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Introduction

arylamidines in neat thionyl chloride at reflux. The S(IV) 1-chlorides are readily reduced under mild conditions to persistent 1,2,4-benzothiadiazinyl radicals which have been characterised by EPR spectroscopy and cyclic voltammetry. Crystallographic studies on isolated radicals indicate that the radicals dimerise *via* pancake bonding in the solid-state, resulting in spin-pairing and net diamagnetism.

A short, versatile route towards benzothiadiazinyl

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A family of substituted 1,2,4-benzothiadiazine 1-chlorides have been prepared by treatment of N-

Stable molecular radical species have long been targeted as potential molecular magnets for future magnetic storage applications, and as test-beds for fundamental studies into magnetic communication.¹ Several metal-free radical families² have been explored which exhibit divergent properties from metal centred species. These are of particular interest because, in addition to their magnetic properties, many exhibit a unique form of bonding wherein they dimerise *via* π - π interactions (termed "pancake bonding") rather than formation of simple $2c2e^-$ bonds.³ These interactions are key to dictating both magnetic and electronic properties of organic systems, and represent a versatile and important motif in supramolecular recognition.⁴

radicals[†]

and Jeremy M. Rawson D*c

This pancake bonding mode is accessible because many of the "organic" radical families known utilise π -delocalisation, typically onto electronegative elements or extended systems, to achieve radical stability, as exemplified by the verdazyl⁵ (N centred radicals), nitroxyl⁶ (N–O centred radicals), and dithiazolyl, and dithiadiazolyl (S–N centred radicals) systems.⁷ The five-membered ring S–N radicals provide a particularly rich vein of potential radical systems due to their amenability to isoelectronic substitutions and modular synthesis. For example, the 1,2,3,5-dithiadiazolyl class incorporates a substituent at the 4-position which is not directly conjugated into the radical heterocycle and whose influence on properties is therefore limited to steric and inductive effects.⁸ However,

^aSchool of Physical Sciences, University of Kent, Ingram Building, Canterbury, Kent, CT2 7NH, UK comparatively few S–N radicals based on six-membered rings are known, and studies on the benzo-1,2,4-thiadiazinyl class are sparse, with only two examples crystallised to date;⁹ some mesophases containing these ring systems have also been characterised.¹⁰

The benzo-1,2,4-thiadiazine heterocyclic system is accessible in a range of oxidation states from S(u) to $S(v_I)$, and incorporation of 2-pyridyl moieties at the pendant 3 position gives rise to chelating ligands for which first row transition metal¹¹ and $Ir(m)^{12}$ complexes are known. The S(m) radicals (see Scheme 1a) are accessible through one-electron oxidation of the S(n)systems,⁹ or more conveniently by one-electron reduction of S(m) precursors.¹³ Work by Oakley has allowed the isolation of



Scheme 1 Reported synthetic routes towards 1,2,4-benzothiadiazines and related systems.

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a range of mixed valent S(II)/S(III) thiadiazine based systems; in these cases, an extended π -system containing an additional S–N heterocycle is used to provide stability.^{14,15} Overall, these systems are comparatively unexplored and offer great potential as molecular radical building blocks as the substituents at the 3 position are not directly conjugated into the singly occupied molecular orbital (SOMO), analogous to the dithiadiazolyl radicals. The radical properties can therefore in principle be tuned as desired by chemical modification of both the benzofused ring, affecting the radical electronic structure, and the 3-substituent whose modification is expected to affect steric demand and packing interactions predominantly.

The expansion of this class of radicals is hampered by the lack of general synthetic methodologies available. The radicals themselves may be formed by either 1e⁻ oxidation¹⁶ or reduction of appropriate closed shell precursors,¹⁴ but few synthetic routes towards these precursors are known and these are not particularly general (see Scheme 1), often involving long, multistep syntheses. Indeed, for the five radicals reported by Kazsynski in 2004, five bespoke synthetic routes were required.⁹ The three points in common across these synthetic routes are the presence of an amidine intermediate to provide the NCN fragment of the heterocyclic ring, ring-closure effected by nucleophilic attack on an S(IV) species which is in turn generated by in situ oxidation of a S(II) precursor, and halogenation of the benzo-fused ring to stabilise the resultant radicals and enable their isolation. This last point introduces an additional synthetic consideration, necessitating pre-halogenated precursors, or exhaustive chlorination after ring-closure using Cl₂. In Levchenko's original 1984 work,17 SCl2 acted simultaneously as the sulphur source, oxidising agent, and chlorinating agent to give benzothiadiazine 1-chlorides with varying degrees of chlorination about the benzo-fused ring, followed by direct chlorination with Cl₂, whilst Oakley's mixed S(II)/(IV) parent species use S₂Cl₂ in the same role.¹⁴

Recognising this, we sought a simple, direct route to the required heterocyclic ring starting from the easily handled and cheap S(w) source, thionyl chloride. We report here the development of a SOCl₂-based route towards 1,2,4-benzothiadiazine 1-chlorides and studies on the derived S(m) radicals.

