

Synthesis and characterization of [2-(2-phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)] tellurenyl chloride

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Abstract

The synthesis and characterization of the first examples of two tellurium compounds based on 2-phenyl-5,6-dihydro-4*H*-1,3-oxazine substrate are described. Intramolecular Te···N interaction in [2-(2-phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)] tellurenyl chloride is established by single X-ray crystallography.

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1. Introduction

Recently, we have reported the *ortho*-lithiation and selenation of 2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (**1**) and compared its reactivity with 4,4-dimethyl-2-phenyl-2-oxazoline (**2**) [1]. The selenation reaction in **1** (where the sp²-N donor atom is a part of a six-membered oxazine ring instead of a five-membered oxazoline ring), gave a mixture of diselenide (**3**), triselenide (**4**) and other polyselenides whereas the analogous reaction of **2** gave the diselenide (**5**) (Chart 1).

In this brief paper, we report the ring size effect of the oxazine ring on the telluration reaction. The synthesis and characterization of ditelluride (**8**) and tellurenyl chloride (**9**) incorporating 2-phenyl-2-oxazine (**1**) containing a six-member heterocyclic ring are described. The intramolecular Te···N interaction in **9** has been studied by X-ray crystallography.

2. Results and discussion

2.1. Synthesis

Ditelluride (**8**) was synthesized by the *ortho*-lithiation route (Scheme 1).

ortho-Lithiation of **1** gave the lithiated intermediate (**6**). Subsequent quenching with tellurium followed by oxidation of the lithium telluroate (**7**) gave the ditelluride (**8**). It is worth comparing here the analogous reaction of **6** with selenium powder. The oxidative work up of reaction under similar conditions afforded the triselenide (**4**) as a major product. This probably is either due to the greater tendency of selenium to catenate or longer Te–Te bond which reduces repulsions between substituents on telluriums. Our attempts to grow single crystals of the ditelluride (**8**) using hexane/Et₂O were unsuccessful and the use of hexane/CH₂Cl₂, CHCl₃ led to the isolation of the tellurenyl chloride (**9**). The tellurenyl chloride, presumably results from the oxidation of ditelluride (**8**) with CH₂Cl₂. Similar observations have been made by Engman et al. [2] for bis[2-(*N,N*-dimethylamino)methyl]phenyl] ditelluride bis(hydrochloride). The attempted recrystallization of diorganodiselenide

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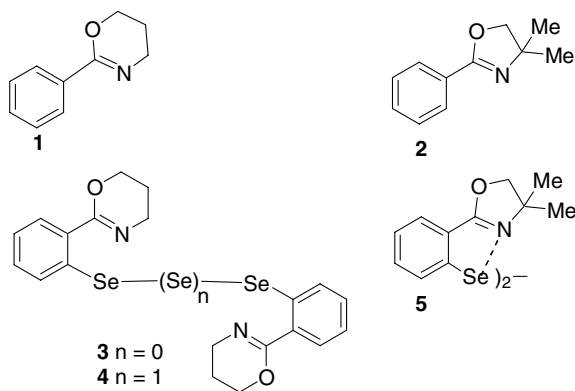
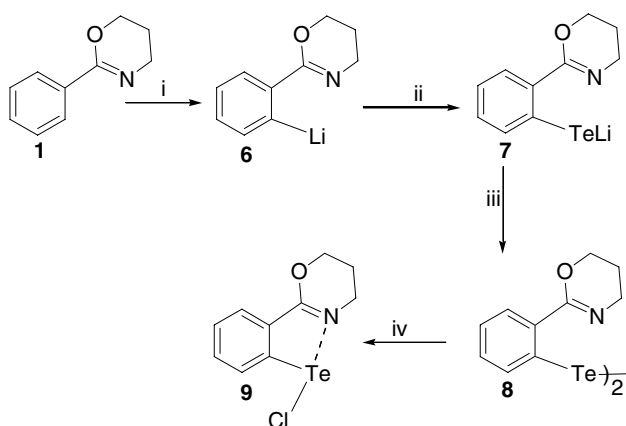


Chart 1

Chart 1. 2-Phenyl-2-oxazoline (1) and 4,4-dimethyl-2-phenyl-2-oxazoline (2) and their diselenide, triselenide (3–5).



