Structure and Formation of the First (-O-Te-N-)$_4$ Ring

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Supplementary Information

Experimental Details

The manipulation of air- and moisture-sensitive materials was carried out in an anhydrous atmosphere; solvents and reagents were purified and dehydrated following standard techniques. Solution NMR spectra were recorded in a Bruker Avance 500 (500.13 MHz) spectrometer. ^{1}H and ^{13}C{^{1}H} δ chemical shifts are referenced to TMS and were measured using the deuterated solvent as a secondary reference. ^{13}C{^{1}H} δ chemical shifts assignments were confirmed using HSQC and HMBC 2-D techniques. The ^{125}Te NMR δ chemical shifts were referenced to Me_2Te and were recorded in a Bruker Avance 500 spectrometer with an external standard solution of Ph_2Te_2 in CH_2Cl_2 (δ 420.36).[S1] Low resolution Mass spectra were obtained in a Micromass GCT (GC-EI/CI TOF) Mass Spectrometer. High resolution Mass spectra were obtained in a Waters/Micromass Q-Tof Ultima Global (ES TOF) Mass Spectrometer. Vibrational spectra were run in a Bio-Rad FTS-40 FT-IR spectrometer.

Z-$C_{11}H_{19}O_2NTe$ (**3**): An excess of sodium borohydride (63 mg in 5 mL of methanol, 2.2 equivalents) was slowly added to bis(N,N-dimethylcarbamoyl)-ditelluride[S2] (300 mg in 10 mL of DMF, 0.75 mmol) at -78°. The mixture was warmed up to 0°C and 5,5-Dimethylhex-3-yn-2-one (342 mg, 2.2 equivalents) was added dropwise. After 7 h the reaction was quenched by careful addition of 10 mL of water. The mixture was filtered and extracted with toluene multiple times. The organic layer was washed with water, dehydrated and evaporated to dryness. The residue was purified by column chromatography (silica, 95:5 CH_2Cl_2/MeOH). Solvent evaporation afforded a yellow oil (yield 25%). ^{1}H NMR (125.8 MHz, CD_2Cl_2, 5.32 ppm): 6.80 (s, ^{1}H, CH); 2.94 (s, 6H, $N(CH_3)_2$); 2.20 (s, 3H, CH_3); 1.22 (s, 9H, $C(CH_3)_3$). ^{13}C-DEPTq NMR (128.5 MHz, CD_2Cl_2, 54.0 ppm): 199.6 (s, 1C, $\underline{C}(O)CH_3$), 156.9 (s, 1C, NC(O)), 151.6 (s, 1C, Te-$\underline{C}$=C), 133.4 (s, 1C, Te-C=$\underline{C}$), 41.4 ($\underline{C}(CH_3)_3$), 35.9 (s, 2C, $N(CH_3)_2$), 31.2 (s, 1C, C(O)$\underline{C}H_3$), 30.7 (s, 3C, $C(\underline{C}H_3)_3$) ^{125}Te NMR (157 MHz): 656 (d, $|^{3}J(^{125}Te,^{1}H)|$ = 13.6 Hz). MS (ES): m/z: 327.1 ([M]+, ^{129}Te), 325.0

([M]+, ^{127}Te). HRMS (ES): m/z Calculated for [MH]+ ($C_{11}H_{20}O_2N^{129}Te$): 328.0557, Found 328.0549.

$C_{32}H_{52}O_4N_4Te_4$ (**4**). An excess (4.4 equivalents) of hydroxylamine- O-sulfonic acid was added to the tellurocarbamate **3** (280 mg, 0.89 mmol) in 10 mL of anhydrous methanol. The mixture was refluxed for two hours and the resulting yellowish solution was cooled down to room temperature and diluted with water. The aqueous phase was extracted with toluene multiple times. The combined organic extracts were washed with water, dried and evaporated. The solid was extracted with ether two times. The remaining pale yellow solid can be recrystallized from hot chloroform to give small yellow crystals. Yield: 60%. ^{1}H NMR (125.8 MHz, CD_2Cl_2, 5.32 ppm): 7.00 (s, ^{1}H, CH); 2.14 (s, 3H, CH_3); 1.42 (s, 9H, $C(CH_3)_3$). ^{13}C-DEPTq NMR (125.8 MHz, CD_2Cl_2, 54.0 ppm): 168.9 (s, 1C, C-Te), 156.4 (s, 1C, C-N), 122.7 (s, 1C, C=<u>C</u>-C), 41.5 (s, 1C <u>C</u>(CH3)), 32.1 (s, 3C CH_3), 16.0 (s, 1C, CH_3). MS (CI+): 269 ([M¼]+, ^{129}Te), 253.0 ([M¼-O]+, ^{129}Te). HRMS (ES): m/z Calculated for [M¼H]+ ($C_8H_{14}ON^{129}Te$): 270.0138, Found 270.0122. IR (cm^{-1}): 2953(s), 2912(m), 2865(m), 1565(m), 1466(m), 1424(w), 1389(w), 1370(m), 1361(m), 1337(w), 1243(w), 1231(w), 1202(w), 1125(vs), 1030(w), 1001(w), 967(mw), 896(m), 842(w), 828(w), 794(w), 760(w), 756(w), 697(m).

Computational Method

All calculations were performed with the ADF package (versions 2008.01d and 2009.01b, www.scm.com), using the PW91 GGA functional, ZORA relativistic corrections, and Quadruple-ζ all-electron basis sets with four sets of polarisation functions. Corrections for BSSE were obviated as they are negligible in the investigated cases. The optimized geometry of **4** reproduced satisfactorily most of the molecular dimensions; the largest deviation was observed in the transannular Te•••Te distance (5.193 Å), which could easily be influenced by packing.

References

S1 A. F. Cozzolino, A. D. Bain, S. Hanhan, I. Vargas-Baca, *Chem. Commun.* 2009**,** 4043.

S2 K. Shimada, S. Oikawa, H. Nakamura, A. Moro-oka, M. Kikuchi, A. Maruyama, T. Suzuki, H. Kogawa, Y. Inoue, Y. Gong, S. Aoyagi, Y. Takikawa, *Bull. Chem. Soc. Jpn.* 2005, **78**, 899.