Results and discussion

Synthesis

Initial studies on the reaction of the prototypical *N*-phenylbenzamidine, **1a**, with stoichiometric SOCl₂ were unsuccessful when performed in DCM, THF, and toluene, in each case producing a copious quantity of **1a** ·HCl as a colourless solid. Addition of stoichiometric base (pyridine, Et₃N and ^{*i*}Pr₂EtN) did not improve matters and, for the trialkylamines, led to a violent side reaction which is likely due to oxidation of the trialkylamine by SOCl₂.¹⁸ It was reasoned that a polar, high-boiling solvent would (i) retain the protonated amidine in solution and (ii) permit the HCl formed to be driven off at elevated temperatures, driving the desired cyclisation process. As thionyl chloride itself fulfils these criteria ($\mu = 1.44$ D, bp = 74.6 °C), the reaction of **1a** in neat SOCl₂ was attempted. After reflux

overnight, the reaction mixture was deep orange, characteristic of benzothiadiazine 1-chlorides. Layering the reaction mixture with ⁿhexane, followed by slow diffusion, led to isolation of analytically pure, crystalline 2a in 71% yield. Reaction of the related amidines 1b-j in refluxing SOCl₂ similarly led to the isolation of benzothiadiazine 1-chlorides 2b-j in moderate to good yields (31-81%) as yellow to red crystalline solids (Table 1). Notably, partial chlorination of both the benzo ring and any methyl substituents on the benzo ring occurs during all these reactions. However, the presence of excess SOCl₂ led to a single product in nearly all cases. For 1d, the chloride salt 2d selectively precipitated from solution in 31% yield, but slow cooling of the mother liquor afforded orange needles which comprised a mixture of the isomeric compound 2s' and the dichloromethyl derivative 2s'' (Fig. 1b) in a *ca*. 44 : 3 ratio based on crystallographic refinement, suggesting the potential for further chlorination when using extended reaction times. Attempts to prepare 2k yielded a yellow solid that was practically insoluble in most organic solvents and only poorly soluble in SOCl₂. ¹H NMR analysis was consistent with the formation of the expected heterocycle and partial chlorination at the 6 position (H : Cl =3:2). Prolonged reflux of $2\mathbf{k}$ in the presence of excess SO_2Cl_2 and larger volumes of SOCl₂ only slightly increased the degree of chlorination (H : Cl = 2:3), possibly due to the poor solubility of the salt, whilst shorter reflux times afforded other unidentified species. Attempts to deprotonate compound 2k with basic amines (pyridine, Et₃N, DABCO) resulted in the immediate formation of a dark blue, EPR active solution from which poor quality crystals of the neutral radical (H : Cl = 4 : 1)could be grown (see ESI[†] for details), indicating that these species are highly oxidising (vide infra).

Selective chlorination of the benzo-fused ring is reminiscent of Levchenko's reaction of N-chloroamidines with SCl2¹⁷ in which the position para to the amidine nitrogen was always chlorinated. Similarly 1,2,3-dithiazolylium salts prepared by Herz from 2-mercaptoanilines and SOCl₂ also undergo chlorination para to the amino group.19,20 For these benzo-fused 1,2,4thiadiazolium salts, chlorination of the benzo ring occurred at all positions except the 8-position and chlorination of methyl groups on the benzo ring typically afforded selectively the chloromethyl derivatives unless the methyl group was at the 8 position where no chlorination was observed. The selectivity leading to retention of the C-H at C(8) is attributed to the combination of successive deactivation by chlorination elsewhere and conjugation into the larger heterocycle, lowering the HOMO energies, directed by the location of C(8) meta to the o,pdirecting amidine group and ortho to the deactivating S(IV) functionality. This is consistent with the exhaustive chlorination reported by Levchenko and Kaszynski which required direct treatment with excess Cl2.9,17 In contrast to the benzo substituents, phenyl and tolyl groups at the 3-position generally appear resistant to chlorination under these conditions. However, activated aryl groups appear to promote chlorination of the 3-aryl group. For example, while 2i formed cleanly, reaction of 1j with SOCl₂ formed 2j selectively under short reaction times but a mixture comprising 2j and up to $\sim 45\%$ of 2q (Fig. 1a) was observed as a by-product under extended

