Resonance stabilized *bis*-thiadiazinyl radicals

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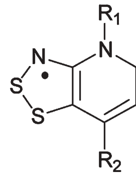
The resonance stabilized *bis*-thiadiazinyl framework holds potential as a stable and versatile building block for the design of radical-based conductors and magnetic materials.

Heterocyclic thiazyl radicals have emerged as versatile building blocks in the development of molecular conductors and magnets.[1–3] Critical to their use in conductive materials is the need for stable, highly delocalized systems which, in the solid state, exhibit a low on-site Coulomb repulsion, U.[4] To this end we have described a series of *bis*-dithiazolyl derivatives, **1**.[1]



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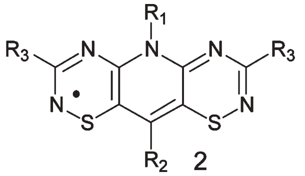

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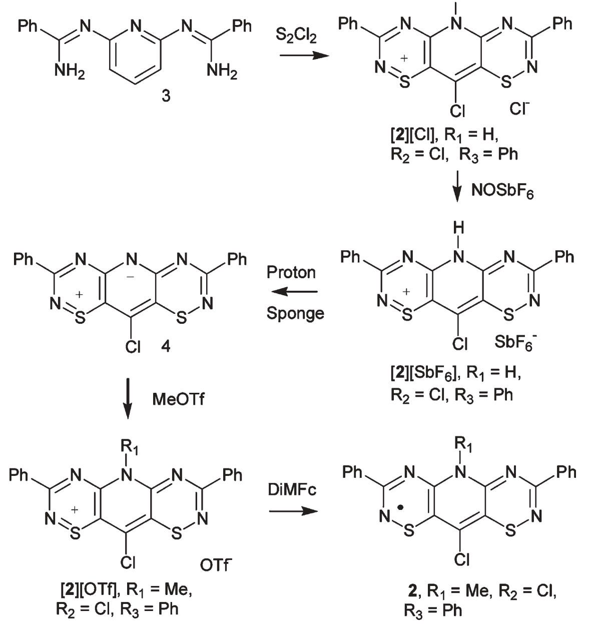
Resonance between the two dithiazolyl rings increases thermal stability, and reduces the computed gas phase disproportionation energies ΔH_{disp} and measured solution electrochemical cell potentials E_{cell}: trends which point to a lower value of U. Consistently, while conductivity in these materials remains activated, the thermal activation energies are lower than for simple non-resonance stabilized radicals.

In the pursuit of new π-radicals with good ion energetics, *i.e.* low ΔH_{disp} and E_{cell} values, we have modified the synthetic procedure used for **1** to allow access to the related *bis*-thiadiazinyl framework **2** (R_1 = Me, R_2 = Cl, R_3 = Ph).[1] While monofunctional thiatriazinyl[5] and thiadiazinyl radicals[6] have been previously described, this is to our knowledge the first report of a resonance stabilized *bis*-thiadiazinyl.

The synthetic sequence begins (Scheme 1) with the cyclocondensation of the bifunctional amidine **3**, itself prepared from 2,6-diaminopyridine, benzonitrile and $AlCl_3$,[7] with sulfur monochloride at reflux in chlorobenzene, to afford the protonated salt [**2**][Cl] (R_1 = H, R_2 = Cl, R_3 = Ph) in >70% yield. Metathesis of the blue-black insoluble chloride with $NOSbF_6$ in MeCN generates a deep blue solution which, upon solvent removal, provides lustrous deep red crystals of the corresponding hexafluoroantimonate salt. Treatment of this salt with Proton Sponge releases the zwitterionic base **4** which, when treated with methyl triflate (MeOTf) in DCE, furnishes the *N*-methyl salt [**2**][OTf] (R_1 = Me; R_2 = Cl, R_3 = Ph), crystals of which can be grown from MeCN. An ORTEP drawing of the asymmetric unit is shown in Fig. 1.



