Electronic Supporting Information

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

Maarit Risto, Robert W. Reed, Craig M. Robertson, Raija Oilunkaniemi, Risto S. Laitinen* and Richard T. Oakley*

Contribution from: Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1 Canada, Department of Chemistry, University of Oulu, P.O. Box 3000, FI-90014 Finland.

Contents

1 Synthetic Details Page S2
2 Physical and Spectroscopic Measurements Page S4
3 Theoretical Calculations Page S6
4 References and Notes Page S7
Synthetic Details

**General Procedures and Starting Materials** All reactions were carried out under an atmosphere of dry nitrogen. Selenium dioxide, tellurium dioxide, 2,1,3-benzothiadiazole, o-phenylenediamine, and methyl trifluoromethanesulfonate were obtained commercially and used as received. 2,1,3-Benzoselenadiazole was prepared by the reaction of SeO₂ with o-diphenyleneamine according to the literature procedure. All solvents were at least the reagent grade; acetonitrile and dichloroethane were dried by distillation over P₄O₁₀ under a nitrogen atmosphere prior to use. Fractional sublimations were performed in an ATS series 3210 three-zone tube furnace, mounted horizontally, and linked to a series 1400 temperature-control system. Melting points are uncorrected. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ.

**Preparation of 2,1,3-benzotellurodiazole 2 (E = Te).** A mixture of tellurium dioxide (3.00 g, 18.8 mmol) and o-phenylenediamine (3.00 g, 27.7 mmol) were melted together at 180 °C for 45 min. The dark red solid was dissolved in hot DMSO (75 mL) and filtered. The filtrate was cooled to the room temperature and 30 mL of toluene was added to complete the crystallization of 2,1,3-benzotellurodiazole. The bronze crystals were filtered off, washed twice with toluene, and dried in vacuo. The crude product (1.60 g, 6.91 mmol, 37 %) was purified by gradient tube sublimation over a range of 50-125 °C/10⁻³ Torr. Yield after sublimation 1.20 g (5.18 mmol, 28 %). IR (cm⁻¹): 3067 (w), 3051 (w), 3007 (w), 1508 (s), 1298 (vw), 1151 (m), 1132 (w), 901 (vw), 778 (w), 740 (s), 730 (vs), 703 (m), 685 (s). ¹H NMR (d₆-DMSO): δ 7.50, 7.49, 7.48, 7.47, 7.26, 7.25, 7.24, 7.23 [4H, AA’BB’, phenyl group]. ¹²⁵Te NMR (d₆-DMSO): δ 1372.²

**Preparation of N-methyl-benzothiadiazolium triflate [1][OTf] (E = S).** Methyl trifluoro-methanesulfonate (1.8 mL, 15.9 mmol) was added slowly to a solution of 2,1,3-benzothiadiazole (2.00 g, 14.7 mmol) in dichloroethane (30 mL). The mixture was stirred overnight at room temperature. The pale yellow crystalline solid obtained by diethyl ether (30 mL) precipitation was filtered, washed twice with diethyl ether, and dried in vacuo. Yield 4.14 g (13.8 mmol, 94 %); mp. 88-90 °C. Anal. Calcd. for C₈H₇F₃O₃N₂S₄: C, 32.00; H, 2.35; N, 9.33 %. Found: C, 33.21; H, 2.47; N, 9.11 %. IR (cm⁻¹): 3101 (m), 3084 (sh), 1602 (w), 1544 (m), 1499 (m), 1329 (m), 1300 (s), 1259 (vs, br), 1222 (s), 1163 (vs, br), 1139 (s), 1056 (m), 1027 (vs), 1003 (m), 927 (m), 864 (vw) 842 (s),
772 (vs), 678 (w), 637 (vs), 576 (m), 493 (w), 414 (m). $^1$H NMR (CD$_3$CN): $\delta$ 8.27-8.00 [m, 4H, phenyl group], 4.59 [s, 3H, N(CH$_3$)]. The X-ray quality crystals of [1][OTf] (E = S) were obtained by recrystallization from dichloroethane layered with diethyl ether.