Reagents and conditions. (i) *n*-BuLi, Et₂O (ii) Te powder 0 °C to r.t. (iii) air oxidation (iv) sulfuryl chloride, CCl₄, r.t.

Scheme 1. Synthetic routes to ditelluride (8) and tellurenyl chloride (9). Reagents and conditions (i) *n*-BuLi, Et₂O, (ii) Te powder 0 °C to r.t., (iii) air oxidation, (iv) sulfuryl chloride, CCl₄, r.t.

(3) from CH₂Cl₂ also led to the formation of the corresponding organoselenenyl chloride [1]. The tellurenyl chloride (9) could also be conventionally synthesized by the equimolar reaction of ditelluride (8) and sulfuryl chloride in good yield. The electrospray mass spectra of the ditelluride (8) and tellurenyl chloride (9) show the corresponding molecular ion peaks with low intensity and the main peaks for RTe⁺ fragment (290, *m/z*). The signals due to the methylene protons in the ¹H NMR spectra of 8 and 9 are shifted downfield as compared with that of the precursor (1).

The ¹²⁵Te NMR signals for 8 and 9 were observed at 500 and 1226 ppm, respectively. The tellurenyl chloride (9) having directly bonded electron withdrawing chlorine atom shows a significant downfield shift compared with the ditelluride (8). The ¹²⁵Te NMR chemical shift for 8 is relatively more downfield shifted

than those of the corresponding reported ditellurides of 1-(*N,N*-dimethylnaphthyl)amine (461 ppm) [3], *N,N*-dimethylbenzylamine (375 ppm) [4] having a sp³-N donor atom and (*R*)-4-ethyl-4-hydro-2-phenyl-2-oxazoline (424 ppm) [4], 2-phenyl-2-oxazoline (420 ppm) [4], 4,4-dimethyl-2-phenyl-2-oxazoline (417) [5] and 2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole (421 ppm) [6] having a sp²-N donor atom. Similarly, the ¹²⁵Te NMR chemical shift of tellurenyl chloride (9) is also more downfield shifted than the tellurenyl chlorides based on the 2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole (1163 ppm) [6] and 4,4-dimethyl-2-phenyl-2-oxazoline (1203 ppm) [7]. These significant downfield shifts indicate a strong interaction between Te···N in 8 and 9 compared to related compounds.

2.2. Crystal structure of 9

The molecular structure of 9 is shown in Fig. 1. There are two molecules in the asymmetric unit as each molecule is chiral and represents one enantiomer. The T-shaped tellurium is formally bonded to a halogen atom and to an aromatic carbon atom, with an additional link to the nitrogen atom *trans* to the chlorine.

The intramolecular Te(1)···N(1) and Te(2)···N(2) bond distances [2.210(3) and 2.193(3) Å] are close to the Te–N single bond covalent radii (2.1 Å). The Te···N bond distances in 9 are significantly shorter than the reported related distance for 2-[(*N,N*-dimethylamino)methyl]benzenetellurenyl chloride [Te···N = 2.362(3) Å] [2] having a sp³-nitrogen donor atom and also shorter than the reported distances for [2-{1-(3,5-dimethylphenyl)-2-naphthyl}-4,5-dihydro-4,4-dimethyloxazole] tellurenyl chloride (Te···N = 2.252(3) Å) [6] and [2-(4,4-dimethyl-2-phenyl)oxazoliny]tellurium chloride [Te···N, 2.241(3) Å] [7] having a sp²-nitrogen donor. However, the Te···N distances in 9 are close to the respective distances of phenylazophenyl-(*C,N'*) tellurium chloride [Te···N, 2.210(7) and 2.23(2) Å] [8], 2-(2-pyridyl)phenyltellurium chloride [Te···N, 2.205(11) Å] [9] and 2-chlorotellurenyl-4'-methylbenzalaniline [Te···N, 2.218 and 2.239 Å] [10]. The Te(1)–Cl(1) and Te(1)–Cl(2) bond distances [2.583(11) and 2.593(10) Å] are in close agreement with those of the corresponding distances of the related organotellurenyl chlorides [Te–Cl, 2.255(2)–2.606(11) Å] [2,6–10]. The angles Cl(1)–Te(1)···N(1) and Cl(1)–Te(1)···N(1) [168.30(8) and 168.22(7)°] are close to the linear arrangement. These parameters clearly indicate that the elongation of the Te–Cl bond that is in *trans* position relative to the N in the N···Te–Cl fragment. The packing pattern of the structure (9) shows interesting intermolecular Te···Te short distances between the two asymmetric molecules (Fig. 1). The intermolecular Te···Te short distance

