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# Structure–property trends in π-stacked dithiazolo-dithiazolyl conductors

**Leanne Beer,[a] Jaclyn L. Brusso,[a] A. Wallace Cordes,[b] Erika Godde,[c] Robert C. Haddon,[c] Mikhail E. Itkis,[c] Richard T. Oakley*[a] and Robert W. Reed[a]**

[a] *Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada. E-mail: oakley@sciborg.uwaterloo.ca*

[b] *Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA*

[c] *Departments of Chemistry and Environmental Engineering, University of California, Riverside, California 92521, USA*

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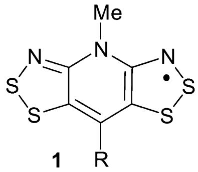
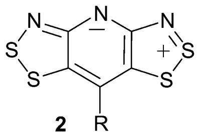
**The resonance stabilized dithiazolo-dithiazolyl radical 1b adopts a slipped π-stack structure exhibiting weak 1-D ferromagnetic coupling; variable temperature conductivity measurements indicate $\sigma_{\mathrm{RT}} = 2 \times 10^{-6}$ S cm$^{-1}$.**

In an ideal neutral radical conductor a stack of π-radicals should function like an array of atoms in an elemental metal; the bulk material would possess a half-filled energy band, as in elemental sodium, and possess a metallic ground state.[1] In practice, however, radicals tend to dimerize (a Peierls instability)[2] and, more importantly, if association can be suppressed, the high on-site Coulomb repulsion $U$ ($\approx$ IP − EA) associated with most stable radicals leads to a Mott insulating state.[3] The design of radicals with good ion energetics, *i.e.*, low disproportionation enthalpies ($\Delta H_{\mathrm{disp}}$ = IP − EA) is therefore crucial to the development of materials with enhanced conductivities.[4] In this regard the resonance stabilized 1,2,3-dithiazolo-1,2,3-dithiazolyl framework **1**, with calculated $\Delta H_{\mathrm{disp}}$ = 4.7 eV, represents an appealing building block.[5] In the solid state, however, the recently reported compound **1a** (R = Cl) is a Mott insulator, as a result of slippage of the radical π-stacks and consequent loss of bandwidth $W$.[5] In an effort to modify the crystal structure, and improve tranpsort properties, we have pursued the prototypal radical **1b** (R = H), in the belief that stack slippage might be reduced, and $W$ increased.

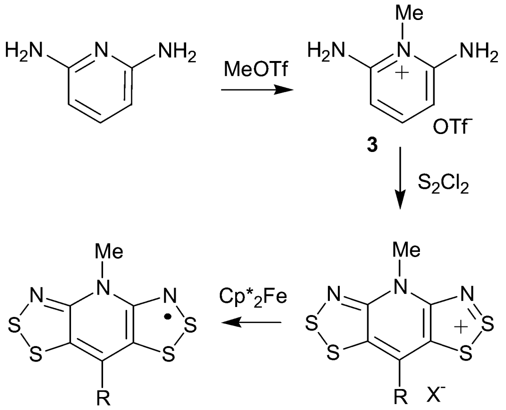


**1**



**2**

The reported preparative route to **1a** involves N-methylation of the zwitterionic heterocycle **2** (R = Cl)[6] with MeOTf followed by reduction of the resulting cation [**1**]$^+$ with Cp*$_2$Fe.[5] We have now developed a much simpler route which provides easy access to both **1a** and **1b**.† Both syntheses involve, as a first step, N-methylation of 2,6-diaminopyridine with MeOTf to give **3**.[7] This reaction affords a mixture of protonated and methylated salts,[8] from which the former can be removed by washing the crude product with NEt$_3$ in C$_2$H$_4$Cl$_2$. Subsequent treatment of **3** (3.02 g, 11.0 mmol) with excess S$_2$Cl$_2$ (17.8 g) at reflux in MeCN for 16 h affords a deep blue solution which, upon cooling, yields lustrous red plates of [**1a**][OTf] (4.38 g, 10.2 mmol, 93%). If **3** (5.1 g, 18.9 mmol) and S$_2$Cl$_2$ (13.5 g) are brought together in CH$_3$CN at room temperature in the presence of NEt$_3$ (11.6 g, 0.114 mmol) as an auxiliary base, and the mixture left to react for 5 days, a blue–black insoluble precipitate of [**1b**][Cl] is formed. Purification[5] and metathesis of the latter with AgSbF$_6$ in CH$_3$CN generates a deep blue solution which, upon solvent removal and recrystallization from HOAc, affords deep red crystals of [**1b**][SbF$_6$]. Subsequent reduction of [**1b**][SbF$_6$] (0.943 g, 1.94 mmol) with Cp*$_2$Fe (0.634 g, 1.94 mmol) in degassed CH$_3$CN affords **1b**, (0.425 g, 1.72 mmol, 89%), which may be recrystallized from degassed toluene as black needles.