Scheme 1

Solutions of both the protonated and methylated salts described above are intensely coloured (λ_{max} = 622 nm, log ε = 4.69 for R_1 = Me) and, like the zwitterionic 16π -hexaaza-anthracene dyes with which they are isoelectronic,[8] are strongly fluorescent (λ_{em} = 642 nm for R_1 = Me). Cyclic voltammetry (Fig. 2) on solutions of [**2**][OTf] (R_1 = Me, R_2 = Cl, R_3 = Ph) in MeCN (with

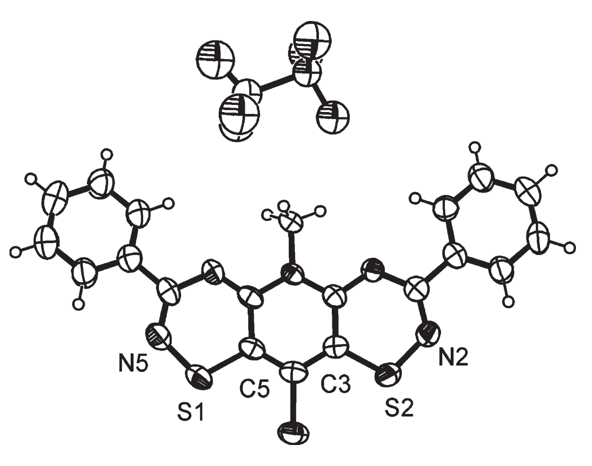


Fig. 1 ORTEP drawing (50% probability ellipsoids) of [**2**][OTf] (R_1 = Me, R_2 = Cl, R_3 = Ph). Selected distances: S1–N5, 1.633(3); S2–N2, 1.612(3); S1–C5, 1.704(3), S2–C3, 1.690(3) Å.

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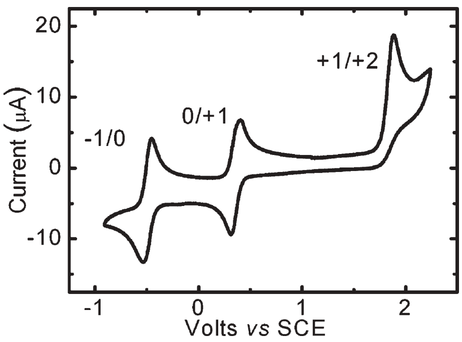

Fig. 2 CV scan of [**2**][OTf] (R_1 = Me, R_2 = Cl, R_3 = Ph) in MeCN.

Pt electrodes and $Bu^n{}_4NPF_6$ supporting electrolyte) reveals two reversible reduction waves for the $\mathbf{2}^{+1/0}$ ($E_{1/2}$ = 0.355 V *vs.* SCE) and $\mathbf{2}^{0/-1}$ ($E_{1/2}$ = −0.476 V *vs.* SCE) couples, as well as an irreversible oxidation wave (E_{pa} = 1.88 V *vs.* SCE) corresponding to the $\mathbf{2}^{+1/+2}$ process.

While these half-wave potentials are more anodic than those observed for **1**, *i.e.* **2** is more electronegative, the cell potential $E_{cell} = E_{1/2}(+1/0) - E_{1/2}(0/-1)$ = 0.83 V is almost identical to that found for **1**.[1] Accordingly the cell potential data, along with the calculated (B3LYP/6-31G**) gas phase ΔH_{disp} value of 4.72 eV obtained for a model **2** (with $R_1 = R_2 = R_3$ = H), represent a significant improvement over monofunctional thiadiazinyls,[6c] and militate in favour of a low on-site Coulomb repulsion, *U*.

Chemical and/or electrochemical reduction of the protonated salt [**2**][SbF_6] (R_1 = H, R_2 = Cl, R_3 = Ph) leads to proton migration (tautomerism)[1a] and degradation of the resulting radical. By contrast, chemical reduction of solutions of [**2**][OTf] (R_1 = Me, R_2 = Cl, R_3 = Ph) with dimethylferrocene (DiMFc) in MeCN affords rust colored fibrous crystals of the corresponding radical **2**. The material is remarkably stable, both in solution and the solid state, towards aerial oxidation and heat. Its EPR spectrum displays a rich hyperfine coupling pattern indicative of a highly delocalized spin distribution. Interpretation of the spectrum and extraction of hyperfine coupling constants was facilitated by deuteration of the phenyl rings, *i.e.* using d^5-benzonitrile, as in Fig. 3. B3LYP/6-31G** calculations on a model ($R_1 = R_2 = R_3$ = H) confirm the b_{1g} SOMO (Fig. 4), and provide spin densities and ^{14}N hyperfine coupling constants that are consistent with the experimental values.