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| Table 1 | Substituted amidines (1) | and corresponding 1 | 2 4-benzothiadiazine | 1-chlorides (2) | after refluxing with SOCIa |
|---------|--------------------------|---------------------|----------------------|-----------------|----------------------------|
| TUDIC 1 | Substituted armanies (±) | and conceptioning i | | | arter renaxing with 50 cl2 |

| Entr | y <i>N</i> -Aryl-amidine | Yield (%) | Benzo-1,2,4-benzothiadiazine 1-chloride | Yield (%) | Entr | y <i>N</i> -Aryl-amidine | Yield (%) | Benzo-1,2,4-benzothiadiazine 1-chloride | Yield (%) |
|------|--------------------------|--------------|--|--------------|------|--------------------------|--------------|--|-----------------------|
| a | NH2 | 90 | | 71 | i | NH2 OMe | 77 | CI N OMe | 81 |
| b | N NH ₂ | 71 | | 61 | j | N NH ₂ | e 74 | CI CI OMe CI S N CI | 63 |
| c | N NH2 | 87 | | 76 | k | NH2 | 88 | X CI S CI CI | а |
| d | N NH ₂ | 79 | | 31 | 1 | N NH ₂ | 85 | CI CI T C | 87 |
| e | N NH ₂ | 78 | | 40 | m | N NH ₂ | 71 | | 0^b |
| f | Ny NH ₂ | 66 | | 46 | n | N NH2 | 72 | | 0^b |
| g | NY NH2 | 63 | | 46 | 0 | Ph NH2 | 68 | | 0 ^{<i>b</i>} |
| h | NH2 | 66 | | 53 | р | NH2 | 41 | | 0^b |

^a Mixture of species. ^b Target product not obtained.



Fig. 1 Partially chlorinated 1,2,4-benzothiadiazine 1-chlorides derived from (a) 1j and (b) 1d.

reaction times. Despite this, attempts to produce pure 2**q** under extended reaction times up to 72 hours was unsuccessful. Attempted purification of 2**q** by recrystallisation from thionyl chloride containing SO_2Cl_2 as stabiliser instead allowed the isolation of a few crystals of 2**r** with additional chlorination of the 6-chloromethyl group. Nevertheless, 2**q** was fully characterised by ¹H and ¹³C{¹H} NMR spectroscopy.

In the case of **1l**, the basic nature of the 3-(4'-pyridyl) group led to isolation of the hydrochloride salt $[2l \cdot H][HCl_2]$. No crystalline products could be isolated for the reactions of **1m–n** with SOCl₂. Since chlorination occurs *para* to the amidine functionality prior to, or at the same time as, ring-closure, it is believed that the presence of a methyl-group at this position inhibits the formation of the desired 1,2,4-benzothiadiazine 1-

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chloride. Attempts to prepare **20** were unsuccessful; yielding a dark brown insoluble solid assigned as a mixture of partially chlorinated species by ¹H NMR spectroscopy. A low yield of pale peach solid was obtained during the attempted synthesis of **2p**; a few, low quality colourless crystals, grown by recrystallisation of the crude solid from boiling SOCl₂, were identified as doubly *ortho*-chlorinated **1p**·HCl by SCXRD but were only a component of a complex mixture as seen by ¹H NMR.

The patterns of partial chlorination observed imply that chlorination is rapid at the 5 and 7 positions, slow at the 6 position, and does not occur for the 8 position. The fact that no products could be isolated when substituents were present para to the amidine nitrogen (the pro-7 position) suggests that chlorination at this position is rapid, as seen for Herz reactions,^{19,20} producing highly reactive intermediates leading to uncontrolled further reactivity and decomposition. The isolation of partially chlorinated 1p·HCl suggests that chlorination of the aryl ring is more rapid than ring-closure and that chlorination at both positions ortho to the amidine nitrogen inhibits the formation of the fused-ring. This would indicate that the rates of chlorination and ring-closure are competitive for these systems. Independent synthesis of 1t, N-(4-chlorophenyl)benzamidine, and reaction in SOCl₂ led cleanly to 2a, supporting this species as an intermediate in ring closure. From these results, it is not possible to fully determine the mechanism, but it is plausible that it occurs by formation of an aminosulphonylchloride, 5 (Scheme 2), and subsequent electrophilic aromatic substitution, either directly or via an intermediate Nsulfinylamine, 6,²¹ followed by deoxygenation of an S(IV) 1-oxide, 7, by reaction with a further equivalent of $SOCl_2$ to give the benzothiadiazine 1-chloride, 2, which may then undergo additional chlorination at carbon, as shown in Scheme 2.

Crystallographic discussion

Single crystals suitable for X-ray diffraction studies were obtained for all derivatives except 2e, either by layering the reaction mixture with dry ^{*n*}hexane or slow cooling of a saturated



Scheme 2 Proposed cyclisation pathway.