**Preparation of N-methyl-benzoselenadiazolium triflate [1][OTf] (E = Se).** Methyl trifluoromethanesulfonate (0.60 ml, 5.30 mmol) was added slowly to a yellow solution of 2,1,3-benzoselenadiazole (0.883 g, 4.82 mol) in dichloroethane (20 mL). The mixture was stirred overnight at room temperature. The yellow solid was filtered off, washed with cold dichloroethane, and dried in vacuo. Yield 1.48 g (4.26 mmol, 88%); mp. 157-158 °C. Anal. Calcd. for C$_8$H$_7$F$_3$O$_3$N$_2$SSe: C, 27.68; H, 2.03; N, 8.07 %. Found: C, 27.92; H, 2.16; N, 7.99 %. IR (cm$^{-1}$): 3095 (w), 3067 (vw), 3018 (vw), 1532 (m), 1503 (w), 1323 (vw), 1258 (vs, br), 1224 (m), 1169 (s), 1159 (sh), 1030 (vs), 761 (s), 638 (vs), 518 (m). $^1$H NMR (CD$_3$CN): $\delta$ 8.06-7.80 [m, 4H, phenyl group], 4.57 [s, 3H, N(CH$_3$)]. $^{77}$Se$^1$H NMR (CD$_3$CN): $\delta$ 1515. The X-ray quality crystals of [1][OTf] (E = Se) were obtained by recrystallization from dichloroethane.

**Preparation of N-methyl-benzotellurodiazolium triflate [1][OTf] (E = Te).** Methyl trifluoromethanesulfonate (1.5 mL, 13.3 mmol) was added slowly to the slurry of benzotellurodiazole (1.50 g, 6.47 mol) in dichloroethane (50 mL). The mixture was heated overnight at 60 °C. The red solid was filtered off, washed twice with dichloroethane, and dried in vacuo. Yield 2.23 g (5.63 mmol, 87%); dec > 125 °C. Anal. Calcd. for C$_8$H$_7$F$_3$O$_3$N$_2$STe: C, 24.28; H, 1.78; N, 7.08 %. Found: C, 24.09; H, 2.01; N, 6.85 %. IR (cm$^{-1}$): 3190 (vw), 3123 (vw), 3067 (vw), 1532 (w), 1511 (m), 1418 (w), 1335 (vw), 1282 (vs), 1234 (vs), 1167 (s), 1152 (s), 1142 (s, sh), 1029 (vs), 799 (vw), 765 (m), 759 (sh), 736 (s), 642 (vs), 596 (m), 574 (m), 568 (m), 518 (s), 495 (vw). $^1$H NMR (CD$_3$CN) 7.78-7.59 [m, 4H, phenyl group], 4.42 [s, 3H, N(CH$_3$)]; $\delta$ (d$_6$-DMSO) 7.74-7.54 [m, 4H, phenyl group], 4.39 [s, 3H, N(CH$_3$)]. $^{125}$Te NMR (d$_6$-DMSO): $\delta$ 1175. The X-ray quality crystals of [1][OTf] (E = Te) were obtained by recrystallization from MeCN.
Physical and Spectroscopic Measurements

**X-Ray Crystallography.** Crystals of [1][OTf] (E = S, Se, Te) were glued to a glass fiber with epoxy. Diffraction data were collected on a Bruker SMART APEX CCD-based diffractometer at 296 K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXL-97 and refined by least-squares methods on F² using SHELXL-97 incorporated in the SHELXTL suite program. After the full-matrix least-squares refinement of non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions in the aromatic rings (C-H = 0.95 Å) and in the methyl groups (C-H = 0.99 Å). In the final refinement the hydrogen atoms were riding with the carbon atom to which they were bonded. The isotropic thermal parameters of the aromatic hydrogen atoms were fixed at 1.2 times and the methyl hydrogen atoms were fixed at 1.5 times to that of the corresponding carbon atom. The scattering factors for the neutral atoms were those incorporated with the programs.