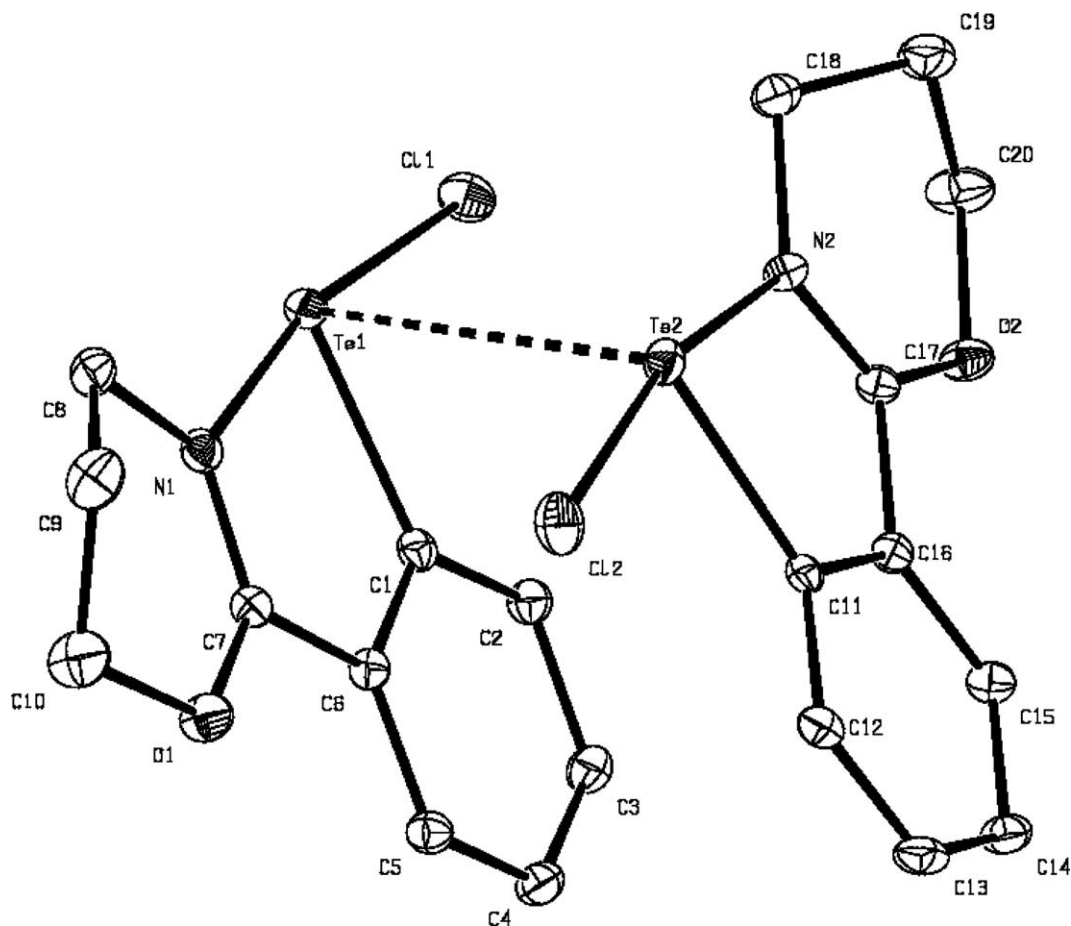


Fig. 1. Molecular structure of **9** showing the Te···Te short distances (hydrogen atoms are omitted for clarity). Significant bond lengths (Å) and angles (°) for **9**: Te(1)–C(1) 2.083(3), Te(1)–N(1) 2.210(3), Te(2)–C(2) 2.079(3), Te(2)–N(2) 2.193(3), C(1)–Te(1)–N(1) 76.65(11), C(11)–Te(2)–N(2) 76.99(11), N(1)–Te(1)–Cl(1) 168.30(8), N(2)–Te(2)–Cl(2) 168.22(7).

