% of **17** from **16**) (Eq. 4) [15] and a disproportionation mechanism was suggested [15]. We propose an alternative mechanism below.



16 16• 17 (4)

Solution UV–vis and EPR studies of $\mathbf{1}^{+\bullet}$, $\mathbf{2}^{\bullet}$ and $\mathbf{3}^{\bullet}$ all indicate that association occurs in solution [1,7,27,28] (despite electrostatic repulsions for $\mathbf{1}^{+\bullet}$) and crystallographic studies indicate that this also occurs in the solid state leading, in the majority of cases, to spin-paired dimers. For $\mathbf{5}^{\bullet}$ (non-fused derivative with $R = CF_3$ and the benzo-fused derivative) the dimerisation enthalpy has been estimated from EPR as ca. 0 kJ mol^{-1} [28] and, whilst association is not particularly favoured, there is no thermodynamic argument for molecules not to associate in solution. In the solid state, some derivatives of $\mathbf{5}^{\bullet}$ are associated, whereas others are not (see Section 3.3.1) whilst in the liquid phase there is ca. 65% dissociation [28] for the non-fused derivative ($R = CF_3$). In $\mathbf{1}^{+\bullet}$, $\mathbf{2}^{\bullet}$, $\mathbf{3}^{\bullet}$ and $\mathbf{5}^{\bullet}$, association occurs through interaction of a pair of singly occupied molecular orbitals (SOMOs), forming dimers and, for $\mathbf{3}^{\bullet}$, this radical association has been linked to a major structural rearrangement; Quantitative conversion of $\mathbf{3}^{\bullet}$, to isomeric $\mathbf{2}^{\bullet}$ has been observed both in solution and in the solid state [7,29]. This type of $\pi^*-\pi^*$ interaction has also been proposed to explain the skeletal scrambling of thiazyl chains in the presence of an alkali metal [30].

Whilst the available data on Herz radicals is extremely limited (there are no crystal structures of simple derivatives nor detailed concentration dependent UV–vis or EPR studies), it does not seem unreasonable, in the light of the above evidence, to believe that these radicals will also associate in solution. In the case of the Herz radical, the SOMO (Section 2.5) indicates an expected weakening of the intramolecular N–S and C–S bonds, and the SOMO–SOMO interaction (Scheme 6) indicates strengthening of the intermolecular S···S and C···N interactions. Subsequent cleavage of intramolecular C–S and S–N bonds, with concomitant formation



Scheme 6.

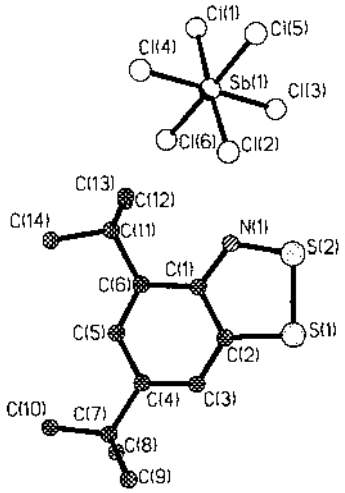


Fig. 2. Crystal structure (**17**) [$SbCl_6$].

of S–S and C–N bonds provides a simple rationale [31] for the generation of phenazines with concomitant extrusion of S_4 units.

2.3. Structures of Herz salts and their derivatives

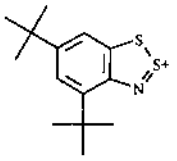
Two fused dithiazolylium salts have been characterised by X-ray crystallography; one is the $SbCl_6^-$ salt **17** [17] (Fig. 2), the second is the $AlCl_4^-$ salt **18** [19]. The cations are essentially planar and the heterocyclic ring geometries (Table 1) are identical within experimental error. The bond lengths and angles are similar to other five-membered heterocycles such as $\mathbf{2}^+$ [1] with bond angles at S slightly

Table 1
Bond lengths and angles for a series of 1,2,3-dithiazolylium salts and dithiazolyl radicals

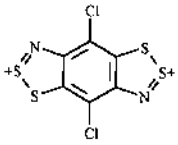
	(**17**) ($SbCl_6$) [17]	(**18**) $(AlCl_4)_2$ [19]	**19** [19]
Bond length (Å)			
C–C	1.435(8)	1.436(6)	1.457(3)
C–N	1.346(7)	1.349(6)	1.306(3)
N–S	1.571(5)	1.567(4)	1.638(2)
S–S	2.022(3)	2.0285(18)	2.0904(9)
S–C	1.704(6)	1.724(4)	1.737(2)
Bond angle (°)			
CCN	115.4(6)		
CNS	117.5(5)		
NSS	99.7(2)		
SSC	92.0(3)		
SCC	15.4(5)		

greater than 90° and with an S–S distance of a little more than 2.0 Å. In both cases the structures are composed of essentially discrete cations and anions, as expected for the harder, non-interacting anions, although there are weak cation–anion contacts. For the $SbCl_6^-$ salt, the cation–anion interactions are manifested as three S···Cl contacts around 3.5 Å. These are in agreement with theoretical calculations (Section 2.5) which indicate the majority of the positive charge is localised on the sulphur atoms, similar to other thiazyl-based cation···chloride interactions [1].

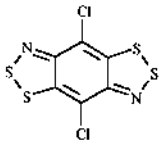
Two-electron reduction of **18** yields the neutral bis(1,2,3-dithiazolyl) [19] which has a singlet ground state ($S = 0$) and should be considered as the quinoid structure, **19**. The structural parameters for this neutral molecule are also given in Table 1. A comparison of the structures of **18** and **19** reveal that, on reduction, there is a clear lengthening of C–N, N–S, and particularly S–S bonds. This is in good agreement with theoretical studies (Section 2.5) which indicate that reduction takes place via addition of electrons into an antibonding orbital [19] which is predominantly based on the heterocyclic ring.



17



18



19

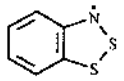
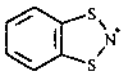
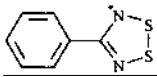
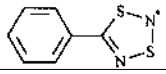
2.4. Physical studies on Herz compounds

A number of physical studies have been carried out on Herz salts and their derivatives, including UV–vis studies on both the cations and radicals, EPR of the dithiazolyl radicals and electrochemical studies of the redox process involved between the dithiazolylium salt and dithiazolyl radical.

2.4.1. Electrochemical studies

Electrochemical studies show that the benzo-1,2,3-dithiazolylium cation undergoes a single, irreversible, $7e^-$ reduction in protic solvents [32]. This has been associated with ring opening, extrusion of the S atom (as S^{2-}) and formation of the aminobenzenethiol, **11**. In acetonitrile, the reduction is stepwise, with an initial, reversible, one-electron reduction of the cation to the radical, followed by an irreversible $6e^-$ reduction. Electro-generation of the dithiazolyl radical, through the $1e^-$ reduction, can be achieved in this manner [32,20], although the colour is rapidly dissipated on admission of air [32]. Mayer also reported that the 1,2,3-dithiazolyls are not stable in protic solvents and, even in $CHCl_3$, the colour of the radical (red–green) is dissipated and 'within a few minutes a salt-like precipitate is formed' [11]. This was assumed in terms of radical oxidation by Mayer, but attempted re-reduction was reported to be unsuccessful by Sutcliffe and co-workers [21]. The second, irreversible, $6e^-$ reduction occurs only in the extremely negative region.

Table 2
Half-wave oxidation potentials for a series of isoelectronic sulphur–nitrogen heterocycles, referenced to SSCE

Compound	$E^{ox}_{1/2}$ (V)	Ref.	Compound	$E^{ox}_{1/2}$ (V)	Ref.
	+0.26	32		+0.15	46
	+0.59	33		+0.33	33

Reduction of these Herz salts to the corresponding radicals would appear facile (Table 2) in comparison to the reduction potentials for other isoelectronic heterocycles such as the dithiadiazolylium salts $\mathbf{2}^+$ and $\mathbf{3}^+$ [1,33], and the isomeric 1,3,2-dithiazolylium cations (Section 3.3.2). Indeed, the tendency of these cations to form radicals is highlighted in the synthesis of the benzo-bis(1,2,3)dithiazolylium salts from diaminobenzenedithiol and S_2Cl_2 [19]; Rather than formation of the bis(dithiazolylium) dication, the radical cation is formed preferentially. Whilst the dithiadiazolyl radicals $\mathbf{2}^\bullet$ and $\mathbf{3}^\bullet$ show only minor variations in redox potential as a function of substituent [1,33], the half-wave oxidation potentials of the fused dithiazolyl derivatives are more substituent sensitive. The ease of the redox process has been associated with the extent of π-delocalisation of the positive charge onto the aromatic ring [32].

2.4.2. UV–vis spectra of Herz salts and radicals

UV–vis spectra of Herz salts have been reported by Heustis [18] and exhibit two absorption maxima, independent of the counterion (BF_4^- or ClO_4^-); one absorption around 350 nm and a weaker one around 440 nm. These maxima exhibit some dependency on the benzo-substituent, the more intense band shifting to longer wavelength on Cl-substitution *para* to the ring N. Reduction of these cations to the corresponding radicals leads to significantly different UV–vis spectra. The benzo-1,2,3-dithiazolyl radical exhibits three absorption maxima (340, 395 and ca. 510 nm) which appear slightly solvent dependent [11,24]. The band to longer wavelength gives rise to their more intense coloration. The solvent dependency could be readily attributed to solvatochromism, or alternatively to a monomer–dimer equilibrium in solution. Association of 1,2,3-dithiazolyl radicals is likely to occur in solution in an analogous fashion to $\mathbf{1}^{+\bullet}$, $\mathbf{2}^\bullet$, $\mathbf{3}^\bullet$ and $\mathbf{5}^\bullet$ (see Section 2.2.2).