**NMR Spectroscopy.** ¹H, ⁷⁷Se{¹H}, and ¹²⁵Te NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300.131, 57.318 and 94.927 MHz, respectively. The spectral widths were 6.61, 56.98, and 75.19 kHz, and the pulse widths were 6.75, 9.70 and 6.30 μs. The pulse delay for proton, selenium, and tellurium was 1.0, 2.0 and 2.0 s, respectively. ¹H NMR spectra are referenced to the solvent signal and are reported relative to Me₄Si. The ⁷⁷Se and ¹²⁵Te NMR spectra are referenced externally to a D₂O solution of SeO₂ and H₆TeO₆, and the chemical shifts are reported relative to neat Me₂Se and Me₂Te, respectively [δ(Me₂Se) = δ(SeO₂) + 1302.6; δ(Me₂Te) = δ(H₆TeO₆) + 712]. Infrared spectra (Nujol mulls, KBr optics) were recorded on a Nicolet Avatar FTIR spectrometer (at 2 cm⁻¹ resolution).

**EPR Spectroscopy.** The X-band EPR spectra of [1] (E = S, Se) were recorded at ambient temperature using a Bruker EMX-200 spectrometer on samples of the radicals dissolved in degassed dichloromethane and/or toluene. Hyperfine coupling constants were obtained by spectral simulation using PEST Winsim³ and Bruker WinEPR Simfonia.

**Cyclic Voltammetry.** Cyclic voltammetry was performed using a PINE Bipotentiostat, Model AFCCIBP1, with scan rates of 50 - 100 mV s⁻¹ on solutions (< 10⁻³ M) of [1][OTf] (E = S, Se, Te)
in oxygen-free MeCN (dried by distillation from P₂O₅) containing 0.1 M tetra-n-butyl-ammonium hexafluorophosphate. Potentials were scanned with respect to the quasi-reference electrode in a single compartment cell fitted with Pt electrodes and referenced to the Fc/Fc⁺ couple of ferrocene at 0.38 V vs SCE. The $E_{pa} - E_{pc}$ separation of the reversible couples was within 10 % of that of the Fc/Fc⁺ couple.
Theoretical Calculations

Density Functional Theory calculations were performed with the Gaussian 03 suite of programs, using on the B3LYP hybrid density functional with the 6-31G(d,p) basis set for light atoms (H, C, N, S). The relativistic effective core potential basis set SDB-cc-pVTZ was used for selenium and tellurium. The gas phase dimerization enthalpy of the \([1]^+\) cations was evaluated in terms of the energetic difference between the cations and their respective dications. Total electronic energies of the gas phase cations \(M^+\) were derived from geometries fully optimized within \(C_s\) (planar) symmetry. That these geometries were stationary points was confirmed by frequency calculations. Total electronic energies of the gas phase dications \([1]_2^{2+}\) were computed using structures optimized within a \(C_{2h}\) symmetry constraint, using the two equivalent intermolecular \(E---N'\) distances as the reaction coordinate. For \(E = \text{Se} \) and \(\text{Te} \), minima were found at \(d(E---N') = 2.811\) and \(2.389\) Å respectively, and frequency calculations confirmed that these were stationary points. The effects of solvation in acetonitrile were investigated using the Polarization Continuum Solvation Model (PCM), with atom radii defined by the United Simple Atom Topological (UA0) Model. Convergence over the \(d(E---N')\) range of 1.8 - 6.0 Å required a solvent-specific scaling parameter set at \(\alpha = 1.0\) (for \(E = \text{S}\)) and \(\alpha = 1.2\) (for \(E = \text{Se}, \text{Te}\)). Given the size of the dications, no attempt was made to probe structural relaxation in solution; instead single point calculations were performed using molecular parameters obtained from the gas phase optimizations over a range of intermolecular distances \(d(E---N')\). Gas phase molecular ion energetics, spin densities and hyperfine coupling constants were evaluated using the same method and basis sets noted above. Adiabatic ionization potentials \((IP)\) and electron affinities \((EA)\) were calculated using \(\Delta SCF\) methods on fully optimized anions, radicals and cations.
References and Notes

1 J. Zhang, W. Zheng, J. Zou, F. Yang, Y. Bai and Y. Li, Chem. J. Internet, 2004, 6, 97

2 This value differs from that (2403 ppm) reported in the literature. See A. F. Cozzolino, J. F. Britten and I. Vargas-Baca, Cryst. Growth Des., 2006, 6, 181.


