The effect of selenium incorporation on the bandwidth and conductivity of neutral radical conductors

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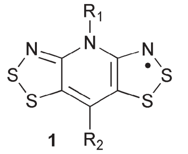
The first example of an undimerized π-stacked *bis*-1,2,3-thiaselenazolyl radical displays improved bandwidth and conductivity relative to an isostructural *bis*-1,2,3-dithiazolyl.

The design of single component molecular conductors based on neutral π-radicals requires the development of building blocks that fulfill stringent molecular and solid state criteria.[1] Dimerization of the radicals must be suppressed, and yet strong lattice wide intermolecular interactions must be maintained in order to generate sufficient electronic bandwidth W to overcome the onsite Coulomb repulsion U, which is a maximum for a half-filled energy band. If $W > U$, a metallic state prevails, but if $W < U$, the system falls into a Mott insulating trap.[2] In pursuit of the metallic state we have developed and explored the resonance stabilized *bis*-1,2,3-dithiazolyls **1**.[3,4] While the computed gas phase disproportionation enthalpies ΔH_{disp} and solution cell potentials E_{cell} found for these materials suggest a lower value for U in the solid state, their bulk conductivities remain activated, with thermal activation energies E_a of 0.4–0.5 eV and room temperature conductivities $\sigma_{\mathrm{RT}} \sim 10^{-6}$ S cm^{-1}, indicating that the bandwidth W is insufficient to offset U.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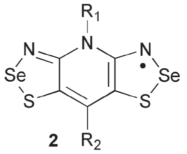
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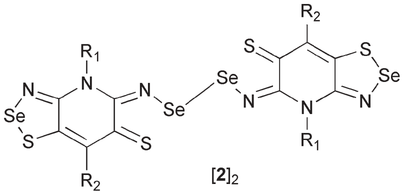
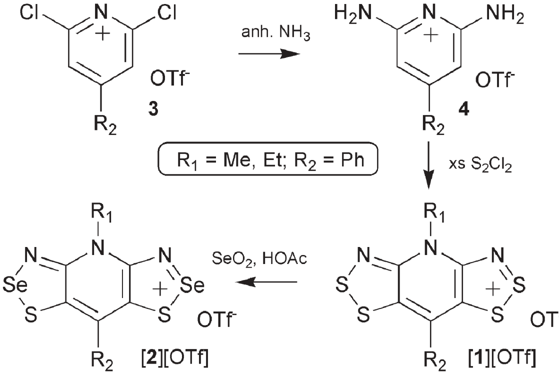

[2]$_2$

In order to address this bandwidth deficiency we have sought to explore the effects on structure and transport properties of the replacement of sulfur by selenium, a design approach recognized early on in the development of CT salts.[5] Recently we described the preparation and structural characterization of the first example of a *bis*-1,2,3-thiaselenazolyl **2** (R_1 = Et, R_2 = H). However, in the solid state this radical associated to produce the σ-bonded dimer **[2]$_2$**, which behaved as a small band gap semiconductor.[6] While cofacial π-dimerization of selenazyl radicals is ubiquitous,[7] the observation of this lateral mode of association was surprising, and prompted the question as to whether it would ever be possible to prevent spin-pairing dimerization of selenazyl radicals. Herein we describe the preparation of **2** (R_1 = Et, R_2 = Ph), the first example of a selenazyl radical to crystallize as an open shell system.