2.4.3. EPR spectra

The EPR spectra of a large number of 1,2,3-dithiadiazolyl radicals have been reported by Mayer and Sutcliffe in a series of comprehensive studies of these radicals [20,21]. Data for a series of benzo-substituted and napthalene derivatives are compiled in Table 3.

In all cases the g-value is close to 2.008, substantially greater than that for the free electron ($g_e = 2.0023$) [23] and is indicative of spin-orbit coupling arising from significant amounts of spin-density at sulphur [19]. This is in agreement with the g-values observed for the radicals $\mathbf{1}^{+\bullet}$, $\mathbf{2}^{\bullet}$ and $\mathbf{3}^{\bullet}$ which have g-values of approximately 2.011, 2.010 and 2.005, respectively [1,27] in which the unpaired spin-density is, to an even larger degree, localised on the heterocyclic ring. The g-values observed for the fused dithiazolyl radicals tend to be a little smaller than the values for the non-fused derivatives which are typically greater than 2.009 [20]. This is in accord with the ability of the fused derivatives to delocalise spin-density away from the sulphur atom, thereby reducing spin-orbit coupling. There is some variation in the N-hyperfine coupling, depending on substituent; A correlation has been observed between the Hammett parameter, σ_p, for the *para*-substituent and the N-hyperfine interaction; the two being inversely proportional [24]; the more extensive the delocalisation, the smaller the N hyperfine coupling constant. Notably the protons *ortho* and *para* to the heterocyclic N exhibit significantly larger coupling constants than the other H atoms, indicative of considerably more unpaired spin density on the aromatic ring C atoms *ortho* and especially *para* to the heterocyclic N atom. ^{33}S labelling experiments [20] indicate that there is more unpaired spin density on $S_{(2)}$, the N-bound S, rather than $S_{(1)}$ and this is in agreement with theoretical studies (Section 2.5).

2.5. Theoretical studies

Whilst theoretical calculations on open-shell molecules, including sulphur–nitrogen compounds, often provide a qualitative analysis (symmetry of the singly occupied molecular orbital and the distribution of the unpaired spin-density), quantitative analyses may be poor and require considerable levels of sophistication to produce results consistent with experimental observation. We take a series of studies on $\mathbf{2}^{\bullet}$ as an example [34–36]. In a comprehensive theoretical study by Oakley and co-workers on derivatives of $\mathbf{2}^{\bullet}$ ($R = Me_2N$ and H_2N), some variation in molecular geometry was observed, dependent on the ab initio basis set used [34]. In particular split-valence basis sets with density-functions for sulphur are required to avoid large distortions to low symmetry structures [35]. In addition, satisfactory agreement between experimental and calculated ionisation potentials [34,35] and dimerisation enthalpies [35,36] could only be achieved, taking into account electron correlation effects, with third and fourth order effects required to produce good agreement between theoretical and experimental data. An analysis of predicted IR data and ionisation energies also require a scaling factor to be incorporated to provide good agreement with experimental data [35]. Similar problems with the prediction of unpaired spin density distributions can be caused by the poor choice of a basis set [27], although more recently, density functional theory has led to quantitative estimates of unpaired spin density in derivatives of $\mathbf{2}^{\bullet}$, in better agreement with observation [36,37]. Nevertheless, whilst quantitative comparisons

Table 3
EPR parameters for some fused 1,2,3-dithiazolyl radicals[a,b]

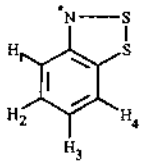
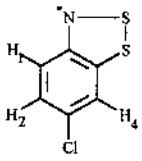
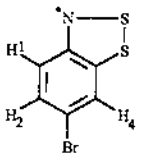
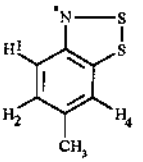
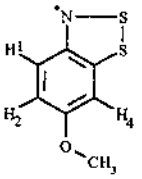
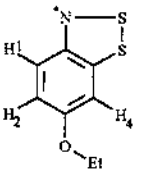
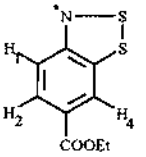
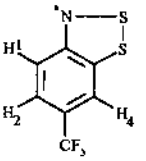
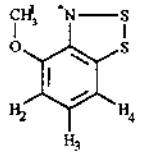
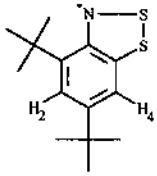
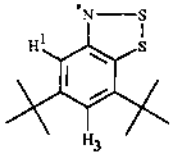
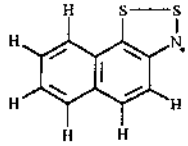
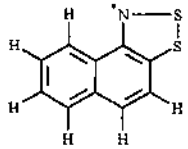
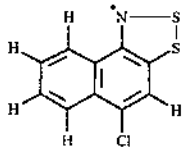
Radical	g-value				a_N	a_S^1	a_s^2	a_H^1	a_H^2	a_H^3	a_H^4
	2.0081	8.13			2.86	0.95			3.62		0.85
	2.0081	8.20	3.51	4.51	2.83	0.88			3.75		0.88
		7.72			2.90	0.90			---		0.90
		7.72			2.93	0.90			---		0.90
	2.0078	7.88			2.94	0.94			---		0.78
	2.0078	8.40			2.90	0.80			3.90 (3xH)		0.80
	2.0083	8.69			2.90	0.90			0.50 (3xH)		0.90
	2.0072	8.50			4.00	1.10			---		1.10
	2.0079	7.40			2.68	0.82			---		0.82
	2.0079	7.25			2.77	1.08			---		0.78
	2.0084	7.45			2.93	0.90			5.50 (3xF)		0.70

Table 3 (Continued)

	2.0076	8.32			---	0.95	3.69	0.95
	2.0076	8.21	3.69	4.51	---	0.95	---	0.75
	2.0081	8.12	3.55	4.51	2.86	---	3.87	---
	2.0079	7.45			1.75	1.55	1.35	0.7 (3xH)
	2.0079	7.30			4.30	0.40 (2xH)	0.80 (3xH)	
	2.0078	8.00						

[a] Hyperfine coupling constants are quoted in Gauss.

[b] Data taken from Refs. [20,21].

between experimental and theoretical parameters may be difficult to make, qualitative analyses, even at the simplest Hückel level can still provide useful estimates of spin-density distributions [27,34–36].

Whilst the dithiadiazolyl radicals **2**• and **3**• have both been shown to have their unpaired spin-density localised on the heterocyclic ring [1], the fused nature of the

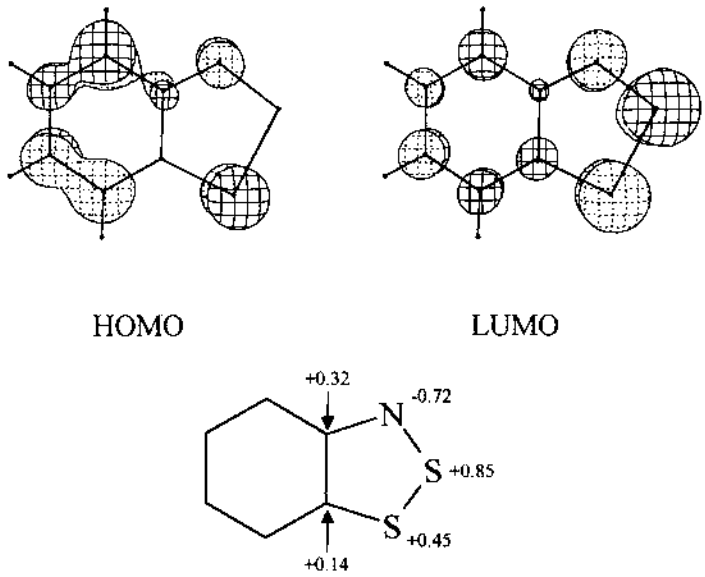
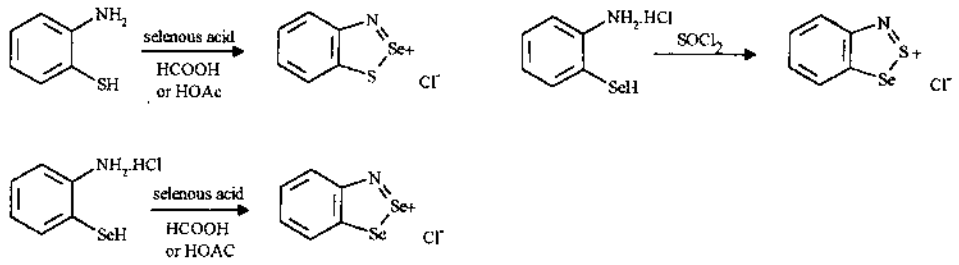


Fig. 3. Frontier molecular orbitals and charge distributions for the benzo-1,2,3-dithiazolium cation, determined from EHMO calculations [38,39].

Herz radicals facilitates π-delocalisation of the unpaired spin density. Thus whilst the spin-density distributions in **2**• and **3**• are almost constant, substituent effects are more likely to play an important role in determining the precise spin-density distribution in derivatives of **4**•. This is highlighted by the variations in N-hyperfine coupling constants and *g*-tensors observed in EPR studies (Section 2.4.3). The frontier orbitals determined [38] at the extended Hückel level [39] (highest occupied molecular orbital, HOMO; and lowest unoccupied molecular orbital, LUMO) of the benzo-1,2,3-dithiazolylium cation are both of π-character and are depicted in Fig. 3.



Scheme 7.

