

Preparation and Characterization of

2-Phenoxyethyl(thiophen-2-yl)tellane ($(\text{C}_4\text{H}_3\text{S})\text{TeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$)

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Z. Naturforsch. **61b**, 61–64 (2006); received August 30, 2005

The synthesis and structure of $(\text{C}_4\text{H}_3\text{S})\text{TeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$ (**1**) ($\text{C}_4\text{H}_3\text{S}$ = thiophen-2-yl) are reported and compared to those of the analogous selenium compound $(\text{C}_4\text{H}_3\text{S})\text{SeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$ previously synthesized by our group. The compound was characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$ -, and ^{125}Te -NMR spectroscopy as well as by X-ray single crystal crystallography. **1** crystallizes in the monoclinic crystal system, space group $P2_1$, with $Z = 2$, and unit cell dimensions $a = 10.618(2)$ Å, $b = 5.357(1)$ Å, $c = 10.684(2)$ Å, $\beta = 96.57(3)^\circ$. The lattice is composed of discrete molecules that are joined together by weak hydrogen bonds into a three-dimensional network. The thiophen-2-yl ring is disordered and shows two alternative orientations with the site occupation factors of 0.70(1) and 0.30(1). All bond parameters are quite normal. The comparison of the lattices in **1** and in its selenium analogue shows that while the closest intermolecular contacts are similar, the packing of the molecules is different.

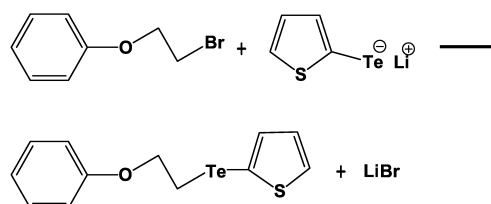
Key words: Telluroether, 2-Phenoxyethyl(thiophen-2-yl)tellane, X-Ray Crystallography, NMR Spectroscopy

Introduction

The organic chemistry of tellurium has seen very rapid progress in the recent decade and tellurium reagents have opened new vistas for designing synthetic methodologies in organic chemistry, as exemplified by the reduction of different functional groups and the reductive cleavage of carbon-heteroatom bonds. Tellurium reagents can be employed in mild conditions. The yields are generally high, the selectivity is good, and many reagents can be generated *in situ* leading to 'one-pot' syntheses (see [1–8], for some recent reviews of this vast field of study).

Organotellurium ligands have also attracted interest in coordination chemistry [9–11] with the goal of designing suitable precursors for chemical vapour deposition processes in order to fabricate thin films that can be utilized in electronic materials such as II–VI semiconductors.

We have recently reported the preparation, structural characterization, and some ligand properties of $(\text{C}_4\text{H}_3\text{S})\text{SeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$ as a part of a systematic study of the structural and bonding trends in chalcogenoethers and chalcogenolates [12]. In this paper we present the synthesis and structural characteriza-



Scheme 1.

tion of a related hybrid chalcogenodiether ($\text{C}_4\text{H}_3\text{S})\text{TeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$.

Results and Discussion

2-Phenoxyethyl(thiophen-2-yl)tellane, $(\text{C}_4\text{H}_3\text{S})\text{TeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$ (**1**) can conveniently be synthesized by the reaction of lithium (thiophen-2-yl)telluroate with (2-bromoethyl)oxybenzene (Scheme 1).

The ^{125}Te resonance of isolated and purified **1** appears as a triplet ($^2J_{\text{Te-H}} = 31.8$ Hz) at 303 ppm. The ^{77}Se chemical shift of $(\text{C}_4\text{H}_3\text{S})\text{SeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$ has been reported to be 183 ppm [12]. The two resonances are consistent with the reported relationship between the ^{125}Te and ^{77}Se chemical shifts in analogous compounds $\{\delta_{\text{Te}} = 1.6 - 1.8 \delta_{\text{Se}} [13]\}$, the current ratio being 1.66.