We have developed a new synthetic sequence (Scheme 1) to the necessary *bis*-1,2,3-thiaselenazolylium triflates **[2]**[OTf] which is significantly simpler than that described earlier.[6] The method takes advantage of the direct insertion of selenium into a *bis*-1,2,3-dithiazolylium cation **[1]**$^+$ by using SeO_2 in refluxing acetic acid.[8] Triflate salts of the latter cation **[1]**[OTf] were prepared by the amination of the *N*-alkylated dichloropyridine **3**, and subsequent double Herz cyclization of the resulting diamino compound **4** with S_2Cl_2.† Initially we pursued this procedure with a view to preparing the known sulfur based radical **1** (R_1 = Me, R_2 = Ph),[4] and hence its selenium containing variant **2**, our intent being to generate and compare the transport properties of an isostructural pair. To our chagrin, reduction of **[2]**[OTf] (R_1 = Me, R_2 = Ph) with octamethylferrocene (OMFc) afforded **2** as a fibrous mass which we were unable to characterize crystallographically. The synthetic sequence was therefore repeated using R_1 = Et, R_2 = Ph and, to our satisfaction, slow diffusion of solutions of **[2]**[OTf] and OMFc afforded **2** as burnished bronze needles suitable for single crystal X-ray work.‡



Scheme 1

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All the radicals **1** and **2** (R_1 = Me, Et; R_2 = Ph) have been characterized by cyclic voltammetry (on their salts in MeCN, Pt electrodes, Bu_4NPF_6 supporting electrolyte) and by EPR spectroscopy (in CH_2Cl_2). Half-wave potentials $E_{½}$ for the three reversible couples (−1/0, 0/+1, +1/+2) are provided in Table 1, along with the *g*-values and hyperfine coupling constants a_N for the two wing (2N) and central (1N) nitrogens. The derived cell potentials E_{cell} are consistent with a slightly lower *U* for the selenium containing radicals.

Table 1 CV[a] and EPR[b] data for **1** and **2** (R_1 = Me, Et; R_2 = Ph)

	R_1 = Me		R_1 = Et	
	1	**2**	**1**	**2**
$E_{½}{}^{+1/+2}$	1.193	1.255	1.295	1.245
$E_{½}{}^{0/+1}$	−0.214	−0.082	−0.118	−0.097
$E_{½}{}^{-1/0}$	−1.064	−0.852	−0.970	−0.974
$E_{cell}{}^{c}$	0.851	0.768	0.852	0.777
g	2.0086	2.0014	2.0086	2.0113
a_N (2N)	0.32	0.32	0.317	0.32
a_N (1N)	0.06	0.06	0.06	0.06

[a] $E_{½}$ values in V *vs.* SCE. [b] Hyperfine coupling constants in mT. [c] $E_{cell} = E_{½}{}^{0/1} - E_{½}{}^{-1/0}$.

Crystals of the *bis*-1,2,3-thiaselenazolyl **2** (R_1 = Et, R_2 = Ph) belong to the trigonal space group $P3_121$ and are isostructural with the *bis*-1,2,3-dithiazolyl **1** (R_1 = Me, R_2 = Ph). Unit cell data for both compounds are compiled in Table 2, along with selected intermolecular chalcogen–chalcogen contacts.

Table 2 Unit cell dimensions[a] and intermolecular contacts[a] for **1** (R_1 = Me, R_2 = Ph)[b] and **2** (R_1 = Et, R_2 = Ph)

	a = *b*	*c*	d1	d2	d3
1	16.182(3)	4.2947(12)	3.287(1)	3.507(1)	3.467(1)
2	15.733(6)	4.973(3)	3.397(2)	3.763(3)	3.595(3)

[a] Distances in Å, angles in °; ESDs in parentheses. [b] Reference 4.

A unit cell drawing of **2** (R_1 = Et, R_2 = Ph) is shown in Fig. 1. The radicals are not dimerized, either in the conventional sense, through overlap of the π-SOMOs,[7] or in the more unusual σ-fashion [**2**]$_2$ found for **2** (R_1 = Et, R_2 = H).[6] Indeed the nesting of the phenyl and ethyl groups and the consequent pinwheel-like packing of the radicals about the 3_1 screw axis militates against this latter mode of association. The radicals lie on a two-fold axis which leads to disorder in the *N*-ethyl groups; this was resolved and refined by standard methods (only one component is shown in the Figures). The tricyclic framework is not completely planar. As in the corresponding sulfur compound **1** there is a slight propeller style warping of the molecular plane about the two-fold axis, creating a dihedral angle of 12.5° between the two five-membered C_2NSSe rings.

