Self-association of the *N*-methyl benzotellurodiazolylium cation: implications for the generation of super-heavy atom radicals†

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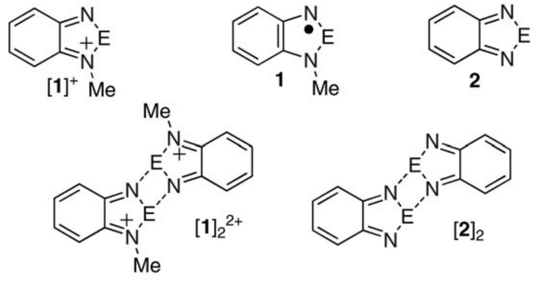
The *N*-methyl benzotellurodiazolylium cation self-associates in the solid state *via* short (2.471(3) Å) 4-center Te···N′ intermolecular contacts; electrochemical data and the results of DFT calculations suggest that the dimers persist in solution.

There is increasing interest in the applications of heavy atom radicals in the design of molecular materials with conductive and magnetic properties.[1] Recently we have demonstrated that the replacement of sulfur by selenium in *bis*-dithiazolyls can lead not only to enhanced conductivity,[2] but also to appealing magnetic effects, *i.e.*, spin-canted antiferromagnetism[3] and bulk ferromagnetism.[4] These findings prompt the question as to whether the incorporation of tellurium will further enhance transport properties. To date, however, there are no examples of neutral tellurium-based radicals.

In order to test the potential stability of tellurazyl radicals we are exploring new families of cationic chalcogen–nitrogen heterocycles which might, upon reduction, afford radicals. To this end we have prepared and characterized the triflate salts of the *N*-methylated benzochalcodiazolylium cations $[\mathbf{1}]^+$ (E = S, Se, Te) (Scheme 1). Reduction of these cations (E = S, Se) affords radicals **1** which can be characterized by EPR spectroscopy. The corresponding Te-based radical cannot, however, be generated in this way. Comparison of the solution electrochemistry of the parent cations $[\mathbf{1}]^+$, and of the solid state structures of the triflate salts [**1**][OTf], indicates that for E = Te, strong intermolecular association of the cation, to form $[\mathbf{1}]_2^{2+}$, alters its redox chemistry and hence its ability to serve as source of the radical **1**.



Scheme 1

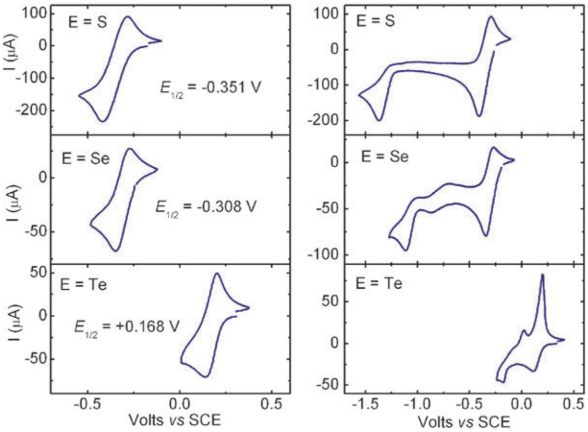


Fig. 1 CV scans on [**1**][OTf] (E = S, Se, Te) in MeCN with restricted (left) and wide (right) scan ranges.

The triflate salts [**1**][OTf] (E = S, Se, Te) were prepared by methylation[5] of the corresponding diazole **2** with methyl triflate.† In the case of E = Te, the parent ring **2** was generated by the direct reaction of *o*-phenylenediamine with TeO_2 at 180 °C, using a method adapted from one used for **2** (E = Se).[6] Cyclic voltammetry (Fig. 1) on the three salts in MeCN (with Pt electrodes and $Bu^n{}_4PF_6$ supporting electrolyte) revealed for E = S a reversible +1/0 wave with $E_{1/2} = -0.351$ V (*vs.* SCE) and an irreversible 0/−1 wave with $E_{pc} = -1.36$ V. For E = Se, a similar +1/0 wave, with $E_{1/2} = -0.308$ V, was observed, but electrochemical reversibility of the +1/0 wave could only be achieved if the negative scan range was not extended too far beyond the half-wave potential. In the case of E = Te, a similar situation was found, but the only reversible reduction wave was found at $E_{1/2} = +0.168$ V, *i.e.*, at a far more anodic potential than those observed for E = S, Se.