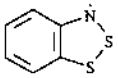
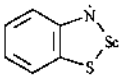
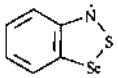
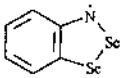
The LUMO is of antibonding character with respect to S–S and S–N. Whilst the majority of the unpaired spin-density (73% on the basis of EHMO calculations) is
localised on the SSN fragment, significant π-delocalisation is observed with large unpaired spin-densities on C atoms *ortho* and *para* to the heterocyclic ring N. This is in good agreement with EPR studies which show significant coupling to ^{1}H nuclei in the *ortho* and *para* positions. (Section 2.4.3). Within the heterocyclic ring, the N-bound S atom exhibits the greatest degree of unpaired spin-density, in agreement with EPR studies. Addition of another electron into the LUMO would form a dithiazolylide anion. Geometry optimisation has indicated [19] that this orbital which is strongly antibonding with respect to S–N would ring-open to form an acyclic anion. Similar studies on the 1,2,3,5-dithiadiazolyl radical, **2**$^{\bullet}$, have indicated that addition of further electron density into its SOMO would lead to weakening of the S–S bond [5]. Indeed reaction of PhCNSSN with low-valent transition metal ions has led to a series of compounds in which the heterocyclic ring has opened at the disulphur bridge and chelated a metal ion [5]. On this basis we might expect 1,2,3-dithiazolyl radicals to undergo oxidative addition reactions to low-valent transition metal ions with insertion of the metal ion into the N–S bond. Interestingly, electrochemical studies (Section 2.4.1) indicate that further reduction of Herz radicals involves a one-step $6e^{-}$ reduction, with loss of sulphide ion, and such complexes may be susceptible to loss of sulphur. Recently, a metal complex containing **2**$^{\bullet}$ has been found to undergo chalcogen abstraction [40].

2.6. Related selenium derivatives

The methodology developed by Huestis [10c] for the synthesis of non-chlorinated Herz compounds (Section 2.1.2) has been adapted [41] to allow the preparation of all the different selenium-for-sulphur substituted derivatives, as outlined in Scheme 7. Oakley recently reported that the 1-thia-2-selenazolylium salts could also be formed by condensation of $SeCl_4$ with *ortho*-aminothiophenols [19], although chlorination of the aromatic ring also occurred in this case.

Electrochemical studies indicate that the redox behaviours of the different derivatives are dominated by the nature of the chalcogen at position 2, with the selenium containing cations more readily reduced (by more than 0.1 V) than the sulphur analogs [32]. The difference for this behaviour has been ascribed [32] to the extent of delocalisation of the positive charge away from the heterocycle, onto the fused aromatic ring; Theoretical calculations indicate that replacement of S by Se, especially at position 2, leads to a substantial increase in the extent of charge delocalisation [32]. UV–vis studies indicate that replacement of S by Se leads to a deepening of the colour and intensity of the salts, consistent with the delocalisation of charge onto the aromatic ring [41]. UV–vis and electrochemical data for the different selenium-for-sulphur substituted derivatives are compiled in Table 4.

Table 4
Half-wave reduction potentials (referenced to SSCE) and absorption maxima for a series of selenium-substituted 1,2,3-dithiazolylium salts[a]

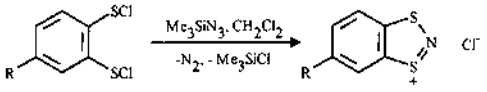
Compound	$E^{ox}_{1/2}$ (V)	λ_{max} (nm) (log ε)	Compound	$E^{ox}_{1/2}$ (V)	λ_{max} (nm) (log ε)
	+0.26	344 (4.15) 423 (3.28)		+0.15	445 (3.59)
	+0.25	361 (3.98) 455 (3.28)		+0.15	400 (4.02) 470 (3.54)

[a] Data from Ref. [42].

3. Fused 1,3,2-dithiazolylium salts and 1,3,2-dithiazolyls

3.1. Syntheses of 1,3,2-dithiazolylium salts

The primary route to benzo-fused 1,3,2-dithiazolylium salts derives from the methodology described by Wölmershauser and co-workers [42]. This approach involves the reaction of *ortho*-bis(sulphenyl chlorides) with trimethylsilyl azide, the chloride salt precipitating from the CH_2Cl_2 solution (Eq. 5). The excellent yields of analytically pure material contrast with the Herz reaction (Section 2.1) in which the isomeric salts are typically contaminated with side-products and require careful purification. Whilst this approach works for simple benzo-fused derivatives [42,43], variations on this synthetic methodology must be applied for other derivatives [44–47], including bis and tris(1,3,2-dithiazolylium) salts [42,46]. In all cases, the primary restriction to this synthetic methodology is the availability of the appropriate 1,2-dithiol precursor. A number of routes are known to 1,2-dithiols and those starting from the chloro-substituents are particularly attractive since they lead to a diverse range of accessible materials [48]. The dithiols, themselves can be readily converted to the sulphenyl chlorides via direct chlorination with Cl_2 or SO_2Cl_2. For aromatics which are susceptible to chlorination, the milder oxidising agent, $PhICl_2$ can be used [45].

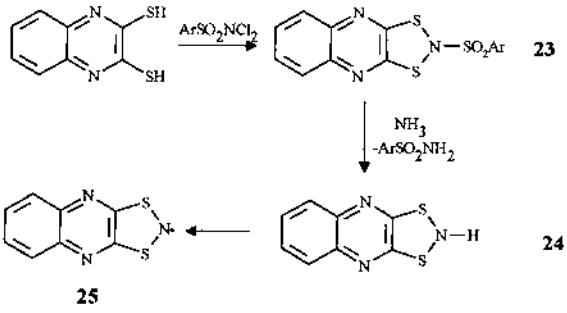


(5)

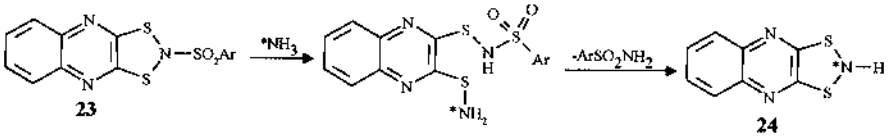
[20]Cl (R=H), **[21]**Cl (R=Me)

In addition, the N-substituted covalently-bonded derivatives can be prepared via condensation of the dithiol or the corresponding silver or titanocene sulphide with dichlorosulphonamides [45,47]. Two sulphonamide derivatives have been character ised by X-ray crystallography; the non-fused derivative, NC·CSN(Ts)SC·CN (**22**)

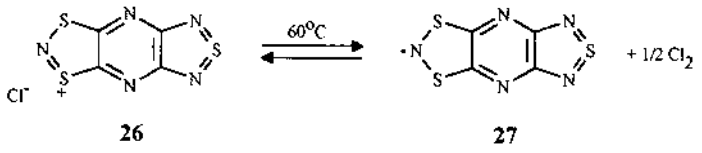
[47] and the fused derivative, **23** [45]. Both structures show the *N*-tosyl group folding out of the molecular plane with a long NS bond between the ring N and the tosylate S atom (1.733 Å for **22**). These *N*-tosylate derivatives can be used as precursors to the 1,3,2-dithiazolyl radicals [42,45,47]. The action of heat is sufficient in some circumstances to generate the corresponding dithiazolyl radical [42,47]. Alternatively, treatment of the sulphonamide **23** with ammonia yields the corresponding amine, **24**, [45] (Eq. 6). Work with ^{15}N-labelled ammonia [47] indicated that the intermediate imide was formed via nucleophilic attack of the heterocyclic S with incorporation of the ^{15}N into the heterocyclic ring and extrusion of the former heterocyclic ring-N atom (Eq. 7). Further treatment of **24** with ammonia is reported to yields the dithiazolyl radical, **25**• (Section 3.2) [47], although more recent work [45] indicates that the oxidation of **24** is facile and can by promoted by molecular oxygen or mild oxidising agent such as $K_3[Fe(CN)_6]$.



(6, 7)



The 1,3,2-dithiazolylium salts can also be prepared by oxidation of the corresponding 1,3,2- dithiadiazolyl radical by, for example, halogens such as Cl_2, Br_2 or I_2 or Lewis acids such as $SbCl_5$ [45,47,49]. Some of the 1,3,2-dithiazolylium salts (e.g. **26**) exhibit a tendency to disproportionate to the corresponding 1,3,2-dithiazolyl radical and elemental halogen [45] (Eq. 8) in an analogous fashion to some of the 1,2,3-dithiazolylium salts (Section 2.4.1). Their ability to undergo disproportionation is related to the ease of reduction of the dithiazolylium cation (Section 3.3.2).

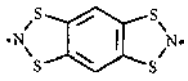


(8)

3.2. Synthesis of 1,3,2-dithiazolyl radicals

In contrast to the isomeric 1,2,3-dithiazolyl radicals which have only been characterised by solution EPR studies, a number of fused-1,3,2-dithiazolyl radicals have been isolated and fully-characterised in the solid state. There are two routes to the 1,3,2-dithiazolyl radicals; either reduction of the corresponding 1,3,2-dithiazolylium cations with reducing agents such as silver powder [42], triphenyl antimony [42,44], sodium dithionite [42]; or via oxidation of the dithiazolyl-imine (such as **24**) using mild oxidising agents such as molecular O_2 or $K_3[Fe(CN)_6]$ [45].

Oakley and other workers have noted [46,50][2] that the reducing conditions must be carefully monitored; for example reduction of benzo-bis(1,2,3-dithiazolylium) dichloride with Ag or Zn yields a black solid and a dark blue solution from which only small quantities of impure diradical, **28••**, could be isolated [46].