Fig. 2 Molecular structure of 2a. Thermal ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity. (a) Top-down view; (b) side view.

thionyl chloride solution. The benzothiadiazine 1-chlorides all adopt solid state structures distorted from planarity, exemplified by 2a (Fig. 2). The heterocyclic ring is not flat but instead bent along the 1,4 S…N axis, with angles between the two halves of the ring ranging from 7.11° to 15.10° (see Table 2). These nevertheless show on average less deviation from planarity than the related S(II) benzothiadiazines,²² likely due to the increased delocalisation in the formally 10π benzothiadiazine 1-chlorides vs. the 12π anti-aromatic S(II) benzothiadiazines. The pendant aryl rings are not coplanar with the heterocycle, showing torsion angles in the range of 0.8(6) to $30.09(3)^{\circ}$; the torsion angles are largest for 2g and 2h with ortho-methyl substituents on the pendant ring. Examination of the S-Cl bonds is informative the bond lengths range from 2.221(2) Å to 2.3412(7) Å, considerably longer than the 2.072 Å expected for a formal S–Cl single bond,23 and comparable to the range seen for thiatriazines (2.283–2.357 Å).^{24,25} In addition to this, the transannular N-S-Cl angles are in a narrow range of $99.84(5)^{\circ}$ to $106.80(5)^{\circ}$, consistent with a rigid and well defined bonding environment. These are therefore elongated and weakened covalent bonds, in contrast to the ionic character seen for dithiadiazolyl chlorides where the S-Cl contacts are much longer at 2.906-2.962 Å,²⁶ albeit still within the sum of the van der Waals radii, 3.55 Å.27 This argues for a comparatively less stable cation following halide abstraction arising from poorer π -delocalisation about the heterocycle.

The benzothiadiazine 1-chlorides are chiral systems and, where partial chlorination of methyl groups occurs, the chloromethyl fragment may therefore lie either *syn* or *anti* to the S–Cl bond. In the case of 2c, 2h, 2j and 2r, the crystal structure shows both C–Cl bonds lying nearly co-parallel, *anti* to the S–Cl bond, whereas for $[2l \cdot H][HCl_2]$, the two chloromethyl groups sit *anti* to one another. In contrast, 2d is polymorphic with the α -phase crystallising with the E–Cl bonds *anti* to one another whilst the β -phase adopts a *syn* configuration. Although not possessing a CH₂Cl group, the OMe group of 2f is disordered equally above and below the plane of the ring relative to the S–Cl bond. In all cases, no splitting of the methylene protons is evident in the ¹H NMR spectrum, consistent with rapid rotation and/or inversion about sulphur on the NMR timescale in solution.

Anion metathesis

Anion metathesis reactions are commonly employed to improve the solubility of S(w) salts prior to reduction to form neutral radicals. With this in mind, some simple tests of the amenability of **2a** towards halide abstraction were performed. Reaction

Table 2 Selected crystallographic parameters for the studied 1,2,4-benzothiadiazine 1-chlorides



| | | Torsion angles/° | | | S-CI angle/° | |
|--------------------|-------------|-------------------------|-------------------------------|-----------------------|------------------------------------|--|
| | planarity/° | $N_2 - C_3 - C_A - C_B$ | N_4 - C_3 - C_A - C_F | S–CI bond length/Å | N ₄ -S ₁ -CI | |
| la | 11.74 | 4.6(6) | 0.8(6) | 2.221(2) | 100.79(8) | |
| | 8.17 | 13.7(6) | 9.9(6) | 2.306(1) | 106.24(7) | |
| ٤b | 11.44 | 11.90(3) | 9.05(3) | 2.2811(8) | 102.58(4) | |
| lc | 7.32 | 6.65(3) | 4.18(3) | 2.3412(7) | 106.11(4) | |
| 2d-α | 10.99 | 8.64(4) | 6.16(4) | 2.2974(9) | 102.32(5) | |
| 2 d -β | 7.11 | 6.1(8) | 1.7(8) | 2.261(2) | 107.0(1) | |
| 2f | 9.61 | 3.83(2) | 0.89(2) | 2.2759(6) | 104.06(3) | |
| lg. | 8.26 | 19.80(1) | 16.08(1) | 2.309(2) | 106.23(1) | |
| 8 | 13.78 | 10.51(1) | 9.96(1) | 2.229(3) | 99.97(1) | |
| 2h | 15.10 | 30.90(3) | 28.91(3) | 2.2689(9) | 99.84(5) | |
| 2i | 7.20 | 9.59(3) | 5.89(3) | 2.3205(8) | 106.80(5) | |
| 2i | 8.25 | 8.25(5) | 5.10(5) | 2.279(1) | 105.33(7) | |
| 7 21 · H][HC]₀] | 13.46 | 20.56(2) | 18.15(2) | 2.238(4) | 100.25(2) | |
| 22 2r | 9.46 | 9.98(1) | 8.45(1) | 2.264(4) | 103.42(2) | |
| 28 | 9.98 | 7.01(9) | 4.03(9) | 2.287(2) | 104.89(1) | |

of 2a with GaCl₃ in DCM resulted in the immediate formation of [4a][GaCl₄] as a dark purple solution whose identity was unambiguously confirmed by growth of single crystals by slow diffusion of ^{*n*}hexane into the reaction mixture (Fig. 3).

benzothiadiazinyl cations are accessible, they are highly reactive and easily reduced to the radical such that judicious choice of weakly coordinating anions is required to allow their isolation.