In order to probe the electronic structures of the putative radicals **1** (E = S, Se and Te) we have carried out a series of DFT calculations using the B3LYP hybrid functional, with 6-31G(d,p) basis sets for C, H, N and S, and SDB-cc-pVTZ effective core potential basis sets for Se and Te.[7] The results, summarized in Fig. 2, indicate remarkably similar spin distributions and (ΔSCF) ionization potentials (IP) for the three radicals, a conclusion which, in the case of E = S and Se, is substantiated by the EPR spectra of the radicals, the latter generated by *in situ* reduction of the corresponding cations with cobaltocene in CH_2Cl_2. As illustrated in Fig. 3, the

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† Electronic supplementary information (ESI) available: Details of synthetic procedures, analytic and spectroscopic characterization, and PCM calculations. Crystallographic data in CIF format (CCDC 680269–680271). See DOI: 10.1039/b803159b

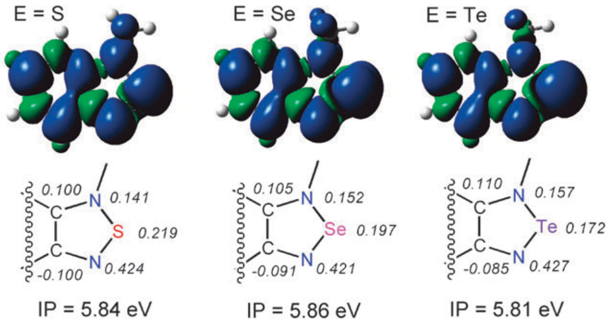

Fig. 2 DFT spin densities and adiabatic IPs for **1** (E = S, Se, Te).

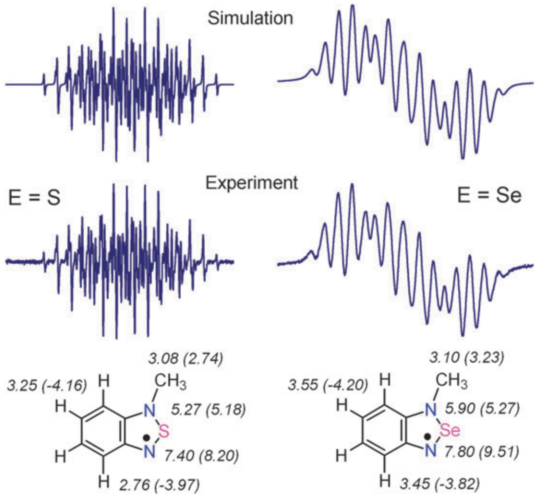

Fig. 3 EPR spectra of **1** (E = S, Se) in CH_2Cl_2; SW = 60 G, g = 2.0039 (E = S), g = 2.0016 (E = Se). Experimentally derived (by simulation) and calculated (in parentheses) coupling constants (in G) are shown below.

hyperfine coupling constants derived by simulation of the spectra are in close agreement with those obtained from the DFT calculations. As expected from spin–orbit effects,[8] there is more line broadening for E = Se. The g-value is, however, lower, although similar trends in g-values have been noted elsewhere.[9] All attempts to observe an EPR signal for the Te-based radical by reduction of [**1**][OTf] were unsuccessful.

While the correspondence between theory and experiment for E = S and Se was satisfying, the inability to generate an EPR spectrum for the Te-based radical and the anomalous CV behavior of $[\mathbf{1}]^+$ (E = Te) were troublesome. Added to these concerns were differences in the response of the ^{77}Se and ^{125}Te NMR chemical shifts occasioned by the methylation of the parent heterocycle **2** (E = Se, Te) to afford [**1**][OTf]. Thus, while N-methylation of **2** (E = Se) induced only a small change in δ (^{77}Se), from 1523 ppm (in d_3-MeCN, *cf.* 1526 ppm in d_6-DMSO)[10] to 1515 ppm in [**1**][OTf], N-methylation of **2** (E = Te) gave rise to a much larger change in δ (^{125}Te), from 1372 ppm (in d_6-DMSO) to 1175 ppm in [**1**][OTf].

