Resonance Stabilized Bisdiselenazonyls 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, E1 = E2 = S).2−4 These resonance stabilized systems enjoy lower molecular disproportionation energies \( \Delta H_{\text{disp}} \) and cell potentials \( E_{\text{cell}} \) 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 \( \pi \)-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 portionation energies \( \Delta H_{\text{disp}} \) on the bis-1,2,3-dithiazolyl framework is to incorporate selenium in place of sulfur. Sequential replacement of both conductive and magnetic materials. 1 In the pursuit to both

1

Chemical reduction of the salts [3][OTf] and [4][OTf] to the respective radicals 3 and 4 (\( R_1 = \text{Me}, R_2 = \text{H} \)) was achieved with octamethylferrocene in MeCN. Single-crystal X-ray analysis7 of the bronze needles of 3 was established that it is essentially isostructural with 1 (\( R_1 = \text{Me}, R_2 = \text{H} \)), both compounds belonging to the orthorhombic space group \( P2_12_12_2 \) 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).

Chart 1

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 (NaBH₄/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] (\( R_1 = R_2 = \text{H} \)) 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] (\( R_1 = R_2 = \text{H} \)) 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] (\( R_1 = \text{Me}, R_2 = \text{H} \)), which crystallizes from hot glacial acetic acid as red needles, \( \lambda_{\text{max}}(\text{MeCN}) = 700 \text{ nm} \) (log \( \epsilon = 4.6 \)). Finally, conversion of [3][OTf] (\( R_1 = \text{Me}, R_2 = \text{H} \)) to [4][OTf] (\( R_1 = \text{Me}, R_2 = \text{H} \)) can be achieved by boiling the former in glacial acetic acid in the presence of SeO₂.6c Recrystallization of [4][OTf] (\( R_1 = \text{Me}, R_2 = \text{H} \)) from MeCN affords deep red flakes, \( \lambda_{\text{max}}(\text{MeCN}) = 736 \text{ nm} \) (log \( \epsilon = 4.7 \)).

Figure 1. Unit cell of 4 (\( R_1 = \text{Me}, R_2 = \text{H} \)), showing intermolecular Se⋯Se contacts.

In contrast to 2 (\( R_1 = \text{Me}, R_2 = \text{H} \)), which associates in the solid state as laterally Se⋯Se \( \sigma \)-bonded dimers,8b all three radicals 1, 3, and 4 (\( R_1 = \text{Me}, R_2 = \text{H} \)) crystallize in an undimerized fashion, the discrete radicals packing in slipped \( \pi \)-stack arrays along the

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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 (R1 = Me, R2 = 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 χP vs T, where χP is the magnetic susceptibility corrected for diamagnetic contributions, are shown in Figure 2. In both cases χP 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 I (R1 = H, R2 = H) exhibited essentially paramagnetic behavior, with weak ferromagnetic coupling at very low temperatures.³

Previous four-probe single-crystal conductivity (σ) measurements on 1 (R1 = Me, R2 = H) as a function of temperature indicated Mott insulator behavior, with a room-temperature conductivity of 2 × 10⁻⁶ S cm⁻¹ and thermal activation energy E₉0 = 0.41 eV.³ The results of four-probe pressed pellet measurements on 3 and 4 (R1 = Me, R2 = H) are illustrated in Figure 3. Sequential incorporation of selenium leads to progressive improvement in the conductivity, with σ(295 K) = 3 × 10⁻⁴ and 1 × 10⁻³ S cm⁻¹ for 3 and 4, respectively. At the same time the value of E₉0 is reduced to 0.24 eV in 3 and 0.17 eV in 4.

In summary, we have developed a general synthetic route to the all-selenium based resonance stabilized radicals 4. Structural analyses on 3 and 4 (R1 = Me, R2 = 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 R₁/R₂ groups and/or the application of physical pressure, as found for derivatives of 2,⁵ may well lead to an even better performance, and perhaps a metallic state.

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Supporting Information Available: Experimental procedures, σ-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.

References

7. Crystal data for 3 at 298(2) K. C₂H₄N₃Se₄MW = 340.16, orthorhombic: space group P2₁₂₁₂, with a = 4.11070(4), b = 11.7953(10), c = 18.6524(2) Å, V = 904.398(12) Å³, Z = 4, D₀calc = 2.498 g cm⁻³, μ = 14.154 mm⁻¹; 123 parameters were refined using 1588 unique reflections to give R = 0.0213 and Rₛ = 0.0579. Crystal data for 4 at 298(2) K. C₂H₄N₃Se₄MW = 433.90, orthorhombic: space group P2₁2₁2₁, with a = 4.199(5), b = 12.181(13), c = 18.642(2) Å, V = 953.1(18) Å³, Z = 4, D₀calc = 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 χ² = 0.0782.

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