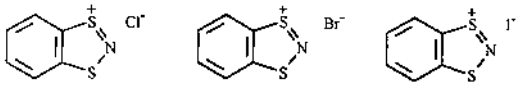
28••

3.3. Physical studies of 1,3,2-dithiazolyl radicals

Unlike the Herz radicals, which have only been characterised in solution (except the quinoidal, diamagnetic **19**, Section 2.3), a number of 1,3,2-dithiazolyl salts have been isolated and characterised in the solid state. These structures are discussed in Section 3.3.1, their EPR spectra are described in Section 3.3.3 and a theoretical analysis of the unpaired spin-density distributions made in Section 3.4. Their electronic properties are described in Section 4.

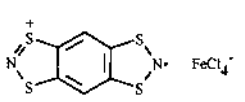
3.3.1. Single crystal X-ray structure determinations

A number of 1,3,2-dithiazolyl radicals have been characterised in the solid state, and the heterocyclic bond lengths and angles are tabulated in Table 5. Table 5 also includes data on some corresponding 1,3,2-dithiazolylium salts for comparison. Within the series of benzo-1,3,2-dithiazolylium salts, **29**–**31** [43,49,51], there are no marked changes in geometry, indicative of completely charge-separated ions. This contrasts with the dithiadiazolylium cations $\mathbf{2}^+$ [1].

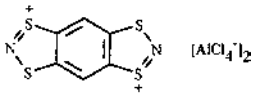


29 **30** **31**

[2] Reduction of tolyl dithiazolylium chloride with Zn/Cu couple yielded a black insoluble product under a pale blue solution from which no pure tolyl-1,3,2-dithiazolyl could be obtained by vacuum sublimation. In contrast, reduction with Ag powder afforded modest yields of tolyl-1,3,2-dithiazolyl which were isolated by careful sublimation (10^{-2} Torr, 50–55°C).



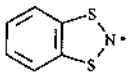
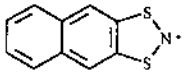
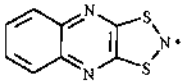
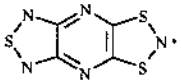
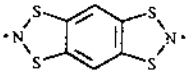
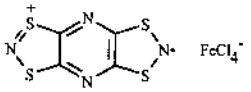
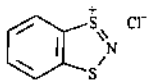
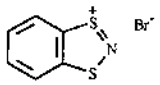
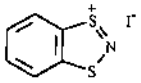
32



33

In comparison, there are some notable changes in geometric features on changing the oxidation state; addition of an electron into the antibonding orbital of the 1,3,2-dithiazolyl ring leads to a lengthening of the C–S and S–N distances (Section 3.4). The bond length changes can also be observed in the fused aromatic substituents and this is clear evidence for extensive delocalisation of the unpaired spin-density [42]. Notably the radical cation, $\mathbf{32}^{+\bullet}$, in which the one electron is shared between two rings is intermediate in nature between the dication, $\mathbf{33}^{2+}$, and diradical, **28**•• [46].

Table 5
Selected bond lengths (Å) and angles (°) for some 1,3,2-dithiazolylium salts and 1,3,2-dithiazolyl radicals

Compound	C–S	S–N	C–C	π*–π*	Ref
	1.741(2) 1.746(2)	1.644(2) 1.648(2)	1.394(3)	3.18	43
	1.748	1.645			44
	1.736	1.649		3.71	44
	1.728(2)	1.636(3)	1.448(2)	3.48	45
	1.729(2) 1.736(2)	1.647(2) 1.648(2)	1.392(2) 1.405(3)	3.49	46
	1.708(7) 1.714(7) 1.711(7) 1.720(7)	1.629(6) 1.618(6) 1.610(6) 1.617(6)	1.435(9) 1.421(9)	3.35	46
	1.708(2)	1.598(2)	1.411(5)	—	43
	1.704(5) 1.700(5)	1.475(10) 1.731(10)	1.395	— —	51
	1.722(6) 1.720(6)	1.584(5) 1.617(6)	1.386(9)	— —	49

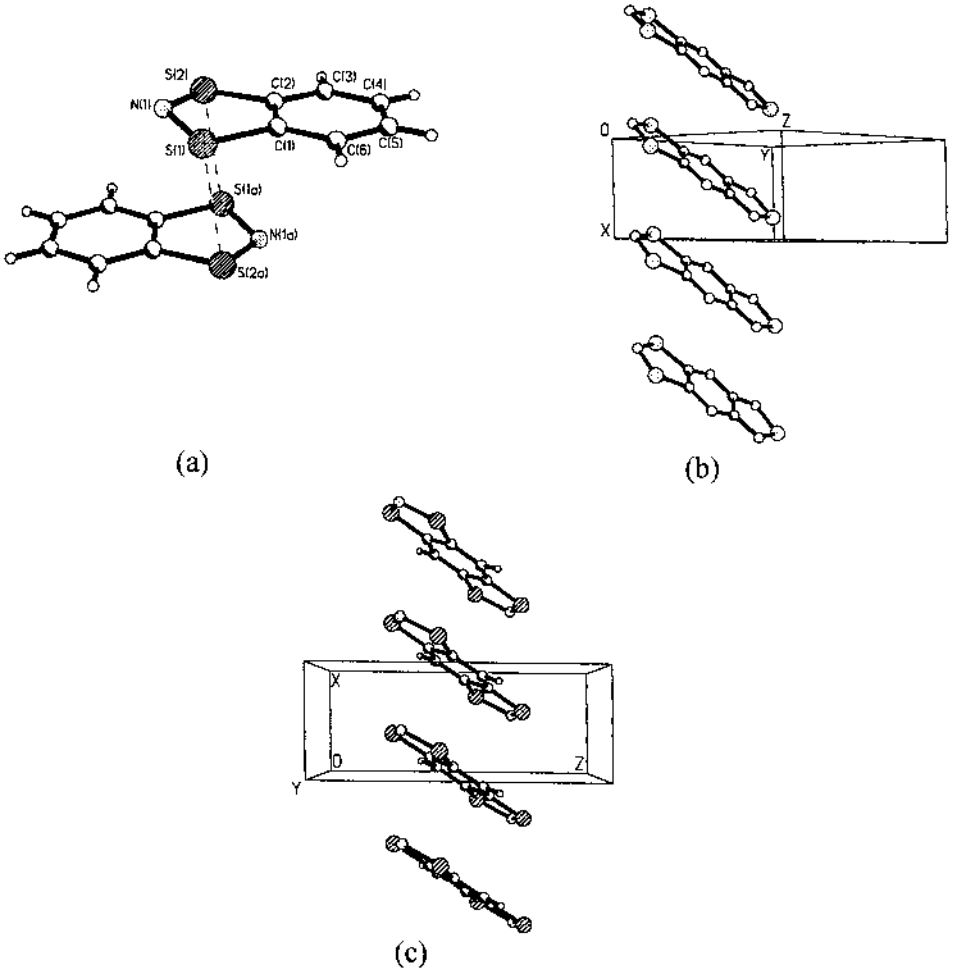
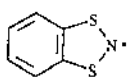


Fig. 4. Solid state structures of (a) dimeric **34**$^{\bullet}$, (b) monomeric **27**$^{\bullet}$ and (c) the diradical **28**$^{\bullet\bullet}$.

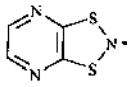
Whilst the structures of 1,3,2-dithiazolyl radicals themselves are similar in terms of their intramolecular geometries, a much wider variation in their *inter*-molecular interactions is found. Packing diagrams for **34**$^{\bullet}$, **27**$^{\bullet}$ and **28**$^{\bullet\bullet}$ are shown in Fig. 4. Typically derivatives of **1**$^{+\bullet}$, **2**$^{\bullet}$ and **3**$^{\bullet}$ associate in the solid state through a π^*–π^* interaction in the range 2.9–3.1 Å [1]. The strength of this π^*–π^* interaction is considerable and has been estimated (from EPR studies) at 45 kJ mol^{-1} for **1**$^{+\bullet}$, 37 kJ mol^{-1} [27] for **2**$^{\bullet}$ (R = Ph and R = CF_3) [7,27], and 19 kJ mol^{-1} for **3**$^{\bullet}$ (R = Ph)[7]. The dimerisation enthalpy is substituent dependent (cf. **2**$^{\bullet}$, R = ^{t}Bu where $\Delta H_{dim} = -31$ kJ mol^{-1} [7]). In the case of both the fused benzo-1,3,2-dithiazolyl radical, and the non-fused bis(trifluoromethyl)-1,3,2-dithiazolyl radical, the dimerisation energy has been estimated [43] to be approximately zero (see Section

2.2.2). As a consequence, there is a much smaller tendency for these radicals to associate in the solid state.

In the case of the benzo- and pyrazine-derivatives, **34**• and **35**•, association is observed, although the association modes for **34**• and **35**• are different; the benzo-derivative associating in a *trans*-antarafacial manner (S···S 3.175(1) Å)[43], whilst the pyrazine derivative forms stacks of cofacial dimers[42]. The non-fused derivative, **5**• (R = CN) also adopts a *cis*-oid dimeric configuration [47] with a S···S separation of 3.14 Å. Similar *cis*- and *trans*- conformers have also been observed in the dithiadiazolyl derivatives **2**• [1]. Notably the intermolecular contacts are a little longer than those observed for derivatives of $\mathbf{1}^{+\bullet}$ and **2**• (typically 2.9–3.1 Å [1]) and this is consistent with the weaker π*–π* interaction caused by more extensive π-delocalisation.