The abstraction results in an almost completely planar system forming, with minimal trans-annular bend (0.51°) and a torsion angle of only 2.57(6)° between the pendant phenyl ring and heterocycle. The S-CAr bond length in [4a][GaCl4] is considerably shorter than that of 2a (1.683(4) Å vs. 1.733(2) Å), with minor alterations in other bond lengths, which coupled with the more planar structure argues for increased delocalization within the ring which is formally a 6π aromatic system $(10\pi$ when considering the benzo-fused substituent). Two long cation-anion interactions of 3.341(1) Å and 3.463(1) Å (cf. 2.2572(7) Å for the S-Cl bond in 2a) are observed between sulphur and the chlorine atoms of two adjacent GaCl₄⁻ anions, confirming the structure as ionic.

Treatment of 2a with NaBAr^{Cl} in DCM resulted in a deep blue, EPR active solution consistent with the formation of the neutral S(III) radical, 3a. Taken together, these results show that whilst



Fig. 3 Molecular structure of [4a][GaCl₄]. Thermal ellipsoids shown at 50% probability. Hydrogen atoms and counter-anion omitted for clarity. (a) Top-down view; (b) side view.

1,2,4-Benzothiadiazinyl radicals

Benzothiadiazinyl radicals have been accessed via one electron oxidation of benzothiadiazines,9 but this requires considerable optimisation for each derivative. An alternative approach is one electron reduction of the benzothiadiazine 1-chloride salts. In our hands, we found that the 1,2,4-benzothiadiazine 1-chlorides (2a-j) were easily reduced to the corresponding radicals with both Ph₃Sb and Fe(η^5 -C₅H₅)₂ but attempts to remove the byproducts and isolate the pure radicals from these reaction mixtures failed. Preliminary small-scale studies utilising Ph₃P as a milder reducing agent in a variety of common organic solvents were promising, immediately yielding dark green, EPR active solutions, and clearly showing the formation of Ph₃PCl₂ (THF, toluene; δ –46 ppm) or [Ph₃PCl]Cl (DCM, MeCN; δ +60 ppm) by ³¹P NMR spectroscopy. Solutions of the radicals generated in DCM, THF, and toluene swiftly discoloured to give yellow-brown suspensions, whilst the radicals were only poorly soluble in MeCN. The green solutions of these benzothiadiazinyl radicals were observed to become a rich blue colour on cooling in liquid nitrogen which is believed to originate from a monomer-dimer equilibrium (vide infra), with the formation of closed-shell dimers being favoured at low temperatures.

EPR spectroscopy

Although concentrated solutions of these radicals decolourise in minutes, dilute solutions proved sufficiently robust in dry,



degassed toluene to allow EPR studies to be performed. This indicates that the short half-life in solution is a result of kinetic instability and subsequent reactivity rather than inherent thermodynamic instability. This is consistent with the thermal stability of the more highly chlorinated analogues reported by Kaszynski which were stable to sublimation at elevated temperature but decomposed over hours in solution.9 They are therefore considerably more reactive than their valence isoelectronic analogues, the Blatter radicals.28 EPR spectra of radicals 3a-j, generated in situ by reduction with Ph₃P, were recorded in toluene at ambient temperature on a continuous wave X-band EPR spectrometer. The EPR spectra for the 1,2,4benzothiadiazinyl radicals are all similar, exhibiting slightly asymmetric 1:2:3:2:1 quintets arising from coupling to two similar but non-identical nitrogen atoms within the heterocyclic ring. Significant line-broadening was observed in all cases due to chlorination of the fused ring; since both ³⁵Cl and ³⁷Cl are quadrupolar nuclei with I = 3/2, the spectra consist of multiple superimposed spectra for each isotopalogue, resulting in net loss of resolution and increased line-broadening, meaning all features beyond nitrogen hyperfine coupling are lost. The EPR spectrum of 3a is shown in Fig. 4 and the g-values and hyperfine coupling constants for radicals 3a-j are summarized in Table 3.

The SOMO geometry of **3a** (Fig. 5), calculated at the UB3LYP/ cc-pVDZ level using a UB3LYP/6-31G optimised geometry,

Table 3 EPR spectral parameters for radicals 3a-j. Assignment of hyperfine coupling to N2 and N4 on the basis of DFT calculations; see ESI for details

| | g-Value | Line-width/MHZ | $a_{\rm N2}/{ m MHZ}$ | a _{N4} /MHZ |
|----|---------|----------------|-----------------------|----------------------|
| | 2 0007 | 0.07 | 15.66 | 10.10 |
| 3a | 2.0037 | 0.27 | 15.66 | 13.13 |
| 3b | 2.0035 | 0.26 | 15.64 | 13.51 |
| 3c | 2.0034 | 0.31 | 15.80 | 13.60 |
| 3d | 2.0043 | 0.31 | 15.10 | 13.10 |
| 3e | 2.0046 | 0.37 | 14.69 | 13.30 |
| 3f | 2.0045 | 0.33 | 14.56 | 13.23 |
| 3g | 2.0046 | 0.27 | 15.88 | 13.35 |
| 3ĥ | 2.0045 | 0.34 | 15.61 | 13.71 |
| 31 | 2.0041 | 0.29 | 15.82 | 12.89 |
| 3j | 2.0041 | 0.38 | 14.73 | 13.98 |
| - | | | | |