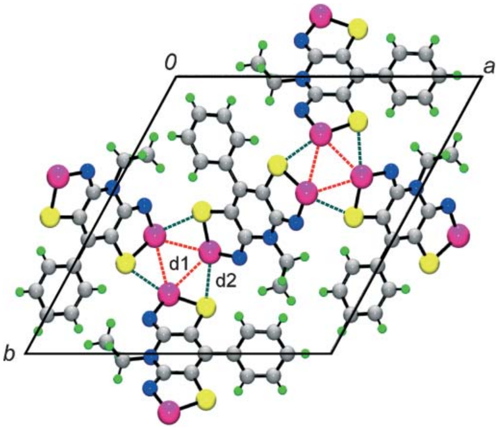

Fig. 1 Unit cell of **2** (R_1 = Et, R_2 = Ph). Intermolecular contacts d1, d2 are defined in Table 2.

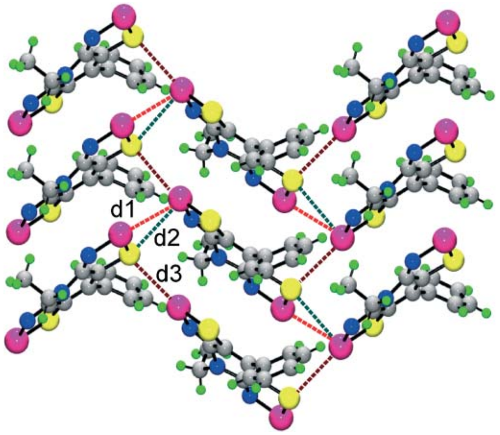

Fig. 2 Herring-bone π-stacks in **2** (R_1 = Et, R_2 = Ph). Intermolecular contacts d1–d3 are defined in Table 2.

The radicals in **2** (R_1 = Et, R_2 = Ph) form slipped π-stacks running along the *z* direction, with a plate-to-plate separation of 3.70(2) Å, *cf.* 3.557(6) Å in **1** (R_1 = Me, R_2 = Ph). These are locked into herring-bone arrays, as shown in Fig. 2. Both compounds display a series of close intermolecular chalcogen–chalcogen contacts d1–d3 (Table 2) which lace the radical termini together around and along the 3-fold screw axis. These values are well within the expected van der Waals separations[9] for S–S′, Se–S′, and Se–Se′ interactions and collectively generate a well-developed electronic structure in three dimensions.

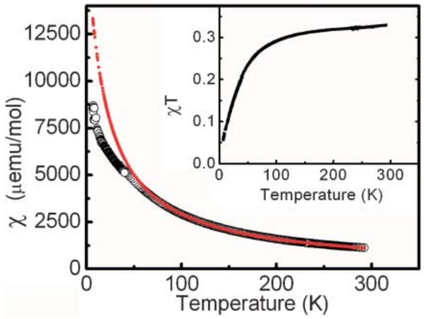

Fig. 3 *χ vs. T* plot for **2** (R_1 = Et, R_2 = Ph). Inset is a plot of *χT vs. T*.

A plot of the magnetic susceptibility *χ* of **2** (R_1 = Et, R_2 = Ph), corrected for diamagnetic contributions, as a function of temperature (Fig. 3) indicates that the material is a paramagnet. A Curie–Weiss fit to the data above 80 K provides values of

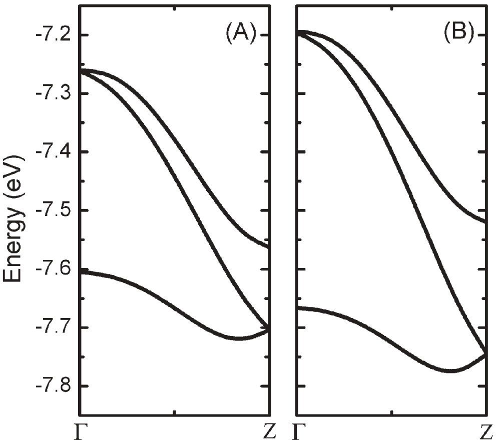

Fig. 4 EHT band dispersion along c^* of the radical SOMOs of (A) **1** (R_1 = Me, R_2 = Ph) and (B) **2** (R_1 = Et, R_2 = Ph).