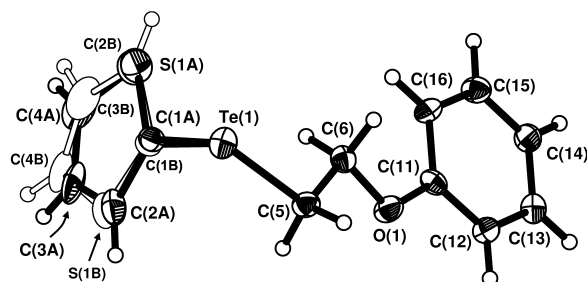


Fig. 1. The crystal structure of $(\text{C}_4\text{H}_3\text{S})\text{TeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$ (**1**) indicating the numbering of atoms. The thermal ellipsoids have been drawn at 50% probability level. The thiophen-2-yl ring is disordered showing two alternative orientations C(1A)-C(2A)-C(3A)-C(4A)-S(1A) and C(1B)-C(2B)-C(3B)-C(4B)-S(1B) (refined site occupation factors are 0.70(1) and 0.30(1) for rings A and B, respectively). Selected bond lengths (\AA): Te(1)-C(1A) 2.086(9), Te(1)-C(1B) 2.147(3), Te(1)-C(5) 2.164(7), C(5)-C(6) 1.508(10), O(1)-C(6) 1.423(8), O(1)-C(11) 1.366(8). Selected bond angles (deg): C(1A)-Te(1)-C(5) 93.4(3), C(1B)-Te(1)-C(5) 92.9(2), C(6)-C(5)-Te(1) 112.2(5), O(1)-C(6)-C(5) 105.5(6), C(11)-O(1)-C(6) 118.9(6). Selected torsional angles (deg): Te(1)-C(5)-C(6)-O(1) $-172.5(4)$, Te(1)-C(1A)-S(1A)-C(4A) $177.0(5)$, Te(1)-C(1B)-S(1B)-C(4B) $-178.4(4)$, Te(1)-C(1A)-C(2A)-C(3A) $-177.2(4)$, Te(1)-C(1B)-C(2B)-C(3B) $178.5(4)$.

The ^{13}C NMR spectrum of **1** is consistent with that recorded for the selenium analogue [12]. Most ^{13}C chemical shifts in the two compounds are close to each other. The most significant difference involves C(5) bound to tellurium in **1** and the corresponding carbon atom bound to selenium in $(\text{C}_4\text{H}_3\text{S})\text{SeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$, the respective chemical shifts being 9.3 and 29.4 ppm [12]. It is expected that selenium, being somewhat more electronegative, moves the chemical shift of the adjacent carbon atom to a lower field. The same trend is observed in the ^{13}C chemical shifts of the methyl carbons of $\text{CH}_3\text{Te}(\text{C}_4\text{H}_3\text{S})$ and $\text{CH}_3\text{Se}(\text{C}_4\text{H}_3\text{S})$ (-13 and 12 ppm, respectively [14]). The smaller differences in the chemical shifts of other carbon atoms of **1** and $(\text{C}_4\text{H}_3\text{S})\text{SeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$ can also be attributed to the electronegativity difference of tellurium and selenium and are also supported by the chemical shifts of $\text{CH}_3\text{Te}(\text{C}_4\text{H}_3\text{S})$ and $\text{CH}_3\text{Se}(\text{C}_4\text{H}_3\text{S})$ [14].

The crystal structure of $(\text{C}_4\text{H}_3\text{S})\text{TeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$ is shown in Fig. 1 together with selected bond lengths and angles. The compound shows normal bond parameters. The thiophen-2-yl ring in the molecule of **1** is disordered with the five-membered ring assuming two alternative orientations A and B with the refined site occupation factors of 0.70(1) and 0.30(1), respec-

tively. To minimize the repulsion with the π -electrons of the phenyl ring the C(5)-C(6)-O(1)-Ph framework is almost planar with a torsion angle Te(1)-C(5)-C(6)-O(1) of $-172.5(4)^\circ$ and the orientation of the thiophen-2-yl ring is almost perpendicular to the Te(1)-C(5) [the angle of the least-squares plane of the disordered thiophen-2-yl groups with respect to the Te(1)-C(5) bond are $71.9(3)^\circ$ (orientation A) and $72.2(2)^\circ$ (orientation B)]. These angles are in qualitative agreement with the values 83.4 and 83.3° between the plane of the aromatic ring and Te-Te bonds in $(\text{C}_4\text{H}_3\text{S})_2\text{Te}_2$, and $(\text{C}_4\text{H}_3\text{O})_2\text{Te}_2$ [14]. The corresponding angles in the selenium analogue of **1** are $75.7(2)$ and $70.8(2)^\circ$ in the two independent molecules of the asymmetric unit [12]. The magnitudes of all these angles are dependent on the electronic and steric factors of the aromatic ring (see discussion and references in [15]).