Fig. 5 Calculated SOMO of 3a (isovalue = 0.04)

reveals that it is largely independent of the substituents around the benzo-fused and pendant aryl rings. This is supported by the similarity of *g*-values and ¹⁴N hyperfine coupling constants observed across the range of 1,2,4-benzothiadiazinyl radicals indicating that the electronic structure is only slightly perturbed by substitution at these positions.

Electrochemical studies

Although all radicals could be generated in situ, pure samples could only be isolated for a minority of the radicals (vide infra). As a result of this and their poor long-term stability in solution, cyclic voltammetry studies were performed on the chlorides 2aj in dry, degassed DCM. The 1,2,4-benzothiadiazine 1-chlorides all displayed similar electrochemical behaviour, and the cyclic voltammogram of 2a is presented as typical of this series (Fig. 6). The two, often-overlapping, reversible processes at positive potentials (vs. Fc/Fc^+) are assigned to S(m)/S(w) couples, whilst the irreversible process at negative potential is attributed to the S(II)/S(III) couple. The two S(III)/S(IV) waves suggest the presence of radical monomers and dimers in solution, as shown in Scheme 3. Similar monomer-dimer equilibria have also been observed for 6-membered thiatriazines and independently confirmed by quantitative EPR measurements.²⁹ Further support for a monomer-dimer equilibrium was observed via variable concentration studies - at low concentrations the



Fig. 6 Cyclic voltammogram of **2a** in DCM with [ⁿBu₄N][PF₆] supporting electrolyte.



Scheme 3 Proposed redox events.

monomer is favoured whilst at high concentrations the cyclic voltammogram is dominated by signals for the dimer. These studies permit initial assignment of the two S(III)/S(IV) redox couples and show that the one electron reduction potential of the monomer is positive relative to the dimer.²⁹ In addition, the S(II)/S(III) reduction wave splits into two well resolved peaks at low concentrations (see ESI[†]).

The irreversibility of the redox event at negative potentials is attributed to a rapid E_rC_i (a reversible electron transfer followed by an irreversible chemical reaction) comproportionation reaction between the electro-generated S(II) anion and the bulk S(IV) species 2a. This has been observed for several S–N systems.²⁹ No evidence of *quasi*-reversibility was observed, even at scan rates up to 2 V s⁻¹, indicating that the comproportionation reaction is extremely rapid. The variable scan-rate data nonetheless show that the S(III)/S(IV) processes for both radical monomer and dimer are reversible electron transfer processes involving a freely diffusing redox species according to the Randles–Sevcik equation,³⁰ and confirm that the analyte is not adsorbed to the electrode surface (see ESI†).

The $E_{1/2}$ potentials for the S(m)/S(rv) couple follow the expected trend (see Table 4), with 1,2,4-benzothiadiazine 1-chlorides bearing electron-withdrawing groups such as **2a**, **2g** and **2i** being more easily reduced than those with electron-donating groups such as **2b–d**. The same trends were also observed for the S(n)/S(m) couple. The substituents on the benzo-fused ring were found to have a greater influence on the electrochemical behaviour and redox potentials compared to substituents on

Table 4 Redox potentials of 1,2,4-benzothiadiazine 1-chlorides 2a–j. Potentials are referenced against the Fc/Fc⁺ couple

| | S(II)/S(III) | S(III)/S(IV) (dimer) | | | S(III)/S(IV) (monomer) | | | |
|----|-----------------|----------------------|----------------------|-------------|------------------------|----------------------|-------------|--|
| | $E_{\rm red}/V$ | $E_{\rm red}/V$ | $E_{\rm ox}/{\rm V}$ | $E_{1/2}/V$ | $E_{\rm red}/V$ | $E_{\rm ox}/{\rm V}$ | $E_{1/2}/V$ | |
| 2a | -1.457 | 0.013 | 0.179 | 0.096 | 0.371 | 0.518 | 0.444 | |
| 2b | -1.511 | -0.112 | 0.084 | -0.014 | _ | 0.449 | _ | |
| 2c | -1.649 | -0.094 | 0.054 | -0.020 | _ | 0.501 | _ | |
| 2d | -1.654 | -0.084 | 0.036 | -0.024 | _ | 0.441 | _ | |
| 2e | -1.473 | -0.027 | 0.142 | 0.057 | 0.336 | 0.469 | 0.403 | |
| 2f | -1.557 | -0.083 | 0.111 | 0.014 | 0.379 | 0.508 | 0.443 | |
| 2g | -1.446 | -0.011 | 0.226 | 0.108 | 0.400 | 0.481 | 0.440 | |
| 2h | -1.599 | -0.040 | 0.123 | 0.041 | _ | 0.479 | _ | |
| 2i | -1.450 | 0.028 | 0.144 | 0.086 | 0.300 | 0.397 | 0.349 | |
| 2j | -1.620 | -0.071 | 0.035 | -0.018 | _ | 0.558 | _ | |