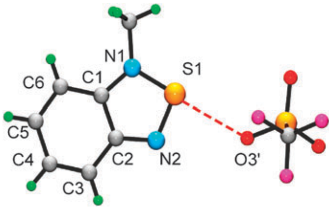

Fig. 4 A single ion pair in [**1**][OTf] (E = S), with atom numbering. Selected distances: S1–N1, 1.656(2); S1–N2, 1.583(2); N1–C1, 1.348(3); N2–C2, 1.353(3); S1···O3′, 2.820(2) Å.

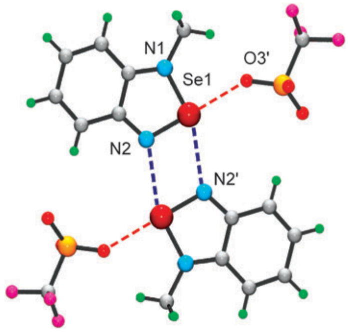

Fig. 5 A dimeric ion pair in [**1**][OTf] (E = Se). Atom numbering follows Fig. 4. Selected distances: Se1–N1, 1.824(5); Se1–N2, 1.765(5); N1–C1, 1.334(7); N2–C2, 1.328(7); Se1···N2′, 2.711(4); Se1···O3′, 2.823(8) Å.

In order to learn more about the structure of the cations $[\mathbf{1}]^+$, we carried out crystal structure determinations of the three salts [**1**][OTf] (E = S, Se, Te). Crystals suitable for X-ray work were grown from $C_2H_4Cl_2$ or MeCN.‡ The crystal structure of [**1**][OTf] (E = S) shown in Fig. 4 holds few surprises. There are several S···O′ cation–anion contacts, the shortest of which is 2.820(2) Å, but no cation–cation contacts. By contrast, the structure of [**1**][OTf] (E = Se) shown in Fig. 5 reveals pairs of cations dimerized across an inversion center and linked by 4-center Se···N′ contacts (2.711(4) Å). Comparable interactions have been observed in the structures of other N-alkylated selenodiazoles[11] and related cations.[12]

The tellurium-based salt [**1**][OTf] (E = Te) also consists of centrosymmetric $[\mathbf{1}]_2^{2+}$ dimers linked by 4-center Te···N′ interactions, as shown in Fig. 6. These contacts (2.417(3) Å) are, however, extremely short, well inside the van der Waals separation,[13] and even shorter than the corresponding contacts in the parent heterocycle **2**.[14] In the present case, the usually easy distinction between intramolecular (primary) and intermolecular (secondary) bonding[15] has broken down.

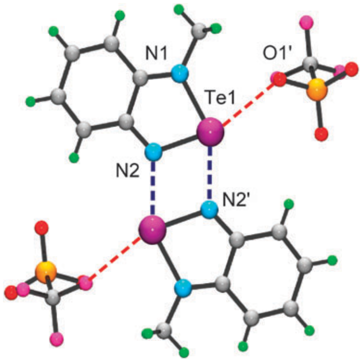

Fig. 6 The dimer $[\mathbf{1}]_2[\mathrm{OTf}]_2$ (E = Te). Atom numbering follows Fig. 4. Selected distances: Te1–N1, 2.093(3); Te1–N2, 1.990(4); N1–C1, 1.317(6); N2–C2, 1.319(5); Te1···N2′, 2.417(3); Te1···O1′, 2.869(4) Å.

Recent structural[14,16] and computational[17] studies on the parent benzochalcodiazoles **2** (E = S, Se, Te) and related compounds has provided much insight into their propensity to self-associate in the solid state *via* 4-center E···N′ contacts, as in [**2**]$_2$. Solid state packing patterns are influenced by these interactions, which increase in strength from S to Se to Te.[17] The observation of even tighter 4-center contacts between cations is at first surprising, as electrostatic repulsion would militate against such pairings. But there are numerous examples of Group 16 cation–cation pairs, *e.g.*, $S_2I_4^{2+}$,[18] and anion–anion pairs, *e.g.*, $S_2O_4^{2-}$,[19] which are stabilized in the solid state by lattice effects.

