The condensation reaction of 2-aminobenzenethiols and 3-aminopyrazinethiols with 2-amino-6-fluoro-N-methylpyridinium triflate afforded thioether derivatives that were found to undergo Smiles rearrangement and cyclocondensation with sulphur monochloride to yield new hybrid 1,4-thiazine-1,2,3-dithiazolium cations. The synthesized cations were readily reduced to the corresponding stable neutral radicals with spin densities delocalized over both 1,4-thiazinyl and 1,2,3-dithiazolylium moieties.

Regardless of the wealth of data on cation radicals of phenothiazine, little is known about neutral phenothiazinyls even though these radicals were reported in the early 1960s. The majority of data on phenothiazinyl radicals are limited to spectroscopic studies and, to the best of our knowledge, there are no reports of X-ray crystallographic investigations. This is surprising considering that the related heterocyclic 1,2-thiazinyl radicals have been thoroughly characterized despite their persistent nature. Consequently, in an effort to extend the chemistry of neutral phenothiazinyl derivatives, we report the use of the Smiles rearrangement reaction to prepare new stable radicals \(5'\) that fuse the 1,4-thiazinyl and 1,2,3-dithiazolyl moieties into a single framework (Scheme 1).

The molecular scaffold in radicals \(5'\) was chosen because of the wide range of physical and chemical properties of thiazyli-based radicals that make them useful building blocks for...
molecular materials, both as free species and as coordinating ligands. While the first examples of closely related hybrid 1,2,3-dithiazolo-1,2,4-thiadiazinyl radicals have only been reported in the last few years, N-alkylpyridinium bridged bis-1,2,3-dithiazolyls and their selenium variants, with mirror plane symmetry, have been extensively explored. Many of these radicals were initially pursued as possible single component molecular conductors. However, their diverse magnetic properties, including ferromagnetic ordering, are notable compared to related classes of light atom molecular radicals such as nitroxides, triazinyls, and verdazyls. Thus, the pursuit of new molecular thiazyl radicals continues to attract considerable attention, which has now lead us to explore new extended aromatic systems based on the synthetically useful N-alkylpyridinium template.

The condensation reaction of 2-aminobenzenethiols (1a,b) and 3-aminopyrazinethiols (1c,d,e) with 2-amino-6-fluoro-N-methylpyridinium triflate (2[OTf]) in the presence of excess anhydrous Na₂CO₃ in acetonitrile (MeCN) afforded N-methylpyridinium thioether salts 3a–c[OTf] (Scheme 1, step i). Recrystallization of 3[OTf] from appropriate solvents gave analytically pure crystalline solids, which were characterized by IR and NMR (1H, 13C{1H}) spectroscopy as well as by single crystal X-ray diffraction analysis (for 3c[OTf], Fig. 1a).

It was anticipated that the salts 3[OTf] would undergo S → N Smiles rearrangement (SR) reaction by intramolecular nucleophilic attack of the benzo/pyrazine NH₂ group to form cationic Meisenheimer complexes Int1. This step has a very high activation barrier, TS1, in agreement with experimental observations. Furthermore, the formation of 4a and 4c is in both cases an essentially energy neutral process. However, what drives the SR reaction forward in the case of 4c is the possibility for 4c to tautomerize to the experimentally characterized form 4c, which renders the overall reaction exergonic by 43 kJ mol⁻¹. In this respect, it is surprising that no SR reaction was realized for 3d and 3e even though these derivatives are also able to tautomerize to the corresponding pyrazinethiones. A computational analysis of their reaction pathways showed that the formation of both 4d and 4e is exergonic, though only by 20 and 11 kJ mol⁻¹, respectively. Hence, the SR

![Fig. 1 ORTEP plots (left, thermal ellipsoids at 50% probability) and line drawings (right) of the cations in (a) 3c[OTf] MeCN and (b) 4c[OTf].](image)

![Fig. 2 Reaction coordinate diagram (PBE1PBE-IEFPCM/def2-TZVP) for the Smiles rearrangement reaction of 3a (red) and 3c (blue). For clarity, the structures of intermediates and transition states are only shown for the pathway from 3c to 4c.](image)
reaction becomes less-favoured for each chlorine substituent added, making 4c+ the most favourable product of the different derivatives a-e considered. Consequently, 4c+ is the only species generated under the experimental reaction conditions.