the pendant aryl ring. This is in good agreement with DFT studies which indicate that there is negligible delocalisation of the unpaired electron onto the pendant aryl ring but significant π -delocalisation across the benzo-fused and heterocyclic rings. There are, however, only minor changes observed across the $E_{1/2}$ potentials for substituted benzothiadiazine 1-chlorides.

Solid state studies of 1,2,4-benzothiadiazinyl radicals

Isolated 1,2,4-benzothiadiazinyl radicals, 3a-j, were prepared by treatment of the S(IV) 1-chlorides with half a molar equivalent of Ph₃P in thoroughly degassed and anhydrous MeCN (Scheme 4). Exploiting the poor solubility of radicals in MeCN, the radicals formed cleanly and rapidly, and precipitated as dark purplegreen solids that were subsequently isolated by filtration and washed prior to drying under vacuum. The stability is significantly enhanced in the solid state, with samples giving clean elemental analysis and remaining spin active even after storage for several weeks at room temperature in an argon glove box. In contrast, the washings were found to swiftly discolour, even when stored at -20 °C. The growth of crystals suitable for SCXRD analysis was severely hampered by the poor stability of the 1,2,4-benzothiadiazinyl radicals in solution, with several approaches (slow cooling, vapour diffusion) and solvents (DCM, THF, toluene, pyridine, ^{*n*}hexane, Et₂O) giving only rapid discolouration and formation of yellow-brown precipitates. Ultimately, single crystals suitable for SCXRD analysis of 3a and 3c were successfully grown by rapidly mixing the parent S(IV) 1chloride and reducing agent in DCM and allowing the radical to slowly crystallise out of solution. This method, however, was found to be unreliable in forming X-ray quality crystals and often afforded just micro-crystalline material unsuitable for single crystal diffraction studies. Single crystals of 3e grew readily from saturated toluene solutions. A few, poor quality crystals of 3k could be isolated after attempting to dissolve 2k in pyridine.

The discussion herein focuses on the thiadiazinyl ring (see ESI[†] for full structures). The structurally characterised 1,2,4benzothiadiazinyl radicals are notably closer to planarity than the S(IV) 1-chlorides; the deviation from planarity for the heterocyclic ring ranges from 1.22° to 5.78° (*cf.* 7.11–15.10° for **2a–s**), although the torsion angles for the pendant aryl ring are comparable $0.3(3)^\circ$ to $9.6(5)^\circ$ (*cf.* $0.89(2)-11.90(3)^\circ$ for **2a–f**). Crystallisation of **3a** allows direct comparison of changes in heterocyclic ring structure between **2a**, **3a**, and [**4a**]GaCl₄, as shown in Table 5. For **3c**, the two CH₂Cl groups adopt an *anti* configuration, in contrast to the *syn* configuration observed in **2c**. Unlike Kaszynski's perfluoro- and perchloro-radicals which are monomeric in the solid state,⁹ radicals **3a**, **3c**, **3e**, and **3k** all



Scheme 4 Synthesis of 1,2,4-benzothiadiazinyl radicals 3a-j.

Table 5 Comparison of heterocyclic bond parameters for ${\bf 2a},\,{\bf 3a}$ and $[{\bf 4a}]^+$

| | | Bond length/Å | | | | | |
|----------------------------------|--------------------------------|---------------|----------|------------|--|--|--|
| | Bond | 2a | 3a | $[4a]^{+}$ | | | |
| N^4 | S_1-N_2 | 1.564(2) | 1.615(2) | 1.574(4) | | | |
| xC ^{-''} C ₃ | N_2-C_3 | 1.382(2) | 1.349(5) | 1.347(5) | | | |
| | $C3-N_4$ | 1.307(2) | 1.323(5) | 1.339(5) | | | |
| $^{\rm YO}$ $S_1^{\rm N_2}$ | N_4-C_X | 1.371(3) | 1.377(5) | 1.324(5) | | | |
| U I | C _X -C _Y | 1.403(3) | 1.405(5) | 1.442(5) | | | |
| | $C_{Y}-S_{1}$ | 1.733(2) | 1.735(4) | 1.683(4) | | | |

crystallise as pancake dimers featuring short contacts between the heterocyclic rings.