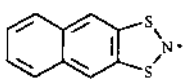


34

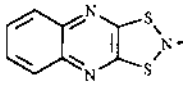


35

Here the similarity between 1,3,2-dithiazolyl derivatives and the isoelectronic radicals, $\mathbf{1}^{+\bullet}$, **2**• and **3**• ends. Almost without exception, derivatives of $\mathbf{1}^{+\bullet}$, **2**• and **3**• are dimeric in the solid state with intermolecular S···S separations around 2.9–3.1 Å, although several derivatives of **2**• have recently been found to retain some [52] or all [53] of their paramagnetic nature in the solid state. In comparison many 1,3,2-dithiadiazolyl derivatives exhibit much longer out-of-plane π–π interactions, ranging from 3.1 to 3.7 Å; The radical cation derivative, $\mathbf{32}^{+\bullet}$, crystallises as loosely associated dimers with a mean interplane separation of 3.35 Å [46]. The related diradical, **28**••, forms a regular slipped π-stack structure, with a longer π*–π* interaction down the stacking direction (3.49 Å)[46]. The more conjugated derivatives, **36**• and **37**•, in which there is increased delocalisation of the unpaired spin density, compared to dimeric **34**• and **35**•, do not dimerise in the solid state [44]. In **36**• the closest intermolecular contact is 3.602 Å, although variable temperature magnetic studies indicate [44] that a structural phase transition may occur around 200 K, in an analogous fashion to **27**• (see below). For **37**• the molecules pack with a slipped π-stack structure with closest intermolecular contact of a π*–π* type at 3.7105(8) Å.



36•



37•

The structure of **27**• appears complex. At room temperature the radicals are packed in a slipped π-stack fashion with a regular separation, but at 150 K, the structure is composed of dimers with the closest inter-annular contacts at 3.401(5) Å at the thiadiazolyl ring and 3.48(5) Å at the dithiazolyl ring. This type of Peierls distortion

is not uncommon [3], although, in this case, it does not lead to complete quenching of the paramagnetism, with approximately 0.1 unpaired spin per molecule below 50 K and about 0.4 unpaired spins at 200 K, rising to 0.6 at 300 K (see Section 4.2). The greater range of intermolecular contacts leads to a wide variation in electronic properties (Section 4).

3.3.2. Electrochemical studies on 1,3,2-dithiazolyl radicals

Electrochemical studies on a number of 1,3,2-dithiazolyl radicals have been undertaken [45,46] and the data is summarised in Table 6. Whilst **34•**, **36•** and the first E_{ox} of **28•** all exhibit similar $E_{1/2}$ values, **27•**, **37•** and the second E_{ox} of **28•** are substantially higher, indicative that the latter compounds are substantially resistant to oxidation. This is in agreement with experimental studies (Section 3.1) which indicate that **27•** readily disproportionates on heating to liberate the radical. The ease with which these radicals are formed (i.e. their ability to act as electron donors) is substantially greater than the dithiadiazolyls **2•** and **3•** and comparable to the 1,2,3-dithiazolyls (Section 2.4.1)[43].

3.3.3. EPR studies

A number of EPR studies have been undertaken on the 1,3,2-dithiazolyl radicals [39,41,42,47]; the most comprehensive being the report by Sutcliffe and co-workers [41] on three different dithiazolyl radicals. Compilations of reported isotropic and anisotropic EPR data are given in Tables 7 and 8, respectively. The g-values range from 2.006 to 2.007. The spectra are normally observed as 1:1:1 triplets (due to coupling to the unique N atom of the dithiazolyl ring) with smaller coupling constants to other elements in the fused substituent. The coupling constants for the N atoms of the dithiazolyl ring range from 9.5 to 11 G, depending on the extent of delocalisation onto the fused aromatic ring. The spectra reveal a general decrease in a_N with the increasing electron-withdrawing power of the fused aromatic and a concomitant decrease in the g-tensor. The exception being the fused thiadiazole/

Table 6
Oxidation potentials for a series of 1,3,2-dithiazolyl radicals and referenced to SSCE

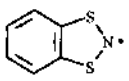
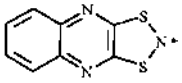
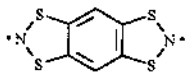
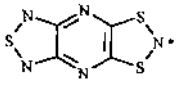
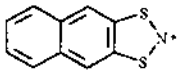
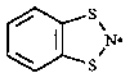
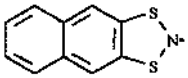
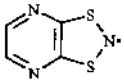
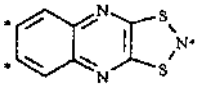
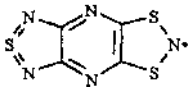
Compound	$E^{ox}_{1/2}$ (V)	Ref.	Compound	$E^{ox}_{1/2}$ (V)	Ref.
	+0.15	46		+0.62	45
	+0.16, +0.74	46		+1.00	45
	+0.27	45			

Table 7
Isotropic EPR parameters for some fused 1,3,2-dithiazolyl radicals[a]

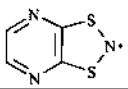
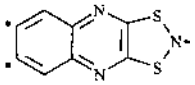
Compound	g	a_N ($a_{N\text{-}15}$)	a_S	a_H	$a_{N'}$	Ref.
	2.0069	11.01				44
	2.0067	11.06				44
	2.00605	(− 15.7)	4.01	1.308	0.654	44
	2.00651	10.89		0.636 ∗0.251	1.272	44
	2.0065 2.0071	10.89 (15.32) 9.50		0.645 ∗0.227 2.07	1.288	47 45

[a] Hyperfine coupling constants are quoted in Gauss.

dithiazolyl derivative **27•**, which exhibits a larger g-value, arising out of extensive delocalisation onto the second heterocyclic ring (notably large $a_{N'}$ hyperfine interaction) with additional spin-orbit coupling from S.

An analysis of the anisotropic EPR data obtained from frozen solutions indicate a large degree of anisotropy in the EPR spectrum, consistent with the localisation of the unpaired spin-density in a π* orbital, with a large N-hyperfine interaction

Table 8
Anisotropic EPR data for **35** and **37**. * indicates N^{15} coupling constants, N′ refers to the N atoms of the pyrazine and quinoxaline rings[a]

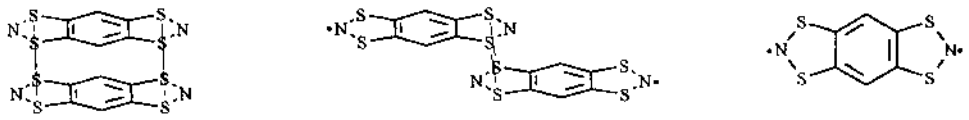
		
g_{xx}	2.0022	2.0014
g_{yy}	2.0060	2.0058
g_{zz}	2.0106	2.0114
$a_N + A_{xx}(N)$	−42.14*	28.81
$a_N + A_{yy}(N)$	−3.90*	1.85
$a_N + A_{zz}(N)$	−1.80*	1.85
$a_{N'} + A_{xx}(N')$	0	3.85
$a_{N'} + A_{yy}(N')$	0	0.14
$a_{N'} + A_{zz}(N')$	0	0.14

[a] Data taken from Ref. [44].

associated with the x-direction (perpendicular to the ring plane). Analysis of the EPR spectrum of **34**$^{\bullet}$ [46] indicates that 54% of the radical electron density resides in the N p-orbital, with 2% in the N s-orbital. In addition (from McConnell's relationship between a_H and the spin-density on the neighbouring C), the spin-density on each of the C–H carbon atoms of the benzo-ring is ca. 2%, consistent with delocalisation of the spin density away from the heterocyclic ring. Thus the remaining two C atoms and two sulphur atoms must comprise the remaining 46% of the spin density [46].

The benzo(bis-1,3,2-dithiazolyl) radical, **28**$^{\bullet\bullet}$ and the related radical cation, **32**$^{+\bullet}$ have received considerable attention and a number of attempts have been made to rationalise their EPR spectra [46]. The EPR spectrum of $32^{+\bullet}$ [46a–c] appears well defined with the spectrum comprising a quintet of triplets consistent with delocalisation of the unpaired electron over the two heterocyclic rings. The N-hyperfine coupling ($a_N = 6.4$ G) is approximately half that observed for a typical dithiazolyl radical, consistent with this interpretation. The additional triplet structure arises from hyperfine interactions to the benzo-bridged protons.

In contrast to **32**$^{+\bullet}$, the diradical **28**$^{\bullet\bullet}$ has been more controversial. Initial reports by Sutcliffe [46a] indicated that the ESR spectrum of **28**$^{\bullet\bullet}$ comprised a triplet of triplets with 'weaker lines varying in intensity ….. sometimes observed'. A subsequent ESR study by Wudl and co-workers [46c] confirmed this observation. The data were interpreted as the ESR spectrum of a single, isolated radical ion giving rise to the triplet of triplets (*tot*) spectrum (coupling to one N, $a_N = 11.2$ G, and two H); the spectrum arising from dimers of higher oligomers in which the radical centres are essentially non-interacting, **38**$^{\bullet\bullet}$, due to the large separation which renders the exchange interaction negligible. A further analysis of the line-broadening of the powder patterns in frozen solutions indicated a minimal distance of almost 10 Å between magnetic point dipoles, consistent with dimers, e.g. **38**$^{\bullet\bullet}$ and higher oligomers in solution [46c]. In addition integration of the ESR signal indicated only ca. 1% of the anticipated intensity, consistent with spin-paired dimers in solution, **39** (or alternatively a large percentage with a strongly antiferromagnetically coupled $S = 0$, ground state) [46c]. The weaker lines centred between the *tot* signals form part of a quintet structure ($a_N = 5.6$ G) with the remaining three resonances masked by the dominant *tot* pattern. These lines varied in intensity between 2 and 7% of the intensity of the main *tot* pattern and are associated with the $S = 1$ triplet state associated with the exchange interaction between radical spins at the ends of oligomers [46c]. More recently, further studies by Oakley have indicated that the ESR spectrum of **28**$^{\bullet\bullet}$ is both solvent and sample dependent [46e]. Whilst they associated the *tot* spectrum to partly associated species in solution (e.g. **38**$^{\bullet\bullet}$) in which the spins are non-interacting, they assign the bands of weaker intensity to isolated **28**$^{\bullet\bullet}$ on the basis of solvent effects in which the intramolecular exchange interactions (J_{ex}) are much larger than the N-hyperfine interaction, a_N [46e]. By changing the solvent the degree of association is varied and this produces differing intensities for the *tot* and exchange bands [46c].