The structural results on [**1**][OTf] (E = Te) prompt a reappraisal of its solution properties, namely its anomalous redox behavior and the large shift in δ (^{125}Te) upon alkylation of **2**. Both these findings could be rationalized if the strong Te···N′ interactions observed in the solid state were also present in solution. To test this possibility, we have carried out a series of DFT calculations using the Polarized Continuum Model (PCM)[20] to simulate the effects of solvation on the equilibrium between [**1**]$^+$ and the ion-pair [**1**]$_2^{2+}$ (E = S, Se, Te). The results are shown in Fig. 7, which shows a plot of the free energy of dimerization ΔG_{dim} of [**1**]$^+$ in MeCN as a function of the E···N′ distance. It must be noted that in the gas phase all of the dimers are unstable, although local potential energy minima are found for E = Se and Te. In the case of E = S the inclusion of solvation is insufficient to offset electrostatic repulsion, and association in solution is neither expected nor observed. For E = Se, the situation is less clear-cut. The calculations are marginally in favor of the retention of dimers [**1**]$_2^{2+}$ in solution, with ΔG_{dim} reaching a shallow minimum of −3.2 kcal mol^{-1} near 2.6 Å. The CV and NMR data (in MeCN) are nonetheless consistent with an equilibrium which favors discrete [**1**]$^+$ cations. When E = Te, however, the results are unequivocal; solvation is more than sufficient to overcome mutual cation–cation repulsion, and the dimer dication [**1**]$_2^{2+}$ displays a well-defined minimum near 2.4 Å with ΔG_{dim} = −11.1 kcal mol^{-1}.

Based on these results, we conclude that in high dielectric solvents the tellurium cation [**1**]$^+$ exists as a dimer [**1**]$_2^{2+}$. Accordingly, electrochemical reduction in MeCN should occur at more anodic potentials, and a large change in δ (^{125}Te) upon methylation of **2** (in DMSO) is not unexpected. The larger issue, of how to generate the neutral radical **1**, remains unresolved. We are currently pursuing the design of tellurium-based heterocycles in which the cationic state is less prone to self-association, so that direct one-electron reduction to a radical can be effected.

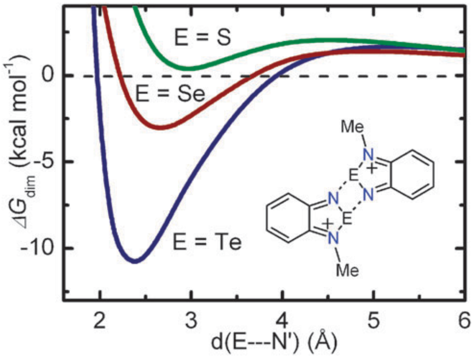

Fig. 7 Calculated ΔG_{dim} of [**1**]$^+$ in MeCN as a function of E···N′ separation in [**1**]$_2^{2+}$ at PCM/B3LYP/6-31G(d,p) (E = S) and PCM/B3LYP/6-31G(d,p)/SDB-cc-pVTZ (E = Se, Te) levels.

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Notes and references

‡ Crystal data at 296(2) K for [**1**][OTf]. E = S: $C_8H_7F_3N_2O_3S_2$, M = 300.28, space group $P2_1/c$, a = 6.495(2), b = 11.427(4), c = 16.481(6) Å, β = 99.424(7)°, V = 1206.6(7) Å^3, Z = 4, D_{calcd} = 1.653 g cm^{-3}, μ = 0.48 mm^{-1}; 163 parameters were refined using 2629 unique reflections to give R = 0.0424 and R_w = 0.1066. E = Se: $C_8H_7F_3N_2O_3SSe$, M = 347.18, space group $P2_1/c$, a = 8.403(2), b = 8.5474(19), c = 16.738(4) Å, β = 95.910(4)°, V = 1195.8(5) Å^3, Z = 4, D_{calcd} = 1.928 g cm^{-3}, μ = 3.355 mm^{-1}; 163 parameters were refined using 2400 unique reflections to give R = 0.0613 and R_w = 0.1437. E = Te: $C_{16}H_{14}F_6N_4O_6S_2Te_2$, M = 791.65, space group $P\bar{1}$, a = 6.8089(5), b = 8.1785(7), c = 11.3633(9) Å, α = 100.884(2), β = 95.645(2), γ = 106.4140(10)°, V = 588.29(8) Å^3, Z = 1, D_{calcd} = 2.234 g cm^{-3}, μ = 2.747 mm^{-1}; 163 parameters were refined using 2379 unique reflections to give R = 0.0325 and R_w = 0.0676.

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