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Resonance Stabilized Bisdiselenazolyls as Neutral Radical Conductors

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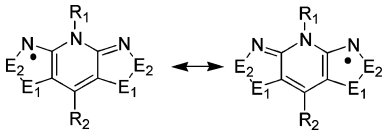
Heterocyclic thiazyl radicals hold considerable potential in the design of both conductive and magnetic materials.[1] In the pursuit of improved conductivity we developed a series of radicals based on the bis-1,2,3-dithiazolyl framework **1** (Chart 1, $E_1 = E_2 = S$).[2−4] These resonance stabilized systems enjoy lower molecular disproportionation energies ΔH_{disp} and cell potentials E_{cell} than their monofunctional counterparts and, as a result, a reduced solid-state on-site Coulomb repulsion U. However, the steric bulk of the substituents R_1 and R_2 forces the radicals to crystallize in slipped rather than superimposed π-stack arrays. The resultant loss in intermolecular overlap between neighboring radicals reduces the bandwidth W of the associated half-filled energy band, and a Mott insulating ground state prevails. One approach to improving W is to incorporate selenium in place of sulfur. Sequential replacement of sulfur by selenium affords, in principle, the three selenium based radicals **2**−**4**. We recently described methods for the partial introduction of selenium, as in **2**,[5] but to date methods to access the isomeric mixed S/Se materials **3** and the all-selenium radicals **4** have been elusive. Herein we report the preparation and solid-state characterization of the first examples of **3** and **4** (with R_1 = Me, R_2 = H).

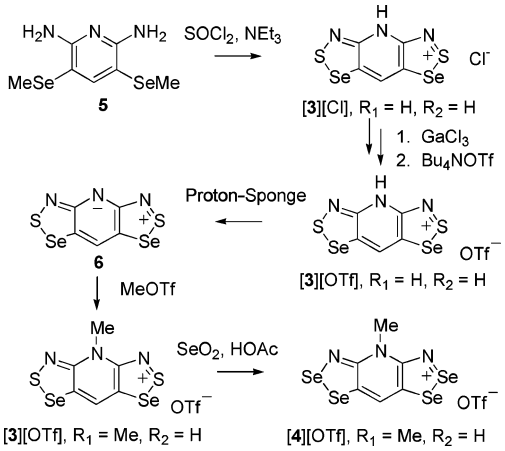
Chart 1



	E_1	E_2
1	S	S
2	S	Se
3	Se	S
4	Se	Se

The critical intermediate in the synthetic sequence (Scheme 1) to both **3** and **4** is diamino-bis(methylseleno)-pyridine **5**. This material is readily generated by reduction ($NaBH_4$/MeOH) and methylation (MeI) of the diaminopyridine-bis(selenocyanate), which itself is prepared in a manner analogous to that used for the corresponding bis(thiocyanate).[3b] Subsequent cleavage of the Se−C(methyl) bonds of **5** and ring closure to the desired heterocyclic framework can be effected with an excess of thionyl chloride[6] in the presence of triethylamine, using MeCN as solvent. The resulting black, insoluble chloride salt [**3**][Cl] ($R_1 = R_2$ = H) is purified by conversion to a tetrachlorogallate and metathesis of the latter to a trifluoromethanesulfonate or triflate (OTf^-) salt. Deprotonation of green solutions of [**3**][OTf] ($R_1 = R_2$ = H) in MeCN with Proton-Sponge affords the zwitterion **6** as a green insoluble powder. Treatment of **6** with methyl triflate in DCE yields a sparkling red precipitate of the *N*-methyl salt [**3**][OTf] (R_1 = Me, R_2 = H), which crystallizes from hot glacial acetic acid as red needles, λ_{max}(MeCN) = 700 nm ($\log \epsilon = 4.6$). Finally, conversion of [**3**][OTf] (R_1 = Me, R_2 = H) to [**4**][OTf] (R_1 = Me, R_2 = H) can be achieved by boiling the former in glacial acetic acid in the presence of SeO_2.[5c] Recrystallization of [**4**][OTf] (R_1 = Me, R_2 = H) from MeCN affords deep red flakes, λ_{max}(MeCN) = 736 nm ($\log \epsilon = 4.7$).