Three different configurations of dimer (Fig. 7) were observed for the radicals. This is analogous to other sulphurnitrogen radicals, especially those based on less delocalised five-membered ring systems such as dithiadiazolyls, for which multiple dimer motifs have been documented.8 Radical 3a dimerises in a twisted, suprafacial motif (Fig. 7a) with the two molecules related via a crystallographic 2-fold rotation axis. The two heterocyclic rings are not quite coplanar, exhibiting an interplanar angle of 7.82° and a pair of crystallographically equivalent S1 ··· N2 contacts at 2.866(4) Å (cf. S…N contacts of 3.193(4) Å and 3.213(4) Å respectively for Kazsynski's monomeric perfluoro-analogue). Radicals 3c and 3k also adopt dimeric structures with molecules related via a crystallographic inversion centre. In this instance, the inversion centre generates a trans-antarafacial dimer motifs (Fig. 7b) featuring two short identical S1...N4 contacts at 3.087(2) Å and 3.010(3) Å for 3c and 3k respectively with parallel heterocyclic rings, whilst 3e dimerised in a trans-suprafacial motif (Fig. 7c) with a single short S1…S1' contact of 2.846(1) Å and a non-parallel

arrangement of the heterocyclic rings; the angle between the mean planes of $10.45^\circ.$

Computational investigation of these binding modes for the prototypical 3-phenyl benzothiadiazinyl radical found dimerization energies to be -14.3 and -14.8 kcal mol⁻¹ for the *trans*-antarafacial and *trans*-suprafacial motifs respectively, approximately twice those seen for the related dithiadiazolyl system³¹ (see ESI[†] for details). No energy minimum corresponding to a pancake dimer could be located for the suprafacial binding mode; instead this geometry was found to correspond to a transition state between S–N bonded σ -dimers. This discrepancy between gas-phase calculated geometries and solid-state structure for this orientation of interaction suggests that this mode of dimerisation depends on additional, second–sphere interactions in the solid state; this is unsurprising as pancake bonding is known to be sensitive to subtle changes in structure.³

Magnetism

Of the structurally characterised radicals, only **3c** and **3e** could be isolated in sufficient purity for magnetic studies, and their magnetic susceptibilities were measured over the temperature range 2–300 K. These confirm that the radicals are diamagnetic in the solid-state, as expected for spin-paired dimers, with no evidence of any magnetic phase transition at high temperature (see ESI†). Broken symmetry calculations^{32,33} have been successfully applied to a variety of heterocyclic sulphurnitrogen radicals,^{34–36} and were performed to explore the nature of the magnetic properties in **3c** and **3e** (see ESI† for details). For both systems, the calculated exchange interaction between the radical pair is strongly anti-ferromagnetic (J/k = -2629 and -6795 K respectively), consistent with observed spin pairing, net diamagnetism, and the large calculated dimerisation energies. The interaction between neighbouring radicals along the



Fig. 7 Dimerisation motifs, shown as side-on and top-down views, observed for 1,2,4-benzothiadiazinyl radicals: (a) **3a** – suprafacial; (b) **3c** and **3k**-*trans*-antarafacial; (c) **3e** – *trans*-suprafacial. The pendant aryl ring and substituents on the benzo-fused ring have been omitted for clarity.

 π -stack are also anti-ferromagnetic, albeit significantly weaker. This is in stark contrast to the behaviour seen for related benzothiadiazinyl radicals which retain their paramagnetism in the solid state^{9,16} and illustrates the sensitivity of these systems to substituents.

Conclusions

A new, efficient route to 1,2,4-benzothiadiazine 1-chlorides is reported wherein the use of neat SOCl₂ leads to reproducible patterns of chlorination on benzo and methyl substituents. This compact route proceeds directly from easily accessible precursors, with no need for pre-functionalisation of the amidines nor subsequent chlorination. Reduction of the benzothiadiazine 1chlorides leads to the formation of persistent benzothiadiazinyl radicals which have been characterised in situ by EPR spectroscopy and cyclic voltammetry. The existence of solution-state monomer-dimer equilibria is supported by both thermochromism and voltametric measurements. Four of these radicals have been structurally characterized by X-ray diffraction and exhibit three differing modes of $\pi^* - \pi^*$ pancake bonding. Two of these radicals were of sufficient purity for magnetic measurements, which confirm that they are diamagnetic in the solid state between 2-300 K, with pancake bonding quenching the inherent magnetism of the radicals. This is markedly different from the behaviour seen for related perhalogenated systems and shows that there remains much to be explored for this tunable radical scaffold.

Data availability

Crystallographic data for all relevant compounds has been deposited at the CCDC; deposition numbers are listed in the ESI.[†] All computational parameters are provided in the ESI.[†]

Author contributions

This work was initially undertaken by E. R. C., A. A., and J. M. R. at the University of Cambridge and completed by A. M. B, P. J. S., and E. R. C. at the University of Kent. Project design and oversight was led by J. M. R. and E. R. C. Synthetic work and physical measurements were completed by E. R. C, A. M. B., and P. J. S. with additional crystallographic measurements by A. A. Initial manuscript drafting was completed by A. M. B. with all authors contributing to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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