**1a** (R = Cl)
**1b** (R = H)

[**1a**][X] (R =Cl)
[**1b**][X] (R = H)

The EPR spectrum of **1b** in CH$_2$Cl$_2$ (Fig. 1) is consistent with the expected spin distribution, and can be simulated in terms of strong coupling from the two wing nitrogens, with weaker coupling to the central N, the unique proton and the N-methyl protons. Cyclic voltammetry on solutions of [**1b**][SbF$_6$] in MeCN (Pt electrodes, $\mathrm{Bu}^{n}{}_4\mathrm{NPF}_6$ supporting electrolyte) reveals a reversible reduction wave (**1b**$^{+/0}$) with $E_{\frac{1}{2}} = -0.130$ V (*vs.* SCE) and an irreversible reduction (**1b**$^{0/-1}$) with $E_{\mathrm{pc}} = -0.952$ V (*vs.* SCE). As expected from the replacement of Cl by H, both these processes occur at slightly more cathodic potentials than those in **1a**.[5] The peak-to-peak separation $E_{\mathrm{pc}}(\mathbf{1}^{+/0}) - E_{\mathrm{pc}}(\mathbf{1}^{0/-1}) = 0.789$ V in **1b** is smaller than **1a** (0.830 V). These data all militate in terms of a low on-site Coulomb repulsion $U$.[9]

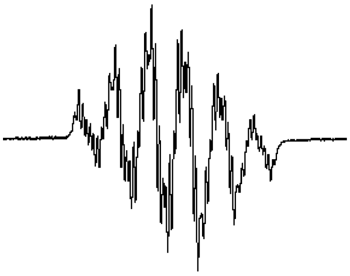


**Fig. 1** EPR spectrum (293 K, CH$_2$Cl$_2$, SW = 3 mT, $g$ = 2.0082) of radical **1b**. Hyperfine coupling constants are $a_{\mathrm{N}}$ = 0.317 (2N) and 0.0620 (1N), $a_{\mathrm{H}}$ = 0.230 (1H) and 0.034 (3H) mT.

The crystal structure of radical **1b**‡ belongs to the orthorhombic space group $P2_12_12_1$, as does that of **1a**.[5] The cell packing (Fig. 2), with radical π-stacks hinged around $2_1$ axes, is similar to that of **1a**. At 293 K the unit cell dimensions $b$ (15.194(5) Å in **1a**, 11.962(3) Å in **1b**) and $c$ (15.069(4) Å in **1a**, 18.262(5) Å in **1b**) are, however, substantially different. The

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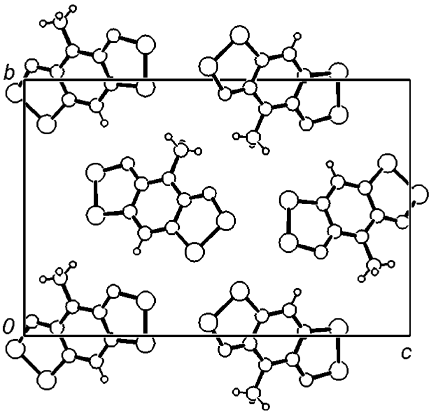

**Fig. 2** Unit cell of **1b**.

cell repeat distances *a* also differ (4.2464(12) Å in **1a**, 3.9626(10) Å in **1b**). The latter parameters herald a change in the degree of slippage in the π-stacks. As illustrated in Fig. 3, the slippage angle $\tau$ (the angle between the mean molecular plane and the stacking axis) is larger for **1b**, *i.e.*, the radicals are more nearly superimposed, as expected from the replacement of Cl by H. However, the plane-to-plane separation $\delta$ is also larger, suggesting that Me···Me repulsions are forcing the molecules apart as they slide on top of one another.§

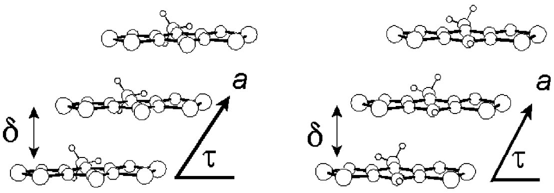

**Fig. 3** Slipped π-stacks in **1a** (left) and **1b** (right) illustrating the plate slippage angles $\tau$ ( = 54.81(13)° in **1a** and 62.04(7)° in **1b**) and mean plane separations $\delta$ ( = 3.470(5) Å in **1a** and 3.500(6) Å in **1b**).