The molecule of **1** is structurally similar to the analogous selenium compound [12]. They are not, however, isomorphic. While both molecules form a continuous three-dimensional network by similar weak hydrogen bonds involving both $\text{H}\cdots\text{O}$ contacts and interaction between the methylene hydrogen atoms and the π -electrons of the phenyl rings, their packing is different, as shown in Fig. 2. The shortest $\text{H}\cdots\text{O}$ contacts show values of $2.614(5)$ – $2.819(4)$ \AA for **1** and $2.671(4)$ – $2.693(4)$ \AA for the selenium analogue.

The investigation of the ligand chemistry of $(\text{C}_4\text{H}_3\text{S})\text{TeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$ (**1**) is currently in progress. A tentative study has shown the compound rather insusceptible for coordination both with hard and soft metal centers.

Experimental Section

The NMR spectra were recorded on a Bruker DPX200 spectrometer operating at 200.13, 50.32, and 63.14 MHz for ^1H , ^{13}C and ^{125}Te , respectively. Tetramethylsilane was used as an internal standard for ^1H and ^{13}C NMR spectra. A saturated solution of $(\text{C}_6\text{H}_5)_2\text{Te}_2$ in CDCl_3 was used as an external standard for the ^{125}Te chemical shift. All spectra were recorded in CDCl_3 that served as an internal ^2H lock. Chemical shifts (ppm) of ^1H and ^{13}C are reported relative to Me_4Si and that of ^{125}Te relative to $(\text{CH}_3)_2\text{Te}$ [$\delta(\text{CH}_3)_2\text{Te} = \delta[(\text{C}_6\text{H}_5)_2\text{Te}_2 + 422]$ [15].

The reaction was carried out in a nitrogen atmosphere. *n*-BuLi (2.5 M solution in hexanes, 3.00 ml, 7.50 mmol, Aldrich) was added to a solution of 0.7 ml (8.74 mmol, Riedel de Haen, dried and distilled before use) of thiophene in 12 ml of tetrahydrofuran (Aldrich, distilled under nitrogen

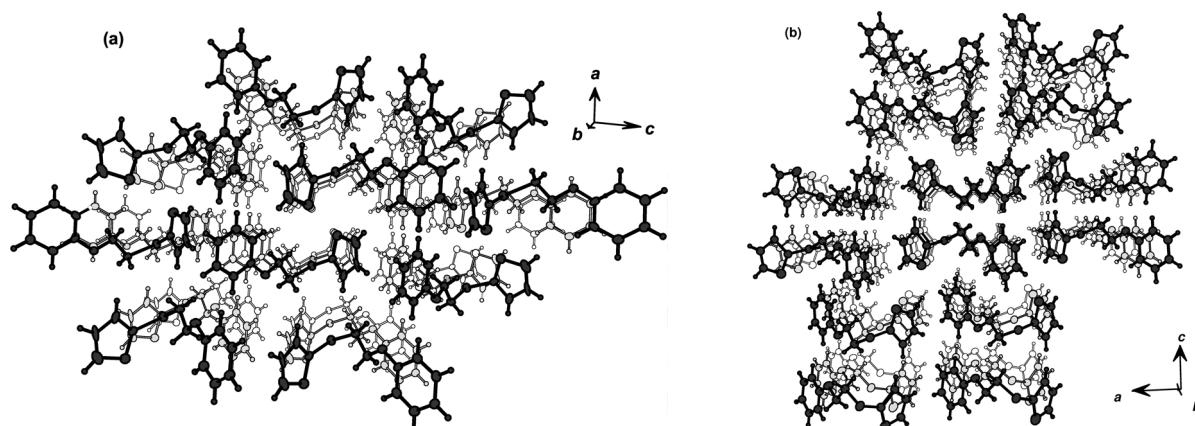


Fig. 2. Comparison of the molecular packing in (a) $(\text{C}_4\text{H}_3\text{S})\text{TeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$ (**1**) and (b) $(\text{C}_4\text{H}_3\text{S})\text{SeCH}_2\text{CH}_2\text{OC}_6\text{H}_5$ (re-drawn from the crystal data given in [12]). For clarity, only the more abundant orientation A of the disordered thiophen-2-yl rings has been presented in both structures.