Closed shell | Non-interacting | Weakly interacting

39 | **38**•• | **28**••

3.4. Theoretical studies on 1,3,2-dithiazolyl radicals

Molecular orbital analysis of the benzo-1,3,2-dithiazolyl, **34**• has been carried out at the STO-3G, STO-3G* and CNDO/2 levels [43] and using the Extended Hückel method [46c] and all gave similar results. The optimised geometry for **34**• is

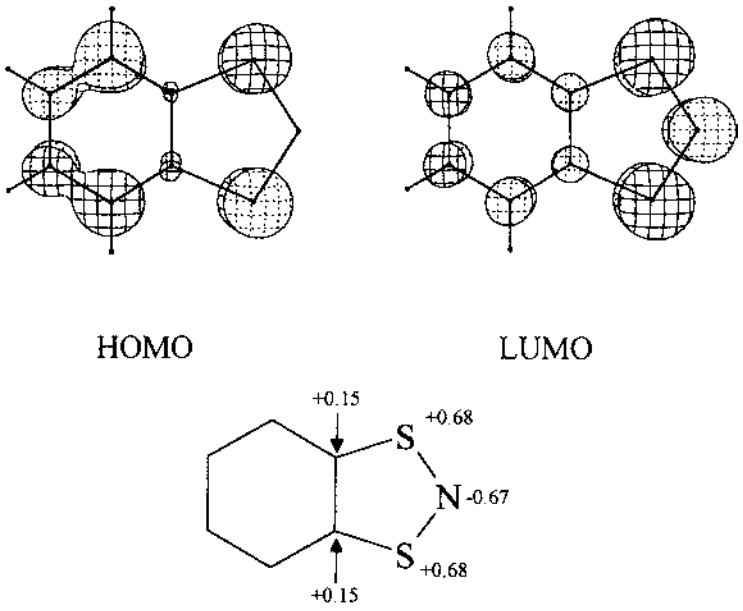


Fig. 5. Frontier molecular orbitals and charge distributions for the benzo-1,3,2-dithiazolylium cation, determined from EHMO calculations [38,39].

essentially planar, with bond lengths and angles in good agreement with observed data. The SOMO of **34**• is a π* orbital, antibonding with respect to S–N and C–S but bonding with respect to C–C [43]. This accounts for the observed increase in S–N and C–S bond lengths on reduction of the dithiazolylium cations to dithiazolyl radicals. In addition, there is considerable mixing of the π* manifold on the dithiazolyl ring with the fused benzene ring [43]. This leads to a notable delocalisation of spin-density away from the heterocyclic ring and is consistent with the observed ^{1}H hyperfine coupling constants (see Section 3.3.3). The frontier orbitals and charge distribution for **20**• are shown in Fig. 5.

Additional studies on the dimerisation process [43] have shown that, in contrast to monomeric **34**•, dimeric $(\mathbf{34})_2$ exhibits an energy minimum when the N atom of the dithiazolyl ring is bent slightly out of the ring plane (ca. 9°), consistent with the structural data (12°). The low level of the calculations indicate that this data should be considered qualitative rather than quantitative [43]. However, the shallowness of the potential energy curve for this deformation, indicate that deformation is facile and an analysis of temperature dependent ESR spectra of acyclic dithiazolyl radicals indicates an out-of-plane bending vibration for the N atom [54]. Addition of a further electron, yielding the hypothetical dithiazolyide anion leads to a more pronounced deviation from planarity with a bending up to 26° [43].

4. A perspective

The recent impetus to study these fused 1,3,2-dithiazolyl radicals stems from the potential use of molecular sulphur–nitrogen radicals in materials applications, in conducting and magnetic devices. Regular stacks of closely-spaced π-radicals are predicted to give rise to conducting materials [55] whilst magnetic exchange interactions between radicals could lead to cooperative magnetic effects such as antiferromagnetism or ferromagnetism [4].

4.1. Conducting dithiazolyl radicals

Overlap of the singly-occupied molecular orbitals of neutral π-radicals in an infinite, regularly spaced stack was proposed by Haddon [50] to give rise to a band structure in which the energy gap between the bonding and antibonding orbitals is extremely small. Since each radical provides one electron, all the bonding orbitals are occupied but, since the energy gap (band gap) to the antibonding orbitals is extremely small, electrons can be readily promoted to the antibonding orbitals and the compound becomes conducting. However, if the inter-molecular spacing is asymmetric i.e. long and short contacts between radicals (such as is commonly encountered because of dimerisation), then this will lead to a modification of the band structure (a Peierls distortion) and the band gap becomes larger. This potential energy barrier to conduction means that the con-

ductivity is reduced [3]. However, doping the sample with acceptors such as I_2, TCNQ or TCNE, places some positive charge on the array of radicals, lowering the orbital energies and reducing the band gap and enhancing conductivity [3].

At a molecular level, good conductivity of electrons requires a small energy barrier to transfer an electron form one molecule to the next. Consequently the energy barrier to electron transfer depends on the electron affinity (EA) of the molecule and its ionisation potential [45]. The disproprotionation energy (IP − EA) provides an estimate of the Coulombic barrier to electron transfer in a neutral radical conductor [45]. Extensive studies by Oakley have concentrated on the use of dithiadiazolyl radicals, **2**$^{\bullet}$, and the isoelectronic diselenadiazolyl radicals as the building blocks for molecular conductors [3,56]. Whilst the electronic properties for **2**$^{\bullet}$ (and **3**$^{\bullet}$) are remarkably insensitive to substituent effects, the efforts in this direction have been successful with a number of iodine-doped derivatives producing conductivities (up to 10^2 S cm^{-1}) reminiscent of the poorer conducting metals [56]. In contrast, the ability to tune the electron affinity and the ionisation potential of the dithiazolyl radicals provides the potential to carefully tune the molecular electronics to provide superior conductivities to other sulphur–nitrogen based materials, including $(SN)_x$ [57].

To date, conductivity measurements have been made on a number of 1,2,3-dithiazolyl radicals and their charge-transfer salts. In a number of cases, e.g. **36**$^{\bullet}$, the molecular packing precludes the formation of a conduction band [44] and room temperature conductivities are typically in the range of 10^{-6} S cm^{-1}. In other cases, such as **37**$^{\bullet}$, regular stacks are observed , but the large intermolecular separation (ca. 3.7 Å) inhibits effective orbital overlap and poor conductivities are observed [44]. The diradical, **28**, is a semiconductor with a band gap of 0.22 eV and a conductivity reaching 10^{-5} S cm^{-1} at 400 K [46]. Partial removal of charge from the band structure by doping, e.g. by forming charge-transfer salts with acceptors such as TCNQ [42,46], leads to enhanced room temperature pressed pellet conductivities ranging from 10^{-4} S cm^{-1} for **28**·TCNQ [46] up to 1 S cm^{-1} for **34**·TCNQ [42].

4.2. Magnetic properties of dithiazolyl radicals

Sulfur–nitrogen radicals of this family, i.e. **1**$^{+\bullet}$, **2**$^{\bullet}$–**5**$^{\bullet}$, have the potential to exhibit unusual magnetic properties and, for example, the dithiadiazolyl radical, **2**$^{\bullet}$ (R = *p*-NCC_6F_4) becomes weakly ferromagnetic at 36 K [53]. (In a weak ferromagnet, spins align essentially antiparallel throughout the solid, but are canted in one direction to give rise to a spontaneous magnetic moment, i.e. the sample exhibits a magnetic memory effect.) In order for these radicals to exhibit any form of magnetic order, they must retain their paramagnetic nature in the solid state, i.e. the dimerisation process must be inhibited. Whilst the dimerisation energies for **1**$^{+\bullet}$, **2**$^{\bullet}$ and **3**$^{\bullet}$ are of the order of 45, 35 and 20 kJ mol^{-1} [7,27], the solution dimerisation energies for the 1,3,2-dithiazolyl radicals are ca. 0 kJ mol^{-1} [43]. Consequently these dithiazolyl radicals would appear excellent candidates for the design of molecular magnets. Whilst the high oxidation potentials, associated with

many of these electronegative sulphur–nitrogen rings, may hinder electron transfer and transport properties, they may benefit the design of molecular magnetic materials in which electron localisation may be beneficial. Because these radicals are sterically unencumbered, they may approach each other closely and, provided the direct bonding interactions can be avoided, the close proximity of the radical centres can lead to strong, magnetic exchange interactions between molecules [4]. The strength of this exchange interaction is influential in determining the magnetic ordering temperature. The majority of organic radicals which order magnetically (and many do not), do so below liquid helium temperature [58]. The observation of magnetic order in *p*-NC·C_6F_4CNSSN at 36 K is indicative of the strength of this exchange interaction [53]. A number of other sulphur–nitrogen radicals which do not undergo long range magnetic order, also exhibit maxima in their susceptibilities at high temperatures (>4 K) indicative of strong short range order [44,45,59]. The evidence for strong, local antiferromagnetic coupling is also evidenced by the value of the Weiss constant, θ (value of the intercept (in K) in a plot of $1/\chi$ vs. T extrapolated from the linear region at high temperature) [4]. Large values of $|\theta|$ are indicative of strong exchange interactions, ferromagnetic for positive θ and antiferromagnetic for negative θ.