Magnetic susceptibility ($\chi$) measurements on microcrystalline samples of **1b** have been performed over the temperature range 320–5 K. Like **1a**, the temperature dependence of $\chi$ for **1b** shows a Curie dependence down to near 100 K, with $C$ = 0.345, $\chi_0$ = 120.4 × $10^{-6}$ emu mol$^{-1}$. Consistently, the number of Curie spins (Fig. 4) remains constant near 0.92 down to 125 K, and then starts to rise. There is slight discontinuity at 85 K, which may signal a subtle phase change similar to that observed for **1a**, after which the free spin count increases more sharply, reaching a value of 7.2 at 5 K. This enhancement is characteristic of weak ferromagnetic coupling along the π-stacks.[5,10]

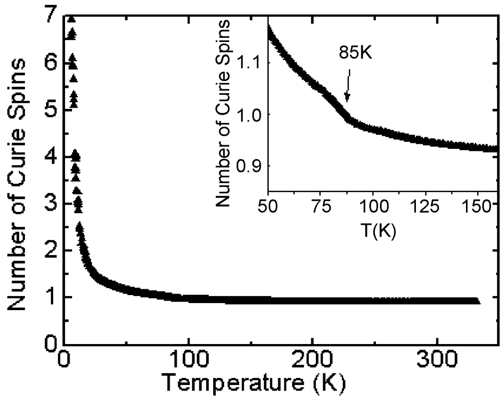

**Fig. 4** Number of Curie spins *vs* *T* for **1b**.

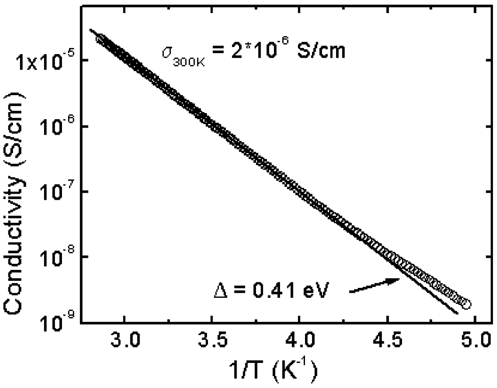

**Fig. 5** Single crystal conductivity of **1b** as a function of 1/*T*.

Single crystal conductivity ($\sigma$) measurements along the needle axis of **1b** over the temperature range 320–150 K indicate (Fig. 5) that the conductivity is activated, with a value of $\sigma$ = 2 × $10^{-6}$ S cm$^{-1}$ at 300 K, *i.e.*, very close to that found for **1a**.[5] The derived activation energy Δ (one-half of the band gap for an intrinsic semiconductor) is 0.41 eV (0.42 eV for **1a**).

We attribute the similarity in the magnetic and conductivity behaviour of **1a** and **1b** to the combined effects of decreases in both $\tau$ and $\delta$. Because the changes offset one another, there is very little difference in (EHT calculated) intrastack overlap, and hence bandwidth *W*, between the two compounds.[5]

## Notes and references

† Satisfactory chemical analyses were obtained for **1b** and [**1b**][SbF$_6$]. The IUPAC name for **1b** is 4-methyl-4*H*-bis[1,2,3]dithiazolo[4,5-*b*:5′,4′-e]pyridin-2-yl.

‡ Crystal data for **1b**: data were collected at 293 K on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.7107 Å) using $\omega$ scans. The structure was solved and refined by full matrix least-squares analysis which minimized $\Sigma w(\Delta F)^2$. $C_6H_4N_3S_4$, $M$ = 246.36, orthorhombic, space group $P2_12_12_1$, with $a$ = 3.9626(10), $b$ = 11.962(3), $c$ = 18.262(5) Å, $V$ = 865.6(4) Å$^3$, $Z$ = 4, $D_c$ = 1.890 g cm$^{-3}$, $\mu$ = 1.044 mm$^{-1}$. 134 parameters were refined using 977 (all) unique reflections to give $R$ = 0.0338 and $R_w$ = 0.0597. CCDC 191497. See http://www.rsc.org/suppdata/cc/b2/b207735n/ for crystallographic data in CIF or other electronic format.

§ Mean intramolecular distances (ranges in parentheses) for **1b**: S–S, 2.097(10); S–N, 1.660(1); N–C, 1.311(6); S–C, 1.727(2) Å.

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