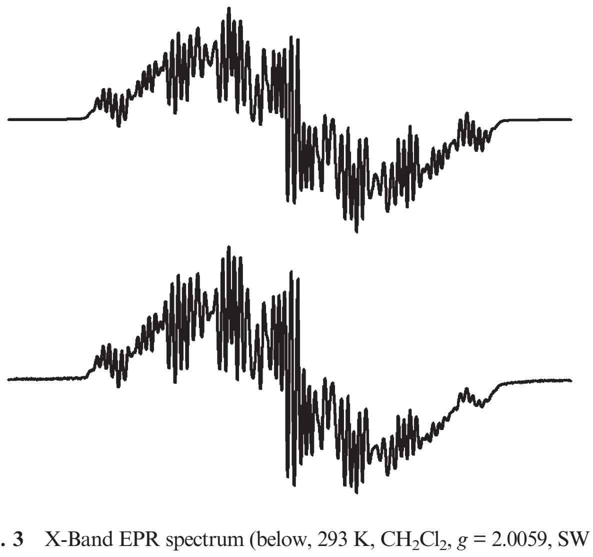

Fig. 3 X-Band EPR spectrum (below, 293 K, CH_2Cl_2, *g* = 2.0059, SW = 3 mT) of **2** (R_1 = Me, R_2 = Cl, $R_3 = C_6D_5$). Simulation (above, LW = 0.016 mT) with a_N = 0.268 (2N), 0.184 (2N) and 0.069 (1N), a_H = 0.033 (3H) and a_{Cl} = 0.029 (1 ^{35}Cl) mT.

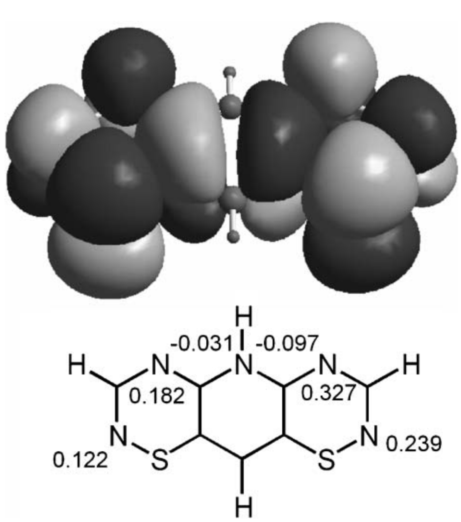

Fig. 4 B3LYP/6-31G** SOMO for **2** ($R_1 = R_2 = R_3$ = H), along with computed spin densities on nitrogen (left) and a_N values (mT, right).

Thin amber needles of the radical **2** (R_1 = Me, R_2 = Cl, R_3 = Ph) can be obtained by sublimation at 200 °C/10^{-4} Torr. A low temperature (173 K) X-ray structure analysis reveals that the radicals do not dimerize, are planar (including the phenyl groups) to within 0.18 Å, and adopt a slipped π-stack arrangement running along the *x* direction (Fig. 5). Temperature differences notwithstanding, the intramolecular distances, notably the S–N and S–C bonds, show slight increases relative to those seen in the cation that are consistent with the antibonding properties of the radical SOMO. Fig. 6 illustrates the slipped π-stack arrays of radicals, which are uniformly separated by an interplanar distance of 3.407(1) Å.

The magnetic susceptibility (χ) of **2** has been measured over the temperature range 4–350 K. A plot of 1/χ *vs.* *T* (Fig. 7) indicates Curie–Weiss behaviour with *C* = 0.360 emu mol^{-1} K^{-1}