Scheme 1



Chemical reduction of the salts [**3**][OTf] and [**4**][OTf] to the respective radicals **3** and **4** (R_1 = Me, R_2 = H) was achieved with octamethylferrocene in MeCN. Single-crystal X-ray analysis[7] of the bronze needles of **3** established that it is essentially isostructural with **1** (R_1 = Me, R_2 = H),[3] both compounds belonging to the orthorhombic space group $P2_12_12_1$ and differing only in the sense of their chirality. In the case of **4**, however, the radical precipitates as brown microcrystals unsuitable for single crystal work. X-ray powder diffraction measurements on this material, followed by Rietveld analysis starting from the coordinates and the space group of **3**,[7] nonetheless allowed us to confirm that this compound is also isostructural with **1** and **3**. A drawing of the unit cell of **4** is shown in Figure 1. Table 1 provides the unit cell parameters of the three isostructural radicals and also provides a summary of the pertinent intermolecular E···E′ contacts (E = S, Se).

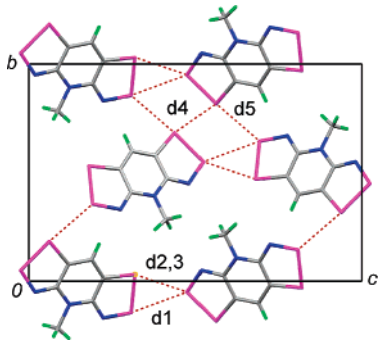


Figure 1. Unit cell of **4** (R_1 = Me, R_2 = H), showing intermolecular Se···Se′ contacts.

In contrast to **2** (R_1 = Me, R_2 = H), which associates in the solid state as laterally Se−Se σ-bonded dimers,[5b] all three radicals **1**, **3**, and **4** (R_1 = Me, R_2 = H) crystallize in an undimerized fashion, the discrete radicals packing in slipped π-stack arrays along the

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Table 1. Crystal Data and Intermolecular Contacts d1−d5

radical[a]	**1**[b]	**3**	**4**
a, Å	3.9626(10)	4.11070(4)	4.199(5)
b, Å	11.962(3)	11.79530(10)	12.181(13)
c, Å	18.262(5)	18.6524(2)	18.64(2)
d1, Å	3.371(1)	3.494(1)	3.479(3)
d2, Å	3.666(1)	3.604(1)	3.692(3)
d3, Å	3.745(1)	3.790(1)	3.834(3)
d4, Å	3.437(1)	3.473(1)	3.561(2)
d5, Å	3.394(1)	3.314(1)	3.335(2)

[a] R_1 = Me, R_2 = H. [b] Reference 3a.

x-direction. These arrays are linked into ribbons running parallel to the *z*-direction by a series of close E···E′ contacts d1−d3. In addition, there are two E···E′ interactions d4 and d5 that bridge neighboring ribbons along the *y*-direction. Collectively, this network of intermolecular interactions generates a closely knit and relatively three-dimensional electronic structure.

The very low solubility of **3** and **4** (R_1 = Me, R_2 = H) in organic solvents precludes their characterization by solution-based EPR methods. Solid-state magnetic measurements as a function of temperature have been performed on both compounds. These experiments confirm that the radicals are not spin paired in the solid state. Plots of $\chi_P T$ versus T, where χ_P is the magnetic susceptibility corrected for diamagnetic contributions, are shown in Figure 2. In both cases $\chi_P T$ approaches 0.375 near room temperature, as expected for undimerized $S = {}^1/_2$ systems, but at lower temperatures its value drops steadily, indicative of strong antiferromagnetic intermolecular coupling. Curie-Weiss fits to the high-temperature data (above 160 K for **3** and above 100 K for **4**) afforded Curie constants $C = 0.377$ and 0.392 emu K mol^{-1}, and θ-values of −78.3 and −44.3 K for **3** and **4**, respectively. By contrast, the all-sulfur radical **1** (R_1 = Me, R_2 = H) exhibited essentially paramagnetic behavior, with weak ferromagnetic coupling at very low temperatures.[3]