The magnetic behaviour of these dithiazolyl radicals is extremely varied and highly dependent on solid state structure. Those compounds which exhibit close association of the radical centres, such as **34•**, can be considered as spin-paired dimers and are essentially diamagnetic, although a small Curie tail may be observed in the susceptibility at low temperature due to small quantities (typically $<1\%$) of monomeric impurity arising at lattice defect sites [43]. At more elevated temperatures close to its melting point, the number of spin carriers increases markedly as the spin-paired dimers begin to dissociate.

For structures which exhibit (slipped) π-stack motifs, the number of free spins is significantly lower than expected. Even when the S···S separation increases up to 3.49 Å (for **28••**) only 6% of unpaired spins are observed at 400 K [43]. For **37•**, the S···S separation is larger at 3.71 Å and the fraction of Curie spins rises from zero at 120 K to 30% at room temperature [41,42]. The 1,3,2-dithiazolyl radical, **27•**, exhibits unusual magnetic properties in that it exhibits two clear regions; up to 50 and above 200 K [45]; between 50 and 150 K thermal hysteresis is observed and the susceptibility depends on the sample history. The origin of the thermal hysteresis is attributed to a kinetic effect associated with a structural phase transition which has been confirmed by single crystal X-ray diffraction experiments [45]. In the low temperature range discrete dimers are observed with an intermolecular S···S contact of 3.48 Å and the fraction of Curie spins is ca. 10%. Above 200 K, a regular slipped π-stack structure is observed with the fraction of spin carriers rising from 40% at 200 K to 60% at 300 K. This compound is reported to possess an antiferromagnetic ground state [45]. In contrast to the π-stacked structures, the magnetic properties of **36•** (intermolecular separation along the stacking direction is 3.7Å) more closely resembles that of a pure paramagnet, with 80% of Curie spins observed at room

temperature [44]. In the high temperature region, the Weiss constant ($\theta = -1$ K) is indicative of weak antiferromagnetic exchange [44]. This compound also undergoes structural transitions; the first at 200 K to a more strongly antiferromagnetically coupled state ($\theta = -11$ K) with only 50% of unpaired spins, before undergoing a further transition at ca. 20 K [44].

The electrochemical data presented on both 1,2,3-dithiazolyl and 1,3,2-dithiazolyl radicals indicate a much greater diversity of physical properties than the corre-sponding dithiadiazolyl radicals **2**• and **3**•. This arises as a result of the more extensive delocalisation possible in **4**• and **5**•, which is observed through the superfine structure in their EPR spectrum. The ability to modulate the electronic properties of the heterocyclic ring through fine tuning of the substituents is key to the success of using these radicals for electronic device applications. Whilst the dithiazolyl radicals, **2**• and **3**•, typically exhibit only minor variation in oxidation potential (± 0.1 V), electrochemical studies indicate that both **3**• and **4**• are much more powerful electron donors. Therefore the dithiazolyl radicals should exhibit much lower barriers to charge transport and have the potential to exhibit superior conductivities to **2**• and **3**•. In addition, the more enhanced delocalisation of the unpaired spin-density leads to a weakening of the dimerisation energy of these radicals and they are therefore more likely to be monomeric in the solid state and could provide convenient building blocks for molecular magnetic materials. The majority of derivatives of **2**•, which have been much more extensively studied than **5**•, are spin-paired and diamagnetic in the solid state. In contrast, the few dithiazolyl structures reported so far indicate a rich magnetochemistry waiting to be discovered. The strength of the short range magnetic interactions promise to give rise to new materials with high magnetic ordering temperatures.

References

[1] J.M. Rawson, A.J. Banister, I. Lavender, Adv. Heterocycl. Chem. 62 (1995) 137.
[2] E. Demarcay, Comp. Rend. 91 (1880) 854.
[3] A.W. Cordes, R.C. Haddon, R.T. Oakley, Adv. Mater. 6 (1994) 798.
[4] (a) G. Antorrena, N. Bricklebank, F. Palacio, J.M. Rawson, J.N.B. Smith, Phos. Sulf. Sil. 133 (1997) 124–125. (b) J.M. Rawson, J.N.B. Smith, F. Palacio, G. Antorrena, J. Mater. Chem. (1999), accepted for publication.
[5] A.J. Banister, I. May, J.M. Rawson, J.N.B. Smith, J. Organomet. Chem. 550 (1998) 241.
[6] S. Parsons, J. Passmore, Acc. Chem. Res. (1994) 101.
[7] (a) N. Burford, J. Passmore, M.J. Schriver, J. Chem. Soc. Chem. Commun. (1986) 140. (b) W.V.F. Brooks, N. Burford, J. Passmore, M.J. Schriver, L.H. Sutcliffe, J. Chem. Soc. Chem. Commun. (1987) 69. (c) J. Passmore, X. Sun, Inorg. Chem. 35 (1996) 1313.
[8] L.I. Khmelnitski, O.A. Rakitin, in: A.R. Katritsky, C.W. Rees, E.F.V. Scriven (Eds.), Comp. Het. Chem., vol. II, 4, Pergamon, Oxford, 1996, p. 409. (b) L.I. Khmelnitski, O.A. Rakitin, in: A.R. Katritsky, C.W. Rees, E.F.V. Scriven (Eds.), Comp. Het. Chem., vol. II, 6, Pergamon, Oxford, 1996, p. 916. (c) L.I. Khmelnitski, O.A. Rakitin, in: A.R. Katritsky, C.W. Rees, E.F.V. Scriven (Eds.), Comp. Het. Chem., vol. II, 6, Pergamon, Oxford, 1996, p. 433.
[9] (a) R. Herz, Chem. Zent. 4 (1922) 948. (b) Cassella, Co. German Patent 360,690 (Oct. 6, 1922).

[10] (a) A.T. Blomquist, L.I. Diuguid, J. Org. Chem. 12 (1947) 720. (b) W.K. Warburton, Chem. Rev. 57 (1957) 1011. (c) L.D. Huestis, M.L. Walsh, N. Hahn, J. Org. Chem. 30 (1965) 2763. (d) P. Hope, L.A. Wiles, J. Chem. Soc. C (1967) 1642.
[11] R. Mayer, Phos. Sulf. 23 (1985) 277.
[12] (a) Y. Inagaki, R. Okazaki, N. Inamoto, Tetrahedron Lett. 51 (1975) 4575. (b) Y. Inagaki, R. Okazaki, N. Inamoto, Bull. Chem. Soc. Jpn. 52 (1979) 1998.
[13] Y. Inagaki, R. Okazaki, N. Inamoto, K. Yamada, H. Kawazura, Bull. Chem. Soc. Jpn. 52 (1979) 2008.
[14] (a) F. Iwasaki, Acta Crystallogr. Sect. B 35 (1979) 2099. (b) F. Iwaski, Acta Crystallogr. Sect. B 36 (1980) 1466.
[15] D.H.R. Barton, M.J. Robson, J. Chem. Soc. Perkin Trans. I (1974) 1245.
[16] Y. Inagaki, R. Okazaki, N. Inamoto, Bull. Chem. Soc. Jpn. 52 (1979) 2002.
[17] J.W. Bats, H. Fuess, K.L. Weber, H.W. Roesky, Chem. Ber. 116 (1983) 1751.
[18] L. Huestis, I. Emery, E. Steffenson, J. Het. Chem. 3 (1966) 518.
[19] T.M. Barclay, A.W. Cordes, J.D. Goddard, R.C. Mawhinney, R.T. Oakley, K.E. Preuss, R.W. Reed, J. Am. Chem. Soc. 119 (1997) 12136.
[20] (a) R. Mayer, S. Bleisch, G. Domschke, A. Bartl, Z. Chem. 21 (1981) 146. (b) R. Mayer, G. Domschke, S. Bleisch, A. Bartl, Z. Chem. 21 (1981) 264. (c) R. Mayer, G. Domschke, S. Bleisch, A. Bartl, Z. Chem. 21, (1981) 325.
[21] S. Harrison, R.S. Pilkington, L.H. Sutcliffe, J. Chem. Soc. Faraday Trans. I 80 (1984) 669.
[22] G.D. McManus, unpublished results.
[23] P.W. Atkins, Physical Chemistry, second ed., Oxford University Press, Oxford, 1984.
[24] Collect. Czech, Chem. Commun. 1984, 684.
[25] R. Mayer, G. Domschke, S. Bleisch, A. Bartl, Tetrahedron Lett. 42 (1978) 4003.
[26] P. Kirby, S.B. Soloway, J.H. Davies, S.B. Webb, J. Chem. Soc. C (1970) 2250.
[27] S.A. Fairhurst, K.M. Johnson, L.H. Sutcliffe, K.F. Preston, A.J. Banister, Z.V. Hauptman, J. Passmore, J. Chem. Soc. Dalton Trans. (1986) 1465.
[28] E.G. Awere, N. Burford, C. Mailer, J. Passmore, M.J. Schriver, P.S. White, A.J. Banister, H. Oberhammer, L.H. Sutcliffe, J. Chem. Soc. Chem. Commun. (1987) 66.
[29] C.Aherne, A.J. Banister, A.W. Luke, J.M. Rawson, R.J. Whitehead, J. Chem. Soc. Dalton Trans. (1992) 1277.
[30] K. Bestari, R.T. Oakley, A.W. Cordes, Can. J. Chem. 69 (1991) 94.
[31] J.M. Rawson, G.D. McManus, unpublished results.
[32] (a) V. S. Tsveniashvili, M.V. Malashkhiya, V.N. Gapriandashvili, B. K. Strelets, M.M. Gel'mont, Y.I. Akulin, Khim. Heterosikl. Soedin. (1985) 181. (b) V.S. Tsveniashvili, M.V. Malashkhiya, Elektrokim. 3 (1984) 357.
[33] (a) C.M. Aherne, A.J. Banister, I.B. Gorrell, M.I. Hansford, Z.V. Hauptman, A.W. Luke, J.M. Rawson, J. Chem. Soc. Dalton Trans. (1993) 967. (b) C.M. Aherne, A.J. Banister, T.G. Hibbert, A.W. Luke, J.M. Rawson, Polyhedron, 16 (1997) 4239. (c) R.T. Boeré, K. Moock, M. Parvez, Z. Anorg. Allg. Chem. (1994) 1589.
[34] (a) R.T. Boeré, R.T. Oakley, R.W. Reed, N.P.C. Westwood, J. Am. Chem. Soc. 111 (1989) 1181. (b) A.W. Cordes, J.D. Goddard, R.T. Oakley, N.P.C. Westwood, J. Am. Chem. Soc. 111 (1989) 6147.
[35] J. Campbell, D. Klapstein, P.F. Bernath, W.M. Davis, R.T. Oakley, J.D. Goddard, Inorg. Chem. 35 (1996) 4264.
[36] H.U. Hofs, J.W. Bats, R. Gleiter, G. Hatmann, R. Mews, M. Eckert-Maksic, H. Oberhammer, G.M. Sheldrick, Chem. Ber. 118 (1985) 3781.
[37] (a) F. Palacio, G. Antorrena, M. Castro, R. Burriel, J.M. Rawson, J.N.B. Smith, N. Bricklebank, J. Novoa, C. Ritter, Phys. Rev. Lett. 79 (1997) 2336. (b) P.J. Alonso, G. Antorrena, J.I. Martinez, J. Novoa, F. Palacio, J.M. Rawson, J.N.B. Smith, J. Am. Chem. Soc. (1999), submitted for publication.
[38] J.M. Rawson, unpublished results.
[39] C. Mealli, D.M. Proserpio, J. Chem. Ed. (PC version 4.0, 1990) 67 (1994) 399.