Having confirmed the identity of 4c+[OTf], its cyclocondensation with excess S2Cl2 was performed by refluxing the reactants in MeCN for 16 h (Scheme 1, step iii). Low-resolution positive ion electrospray ionization mass spectrometry (+ESI-MS) showed that the main products from the reaction were the salt 5c+[OTf] and the doubly chlorinated analogue 5e+[OTf]. Repeated syntheses confirmed that the 5c+[OTf]: 5e+[OTf] ratio is variable and does not depend on the reaction conditions in any obvious manner. However, the chlorinated product 5e+[OTf] could be crystallised from the reaction mixture using MeCN, affording a small amount of purple blocks. Unsatisfied with the low yield of 5e+[OTf], we attempted the direct reaction of S2Cl2 with thiocarbamide 3e+[OTf] that already contains an appropriate substitution of chlorine on the pyrazine ring to potentially afford another route to 5e+[OTf] (Scheme 1, step iv). To our delight, 5e+[OTf] was obtained in good isolated yield (78%) as confirmed by IR spectroscopy and +ESI-MS.

To explore the scope of this alternative pathway to 5+[OTf], the reactivity of 3a+[OTf], 3b+[OTf], 3d+[OTf] and 3e+[OTf] with S2Cl2 was also investigated. In the case of 3a+[OTf], +ESI-MS suggested that the product is a mixture of the non-chlorinated salt 5a+[OTf] with its chlorinated analogues containing one or more chlorine atoms. Hence, 5a+[OTf] was obtained in very low isolated yield (2%). Condensation reactions of S2Cl2 with aromatic amines containing an unsubstituted para-position (or those containing a good leaving group) are well-known to undergo simultaneous chlorination. Consequently, the reaction of S2Cl2 with the chlorinated species 3b+[OTf] and 3d+[OTf] was found to offer a practical route to derivatives 5b+[OTf] and 5d+[OTf] without further chlorination, albeit in moderate yield (43 and 48%, respectively). This further demonstrates that SR and cyclocondensation can take place concomitantly rather than sequentially, providing another route to different derivatives of 5+[OTf].

Cyclic voltammetry performed on solutions of 5+[OTf] in MeCN (with 0.1 M n-Bu4NPF6 as the supporting electrolyte) displayed a reversible +1/0 redox couple with $E_{1/2} = 0.031$ V and 0.220 V (vs. SCE) for 5b+[OTf] and 5e+[OTf], respectively. The cathodic shift in $E_{1/2}$ indicates that the heterocyclic aromatic substituent affects the electrochemical behaviour of the cations by altering the energy of their lowest unoccupied molecular orbital. This provides opportunities to fine-tune the electronic properties of the cations 5+ through careful choice of substituents. Furthermore, the $E_{1/2}$ values for 5b+[OTf] and 5d+[OTf] clearly demonstrate that octamethylferrocene (Me8Fc) is a suitable reducing agent for both cations. The cyclic voltammetry measurements also revealed that the 0/+1 redox couple is irreversible for 5e+[OTf], while 5b+[OTf] appears to undergo significant decomposition under the same conditions. The estimated $E_{\text{cell}}$ of 5c+[OTf] is 0.720 V, which is smaller than those of related bisdithiazolyl radicals ($E_{\text{cell}} = 0.851$ V) but comparable to analogous bishiazelenazolyls ($E_{\text{cell}} = 0.745$ V).14 Reduction of 5b+[OTf] and 5e+[OTf] was performed by slow diffusion of a degassed MeCN solution of the salt through a medium porosity sintered glass frit into a similar degassed MeCN solution of excess of Me8Fc. This afforded the radicals 5b' and 5e' as analytically pure crystalline solids (Scheme 1, step v). In the case of 5b', crystals suitable for single crystal X-ray diffraction were obtained as small lustrous bronze blocks. The crystal structure of 5b' belongs to the centrosymmetric monoclinic space group P21/c. The asymmetric unit consists of two essentially coplanar radicals in trans-coplanar arrangement (Fig. 3) with the shortest intermolecular C⋯C interactions very close to the sum of van der Waals radii.15 This suggests that the radicals are not strongly interacting in the solid state. The radicals in the asymmetric unit of 5b' and those related to them by an inversion centre form π-stacked motifs that are arranged in a herringbone pattern similar to those typically observed for related bisdithiazolyl radicals.14,16