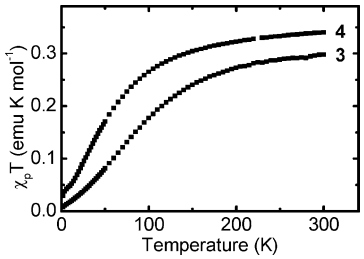

Figure 2. Plots of $\chi_P T$ vs T for **3** and **4** (R_1 = Me, R_2 = H).

Previous four-probe single-crystal conductivity (σ) measurements on **1** (R_1 = Me, R_2 = H) as a function of temperature indicated Mott insulator behavior, with a room-temperature conductivity $\sigma(295\ \text{K}) = 2 \times 10^{-6}$ S cm^{-1} and thermal activation energy E_{act} = 0.41 eV.[3] The results of four-probe pressed pellet measurements on **3** and **4** (R_1 = Me, R_2 = H) are illustrated in Figure 3. Sequential incorporation of selenium leads to progressive improvement in the conductivity, with $\sigma(295\ \text{K}) = 3 \times 10^{-4}$ and 1×10^{-3} S cm^{-1} for **3** and **4**, respectively. At the same time the value of E_{act} is reduced to 0.24 eV in **3** and 0.17 eV in **4**.

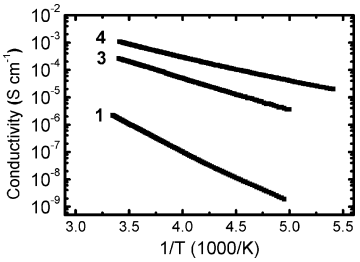

Figure 3. Conductivity of **1**, **3**, and **4** (R_1 = Me, R_2 = H) as a function of inverse temperature. Data for **1** are from ref 3b.

In summary, we have developed a general synthetic route to the all-selenium based resonance stabilized radicals **4**. Structural analyses on **3** and **4** (R_1 = Me, R_2 = H) confirm that lattice and π-delocalization energies are sufficient to prevent solid-state dimerization of the radicals. Incorporation of selenium leads to a dramatic increase in conductivity and reduction in thermal activation energy relative to sulfur based radicals. Modification of the R_1/R_2 groups and/or the application of physical pressure, as found for derivatives of **2**,[5c] may well lead to an even better performance, and perhaps a metallic state.

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Supporting Information Available: Experimental procedures, π-stacking diagram of **4**, and crystallographic data in CIF format for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Crystal data for **3** at 298(2) K: $C_6H_4N_3S_2Se_2$, MW = 340.16, orthorhombic; space group $P2_12_12_1$, with a = 4.11070(4), b = 11.79530(10), c = 18.6524(2) Å, V = 904.398(12) Å^3, Z = 4, D_{calcd} = 2.498 g cm^{-3}, μ = 14.154 mm^{-1}; 123 parameters were refined using 1588 unique reflections to give R = 0.0213 and R_w = 0.0579. Crystal data for **4** at 298(2) K: $C_6H_4N_3Se_4$, MW = 433.96; orthorhombic, space group $P2_12_12_1$, with a = 4.199(5), b = 12.181(13), c = 18.64(2) Å, V = 953.1(18) Å^3, Z = 4, D_{calcd} = 3.024 g cm^{-3}. Powder X-ray data analysed by Rietveld methods based on the coordinates and space group of **3**, allowing for full anisotropic refinement of the selenium atoms and isotropic refinement of all other non-hydrogen atoms gave Rp = 0.0629 and wRp = 0.0782.

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