C = 0.349 and $\Theta = -19.5$ K. The relatively constant value of χT above 100 K indicates that the material behaves essentially as an $S = ½$ spin system, with a free Curie spin count of 88% at 293 K.

In order to compare the extent of electronic interactions found in **1** (R_1 = Me, R_2 = Ph) and **2** (R_1 = Et, R_2 = Ph) we have carried out Extended Hückel Theory (EHT) band structure calculations on the two crystal structures. The results, presented in Fig. 4 as plots of dispersion curves along c^* of the crystal orbitals (COs) arising from the three SOMOs within the unit cell, indicate that while the contacts d1–d3 are collectively longer in **2** than in **1**, they are stronger. As a result the incorporation of selenium in place of sulfur leads to an increase in bandwidth W which, based on the energetic spread of the three COs, we estimate to be from 0.46 eV to 0.61 eV. Variable temperature conductivity measurements on **2** (R_1 = Et, R_2 = Ph) provide a value of $\sigma_{RT} = 5 \times 10^{-6}$ S cm^{-1}. While the conductivity remains activated, the value of E_a = 0.32 eV is markedly lower than in all reported derivatives of **1**.[3]

It is thus apparent that the replacement of sulfur by selenium, *i.e.*, **1** → **2** has the desired effect of increasing bandwidth and hence reducing the thermal activation energy for electronic conduction. Further improvement in performance can be achieved by the use of external (physical) pressure. As shown in Fig. 5 the application of 4 GPa pressure to **1** (R_1 = Me, R_2 = Ph) and 5 GPa to **2** (R_1 = Et, R_2 = Ph) leads to increases in σ_{RT} approaching 3 orders of magnitude, the selenium compound showing a larger response at lower pressures. Variable temperature measurements over the range T = 20 to 90 °C on **1** (at 4 GPa) affords an E_a value of 0.25 eV, while that of **2** (at 5 GPa) is reduced to 0.19 eV, *i.e.*, about one-half that observed at room temperature, and indicative of a close approach to the metallic state.

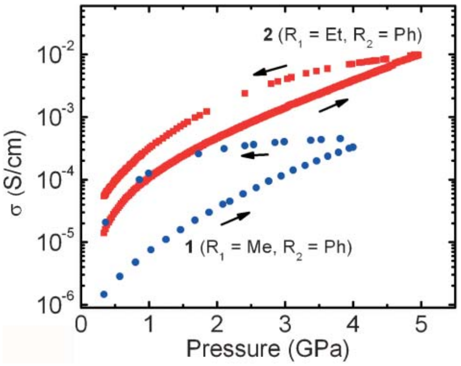

Fig. 5 Conductivity of **1** (R_1 = Me, R_2 = Ph) and **2** (R_1 = Et, R_2 = Ph) as a function of pressure. Arrows denote direction of change in pressure.

Notes and references

† Satisfactory chemical analyses were obtained for compounds **1** to **4**, [**1**][OTf] and [**2**][OTf] (R_1 = Me, Et; R_2 = Ph).

‡ Crystal data at 298(2) K for **2** (R_1 = Et, R_2 = Ph): $C_{13}H_{10}N_3S_2Se_2$, M = 430.28, space group $P3_121$, $a = b$ = 15.733(3), c = 4.973(3) Å, V = 1066.0(9) Å^3, Z = 3, D_{calcd} = 2.011 g cm^{-3}, μ = 5.487 mm^{-1}; 106 parameters were refined using 1401 unique reflections to give R = 0.0607 and R_w = 0.1241. CCDC 281599. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511648a

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