[4.268(5) Å] is larger than the reported for related organotellurium compounds (3.58–4.07 Å) [11], however, shorter than the sum of their van der Waals radii (4.4 Å). The intermolecular Te···Cl distances [5.908(12) and 5.652 (12) Å] between two asymmetric molecules are quite long and do not indicate any interaction. It is interesting to note that the tellurenyl chlorides based on the 4,4-dimethyl-2-phenyl-2-oxazoline containing five-membered oxazoline rings did not show any intermolecular Te···Te short distances but showed the Te···Cl short distances (3.642 Å) [7].

In summary, telluration reaction of **1** gives the ditelluride (**8**). Thus, reactivity of **1** towards the telluration reaction is different than the selenation reaction. However, telluration reaction in **1** is similar to that reported 4,4-dimethyl-2-phenyl-2-oxazoline (**2**). The intramolecular Te···N distances in tellurenyl chloride (**9**) based on the oxazine having six-membered heterocyclic ring, are shorter than the corresponding distance of tellurenyl chloride based on oxazoline ligands containing a five-membered heterocyclic ring [6,7].

3. Experimental

3.1. General comments

All reactions were carried out under nitrogen or argon using standard vacuum-line techniques. Solvents were purified by standard procedures [12] and were freshly distilled prior to use. Melting points were recorded in capillary tubes and are uncorrected. The IR spectra were recorded as KBr pellets on a Nicolet Impact 400 FTIR spectrometer. The ^1H NMR and ^{13}C NMR spectra were obtained at 300 MHz in CDCl_3 on a Varian VXR 300S spectrometer. The ^1H and ^{13}C NMR chemical shifts are cited with respect to SiMe_4 as internal standard. The ^{125}Te NMR spectra were obtained at 94.75 MHz, respectively, in CDCl_3 on a Bruker AMX500 spectrometer using diphenyl ditelluride as external standard. The chemical shifts are reported relative to dimethyl telluride (^{125}Te) by assuming that the resonance of the standard is at 421 ppm. Elemental analyses were performed on a Carlo-Erba model 1106 elemental analyzer. Electrospray mass spectra (ES–MS)

were performed at room temperature on a Q-Tof micro (YA-105) mass spectrometer.

3.2. Synthesis of bis[2-(2-phenyl-5,6-dihydro-4H-1,3-oxazinyl)] ditelluride (**8**)

Addition of *n*-BuLi (6.9 mL, 11 mmol, 1.6 M solution in hexane) to ether (200 mL) solution of **1** (1.61 g, 10 mmol) at 0 °C afforded a brown-coloured solution of **6**. After 30 min, finely ground tellurium powder (1.27 g, 10 mmol) was added at 0 °C. The stirring was continued for 5 h at room temperature. During this time, all the tellurium powder reacted to give a brown-coloured lithium aryltelluroate (**7**). After this, air was bubbled through the brown-coloured reaction mixture for 20 min, and the resulting solution was poured into a beaker and kept overnight. The product was extracted with ether (2 × 25 mL) and the organic layer was separated, dried over sodium sulfate, and evaporated under vacuum to give a yellow oil. Addition of hexane/ether (5:1) to the yellow oil of **8** gave a yellow-coloured solid. Yield: 1.64 g, 57%, m.p. 130–132 °C; Anal. Calc. for C₂₀H₂₀N₂O₂Te₂: C, 41.73; H, 3.50; N, 4.87. Found: C, 41.64; H, 3.11; N, 5.23%. ¹H NMR (CDCl₃) δ 2.48 (m, 4H), 3.62 (t, 4H), 4.31 (t, 4H), 7.24–7.45 (m, 6H), 7.71–7.81 (m, 4H); ¹³C NMR (CDCl₃) δ 22.27, 41.67, 65.41, 125.29, 127.78, 130.40, 132.14, 132.78, 155.41; ¹²⁵Te NMR (CDCl₃) δ 500; ES-MS: 580 (*m/z*); IR (KBr) ν 3059, 2927, 2861, 1618, 1545, 1466, 1275, 1071 cm⁻¹.