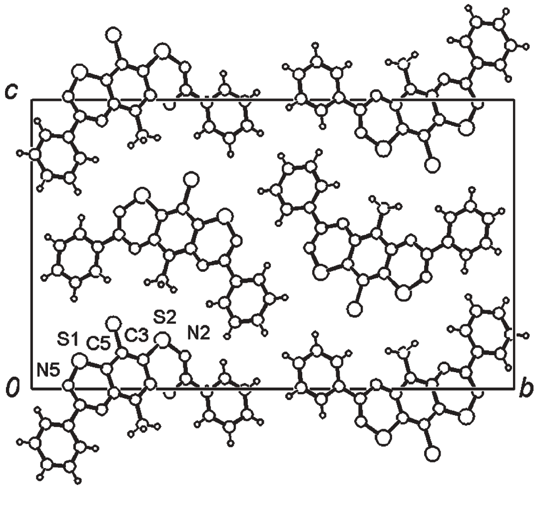

Fig. 5 Unit cell of **2** (R_1 = Me, R_2 = Cl, R_3 = Ph). Selected distances: S1–N5, 1.657(5); S2–N2, 1.662(5); S1–C5, 1.726(5), S2–C3, 1.735(5) Å.

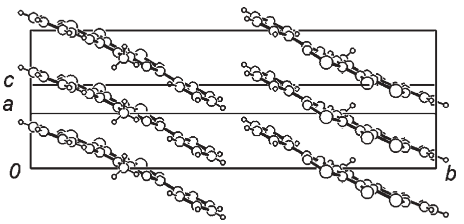

Fig. 6 Slipped π-stacks of **2** (R_1 = Me, R_2 = Cl, R_3 = Ph).

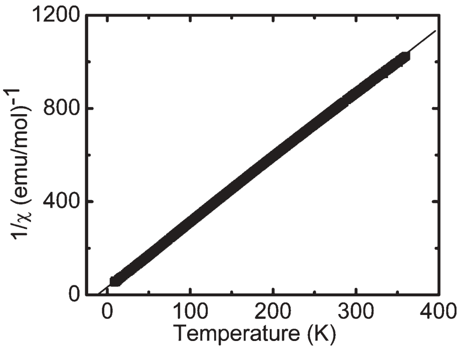

Fig. 7 A plot of 1/χ *vs.* *T* for **2** (R_1 = Me, R_2 = Cl, R_3 = Ph).

and $\theta = -11.9$ K. A pressed pellet conductivity measurement on **2** indicates a room temperature value σ_{RT} below 10^{-7} S cm^{-1}. Presumably the severe slippage of the π-stacks illustrated in Fig. 6 reduces the electronic bandwidth to the point where a Mott insulator state prevails.

Considerable synthetic opportunity nonetheless remains for variation in the nature of the exocyclic substituents R_1–R_3, and such modifications may afford materials with improved solid state structures and transport properties.†‡

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Notes and references

† Satisfactory chemical analyses were obtained for **3**, [**2**][OTf] and **2** (R_1 = Me, R_2 = Cl, R_3 = Ph). The IUPAC name for the radical is 10-chloro-5-methyl-3,7-diphenyl-5H-[1,2,4]thiadiazino[6′,5′:5,6]pyrido-[2,3-*e*][1,2,4]thiadiazin-2-yl.

‡ X-Ray data was collected on Bruker Apex and Rigaku Mercury CCD diffractometers with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å) using ω scans. The structures were solved and refined by full matrix least-squares analysis which minimized $\sum w(\Delta F)^2$. Data for [**2**][OTf] (R_1 = Me, R_2 = Cl, R_3 = Ph) at 295 K: $C_{21}H_{13}ClF_3N_5O_3S_3$, $M = 571.99$, orthorhombic, space group *Pbca*, with $a = 8.4474(6)$, $b = 13.9712(10)$, $c = 40.105(3)$ Å, $V = 4733.2(6)$ Å^3, $Z = 8$, $\mu = 0.486$ mm^{-1}. 329 parameters were refined using 5591 unique reflections to give $R = 0.0587$ and $R_w = 0.1615$. Data for **2** (R_1 = Me, R_2 = Cl, R_3 = Ph) at 173 K: $C_{20}H_{13}ClN_5S_2$, $M = 422.92$, monoclinic, space group $P2_1/c$, with $a = 3.9232(8)$, $b = 27.527(6)$, $c = 16.378(3)$ Å, $\beta = 90.17(3)°$, $V = 786.7(6)$ Å^3, $Z = 4$, $\mu = 0.470$ mm^{-1}. 253 parameters were refined using 3516 unique reflections to give $R = 0.0983$ and $R_w = 0.2159$. CCDC reference numbers 256271 and 256272. See http://www.rsc.org/suppdata/cc/b4/b417236a/ for a crystallographic file in .cif format.

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