The electronic structures of 5b' and 5e' were investigated by a combination of computational (PBE1PBE/def2-TZVP) methods and EPR spectroscopy. The calculations showed that the singly occupied molecular orbital and the spin density of 5' are delocalized over the molecular backbone (Fig. 4). Specifically, natural population analysis assigned 40 and 55% of the α-spin density of 5b' on the 1,4-thiazinyl and 1,2,3-dithiazolyl moieties, respectively; the spin distribution of 5e' is slightly more localised on the 1,2,3-dithiazolyl moiety. Consequently, the radicals 5 can be considered hybrids of 1,4-thiazinyls and 1,2,3-dithiazolyls, which underlines the fact that the line drawing in Scheme 1 is an oversimplified picture of their electronic structure. In this respect, population analyses of 5b'' and 5d'' showed that the sulphur atom on the 1,4-thiazinyl ring is the single most positively charged nucleus in the structures. However, the shortest anion-⋯cation contacts in crystal structures of 5b'[OTf] and 5d'[OTf] involve the two sulphur atoms on the 1,2,3-dithiazolyl moiety.

The room-temperature EPR spectrum of 5b' in CH2Cl2 (Fig. 5a) consists of an eight line pattern with $g = 2.0071$ and no fine-structure. A good simulation of the spectrum was obtained by using hyperfine couplings (hfcs) to the nitrogen nuclei in the dithiazolyl ($a_{N1} = 0.383$ mT) and thiazyl

![Fig. 3 ORTEP plot of the asymmetric unit of 5b' (thermal ellipsoids at 50% probability).](image-url)
The thiazinyl moiety is desired. Thus, we chose the quinoxaline cations, the stability of the radicals is of particular importance. To the pyrazine nitrogen atoms, which also revealed minute coupling of the unpaired electron (based on a computational analysis of line widths (mT) of 0.067/0.092 and 0.090/0.087 for 5b). The identity of 3f[OTf] and 4f[OTf] was confirmed by both NMR spectroscopy and single-crystal X-ray crystallography. This demonstrates that, when using appropriate 3-aminoquinolinethiols, the SR reaction is an extremely viable pathway for the synthesis of salts 4f[OTf], which yield the corresponding stable neutral radicals 5' after ring closure and reduction.

Conclusions

In this communication, we have shown that the Smiles rearrangement reaction, either followed by cyclocondensation or performed concurrently with it, offers a viable and modifiable route to a new class of hybrid 1,4-thiazine-1,2,3-dithiazolyl salts 5'[OTf], which can be readily reduced to yield the corresponding neutral radicals 5' with spin densities delocalized over both 1,4-thiazinyl and 1,2,3-dithiazolyl moieties. Future work will focus on the characterisation of transport properties of 5' and related radicals, along with the exploration of their coordination chemistry. This will provide opportunities for the design of molecular materials that may exhibit novel physical properties.

Conflicts of interest

There are no conflicts to declare.

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