3.3. Synthesis of 2-(2-phenyl-5,6-dihydro-4H-1,3-oxazinyl) tellurium (II) chloride (**9**)

3.3.1. Method A

Crystallization of ditelluride (**8**) from CCl₄ and CH₂Cl₂ (1:1) gave yellow-coloured crystals of tellurenyl chloride (**9**).

3.3.2. Method B

To a solution of **8** (0.14 g, 0.25 mmol) in CCl₄ (25 mL) was added a solution of sulfuryl chloride (0.03 g, 0.25 mmol) in CCl₄ at 0 °C. A yellow precipitate formed after the complete addition of sulfuryl chloride. The volatile impurities were removed by evaporation under reduced pressure to give the desired compound (**9**). Yellow crystals were obtained by recrystallization from dichloromethane/hexane (2:1). Yield: 0.13 g, 83%, m.p. 165–167 °C; Anal. Calc. for C₁₀H₁₀NOTeCl: C, 37.16; H, 3.12; N, 4.33. Found: C, 37.34; H, 3.23; N, 4.54%. ¹H NMR (CDCl₃) δ 2.25 (m, 2H), 3.87 (t, 2H), 4.60 (t, 2H), 7.38 (t, 1H), 7.58 (t, 1H), 7.92 (d, 1H), 8.57 (d, 1H); ¹³C NMR (CDCl₃) δ 21.52, 41.92, 67.13, 124.69, 125.69, 126.10, 128.39, 132.41, 145.38, 1159.89; ¹²⁵Te NMR (CDCl₃) δ 1226; ES-MS: 324 (*m/z*); IR (KBr) ν 3037, 2927, 1499, 1430, 1230, 1030 cm⁻¹.

Table 1
Crystal data and structure refinement for **9**

Compound	9
Empirical formula	C ₂₀ H ₂₀ Cl ₂ N ₂ O ₂ Te ₂
Formula weight	646.48
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
A (Å)	7.9454(5)
B (Å)	14.7149(11)
C (Å)	18.5906(13)
α (°)	90
β (°)	96.679(8)
γ (°)	90
<i>V</i> (Å ³)	2158.8(3)
<i>Z</i>	4
<i>D</i> _{calc.} (mg/m ³)	1.989
Abs. coeff. (mm ⁻¹)	2.969
Obs. reflections	33 378
Final <i>R</i> (<i>F</i>) [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0236
<i>wR</i> (<i>F</i> ²) [<i>I</i> > 2σ(<i>I</i>)]	0.0367
<i>wR</i> ₂ (all data)	0.0398
Data/restraints/parameters	4486/0/253
Goodness-of-fit on <i>F</i> ²	0.752

^a Definitions: $R(F_o) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $wR(F_o^2) = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_c^2)^2]\}^{1/2}$.

3.4. X-ray crystallography

The diffraction measurements were performed on a STOE (Darmstadt, Germany) IPDS imaging plate single crystal diffractometer at room temperature with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The structures were solved by direct methods and full-matrix least-squares refinement on *F*² (program SHELXL-97) [13]. Hydrogen atoms were localized by geometrical means. A riding model was chosen for refinement. The isotropic thermal parameters of the H atoms were fixed at 1.5 times (CH₃ groups) or 1.2 times *U*_{eq} (Ar–H) of the corresponding C atom. Some details of the data collection and refinement are given in Table 1.

4. Supporting material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre: CCDC No. 249598 for compound **9**. Copies of this information may be obtained free of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (Fax: +/44-1223-336033; email: deposit@ccdc.cam.ac.uk. or <http://www.ccd.cam.ac.uk>).

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