from Na/benzophenone) that was cooled in EtOH/N₂ bath. The reaction solution was stirred for 45 min during which time it was allowed to warm to ambient temperature. A slight excess of tellurium powder (1.17 g, 9.17 mmol, Aldrich) was added to the solution under a nitrogen flow and the mixture was stirred for an additional hour. (2-Bromoethyl)oxybenzene (1.69 g, 8.41 mmol, Aldrich) was gradually added into the reaction mixture in small portions. After 30 min, the reaction mixture was poured into water (75 ml) and the product was extracted with two portions of CH₂Cl₂. The combined organic layers were dried over anhydrous MgSO₄ and after filtration the solvent was removed by evaporation affording a pale yellow oil. The oily residue was dissolved in hexane and cooled to -20°C . The resulting pale yellow precipitate was filtered cold, washed several times with cold hexane, and dried. Colorless crystals were obtained from a mixture of methanol and *n*-hexane (1:1) by slow evaporation of the solvent. Yield of the purified product: 1.14 g (46%). ^1H NMR (200.13 MHz): δ = 6.97 (1 H, 2-H), 6.89 (1 H, 3-H), 7.46 (1 H, 4-H), 3.11 (1 H, 5-H), 4.32 (1 H, 6-H), 6.84 (3 H, 12-H, 14-H, 16-H), 7.29 (2 H, 13-H, 15-H) ppm. ^{13}C NMR (50.32 MHz): δ = 120.6 (1-C; 14-C), 134.3 (2-C), 128.6 (3-C), 141.6 (4-C), 9.3 (5-C), 68.5 (6-C), 157.9 (11-C), 114.3 (12-C; 16-C), 129.2 (13-C; 15-C) ppm. ^{125}Te (63.14 MHz): δ = 303 ppm ($^2J_{\text{Te-H}}$ 31.8 Hz) (for numbering of atoms, see Fig. 1). $-\text{C}_{12}\text{H}_{12}\text{OSTe}$ (331.88): calcd. C 43.43, H 3.64, S 9.66; found C 42.36, H 3.23, S 9.58.

Crystal structure determination for $\text{C}_{12}\text{H}_{12}\text{OSTe}$. FW = 331.88, colorless plates, monoclinic space group $P2_1$, a = 10.618(2), b = 5.357(1), c = 10.684(2) Å, β = 96.57(3)°, U = 603.7(2) Å³; Z = 2; D_c = 1.826 g cm⁻³, $F(000)$ = 320; $\mu(\text{Mo-K}\alpha)$ = 2.607 mm⁻¹, T = 120(2) K, crystal dimensions 0.30 × 0.10 × 0.10 mm³. Reflections: 3347 total, 2149 unique, θ range 2.56–25.99°, R_{int} = 0.0527. R_1 = 0.0408

$[I \geq 2\sigma(I)]$, wR_2 = 0.1062 (all data), absolute structure parameter $-0.01(5)$. Diffraction data were collected on a Nonius KappaCCD diffractometer using graphite monochromated Mo- $K\alpha$ radiation (λ = 0.71073 Å).^{*} The data were corrected for Lorentz and polarization effects and the empirical absorption correction was applied to the net intensities. The structure was solved by direct methods using SIR-92 [16] and refined using SHELXL-97 [17]. The thiophen-2-yl ring in **1** was found to be disordered. The disorder was taken into account by refining the site occupation factors of the two alternative orientations and constraining their sums to unity. Since the site occupation factors and thermal parameters of the disordered atoms correlate with each other, the thermal parameters of the corresponding pairs of atoms were restrained to be equal. After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters the hydrogen atoms were placed in calculated positions in aromatic rings (C-H = 0.95 Å) and methylene groups (C-H = 0.99 Å) for the final refinement. The scattering factors for the neutral atoms were those incorporated with the programs.

Acknowledgements

Financial support from Academy of Finland and Finnish Cultural Foundation is gratefully acknowledged.

^{*}Crystallographic information (excluding tables of structure factors) has been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 282494. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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