[40] N. Feeder, R.J. Less, J.M. Rawson, J.N.B. Smith, J. Chem. Soc. Dalton Trans. (1998) 4091.
[41] (a) Y.I. Akulin, B.K. Strelets, L.S. Efros, Khim. Geterosikl Soedin. 2 (1975) 275. (b) Y.I. Akulin, B.K. Strelets, L.S. Efros, Khim. Geterosikl Soedin. 1 (1974) 138. (c) A.M. Evdokimov, Y.I. Akulin, B.K. Strelets, L.S. Efros, Khim. Geterosikl Soedin. 10 (1975) 1429.
[42] (a) G. Wolmershauser, M. Schnauber, T. Wilhelm, J. Chem. Soc. Chem. Commun. (1984) 573. (b) G. Heckmann, R. Johann, G. Kraft, G. Wolmershauser, Synth. Met. 41–43 (1991) 3287.
[43] (a) E.G. Awere, N. Burford, R.C. Haddon, S. Parsons, J. Passmore, J.V. Waszczak, P.S. White, Inorg. Chem. 29 (1990) 4821. (b) E.G. Awere, N. Burford, C. Mailer, J. Passmore, M.J. Schriver, P.S. White, A.J. Banister, H. Oberhammer, L.H. Sutcliffe, J. Chem. Soc. Chem. Commun. (1987) 66.
[44] (a) Y-L Chung, S.A. Fairhurst, D.G. Gillies, G. Kraft, A.M.L. Krebber, K.F. Preston, L.H. Sutcliffe, G. Wolmershauser, Magn. Reson. Chem. 30 (1992) 774. (b) T.M. Barclay, A.W. Cordes, N.A. George, R.C. Haddon, R.T. Oakley, T.T.M. Palstra, G.W. Patenaude, R.W. Reed, J.F. Richardson, H. Zhang, J. Chem. Soc. Chem. Commun. (1997) 873
[45] T.M. Barclay, A.W. Cordes, N.A. George, R.C. Haddon, M.E. Itkis, M.S. Mashuta, R.T. Oakley, G.W. Patenaude, R.W. Reed, J.F. Richardson, H. Zhang, J. Am. Chem. Soc. 120 (1998) 352.
[46] (a) T.M. Barclay, A.W. Cordes, R.H. de Laat, J.D. Goddard, R.C. Haddon, D.Y. Jeter, R.C. Mawhinney, R.T. Oakley, T.T.M. Palstra, G.W. Patenaude, R.W. Reed, N.P.C. Westwood, J. Am. Chem. Soc. 119 (1997) 2633. (b) E. Dormann, M.J. Nowak, K.A. Williams, R.O. Angus, Jr., F. Wudl, J. Am. Chem. Soc. 109 (1987) 2594. (c) G. Wolmershauser, G. Wortmann, M. Schnauber, J. Chem. Res. S (1988) 358. (d) G. Wolmershauser, M. Schnauber, T. Wilhelm, L.H. Sutcliffe, Synth. Met. 14 (1986) 239.
[47] (a) G. Wolmershauser, G. Kraft, Chem. Ber. 122 (1989) 385. (b) G. Wolmershauser, G. Kraft, Chem. Ber. 123 (1990) 881.
[48] (a) L. Testaferri, M. Tingoli, M. Tiecco, J. Org. Chem. 45 (1980) 4376. (b) F. Maiolo, L. Testaferri, M. Tiecco, M. Tingoli, J. Org. Chem. 46 (1981) 3070. (c) C.W. Dirk, S.D. Cox, D.E. Wellman, F. Wudl, J. Org. Chem. 50 (1985) 2395.
[49] R.T. Oakley, R.E. von, H. Spence, J.F. Richardson, Acta. Crystallogr. Sect. C 51 (1995) 1654.
[50] (a) R.C. Haddon, Nature 256 (1975) 394. (b) G.D. McManus, J.M. Rawson, N. Feeder, F. Palacio, unpublished results.
[51] A.M.Z. Slawin, D.J. Williams, Department of Chemistry, Imperial College of Science and Technology, London, unpublished results.
[52] R.A. Beekman, R.T. Boeré, K.H. Moock, M. Parves, Can. J. Chem. 1 (1998) 85.
[53] (a) A.J. Banister, N. Bricklebank, W. Clegg, M.R.J. Elsegood, C.I. Gregory, I. Lavender, J.M. Rawson, B.K. Tanner, J. Chem. Soc. Chem. Commun. (1995) 679. (b) A.J. Banister, N. Bricklebank, I. Lavender, J.M. Rawson, C.I. Gregory, B.K. Tanner, W. Clegg, M.R.J. Elsegood, F. Palacio, Angew. Chem. Int. Ed. Engl. 35 (1996) 2533. (c) F. Palacio, G. Antorrena, M. Castro, R. Burriel, J.M. Rawson, J.N.B. Smith, N. Bricklebank, J. Novoa, C. Ritter, Phys. Rev. Lett. 79 (1997) 2336.
[54] S.A. Fairhurst, R.S. Pilkington, L.H. Sutcliffe, J. Chem. Soc. Faraday Trans. I (1983) 925.
[55] R.C. Haddon, Nature 256 (1975) 394.
[56] (a) C.D. Bryan, A.W. Cordes, R.M. Fleming, N.A. George, S.H. Glarum, R.C. Haddon, C.D. MacKinnon, R.T. Oakley, T.T.M. Palstra, A.S. Perel, J. Am. Chem. Soc. 117(1995) 6680. (b) C.D. Bryan, A.W. Cordes, .C. Haddon, R.G. Hicks, D.K. Kennepohl, C.D. MacKinnon, R.T. Oakley, T.T.M. Palstra, A.S. Perel, S.R. Scott, L.F. Schneemeyer, J.V. Wasczak, J. Am. Chem. Soc. 116 (1994) 1205. (c) C.D. Bryan, A.W. Cordes, N.A. George, R.C. Haddon, C.D. MacKinnon, R.T. Oakley, T.T.M. Palstra, A.S. Perel, Chem. Mater. 8 (1996) 762.
[57] A.J. Banister, I.B. Gorrell, Adv. Mater. 10 (1998) 1415.
[58] (a) H.Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M.Iwamura, M. Takabashi, M. Kinoshita, Chem. Phys. Lett. 186 (1991) 401. (b) R. Chiarelli, M.A. Novak, A.Rassat, J.L.

Tholence, Nature 147 (1991) 363. (c) T.C. Koboyashi, M. Takiguchi, C.U. Hong, K. Amaya, A. Kajiwara, A. Harda, M.Kamachi, J. Magn. Mat. 140–145 (1995) 1447. (d) K. Takeda, M. Mito, H. Nakano, T. Kawae, M. Hitaka, S. Takagi, H. Deguchi, S. Kawasaki, M. Mukai, Mol. Cryst. Liq. Cryst. 306 (1997) 431.

[59] (a) T.S. Cameron, R.C. Haddon, S.M. Matter, S. Parsons, J. Passmore, A.P. Ramirez, Inog. Chem. 31 (1992) 2274. (b) A. Berces, G.D. Enright, J.R. Morton, J. Passmore, K.F. Preston, R.C. Thompson, D.J. Wood, Phos. Sulf. Sil. 124–125 (1997) 331.