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## Preparation and structural characterization of bis(trimethylsilylmethyl) tellurium diiodide

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**Abstract:** The telluroether  $\text{Te}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$  (**1**) has been prepared in a good yield by the reaction of  $\text{Na}_2\text{Te}$  and  $\text{ClCH}_2\text{SiMe}_3$  in aqueous solution. The reaction of **1** with  $\text{I}_2$  affords  $\text{TeI}_2[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$  (**2**). The compounds have been characterized by  $^{13}\text{C}\{^1\text{H}\}$ - and  $^{125}\text{Te}$ -NMR spectroscopy. The crystal structure of **2** shows the presence of weak  $\text{Te}\cdots\text{I}$  and  $\text{I}\cdots\text{I}$  secondary bonding interactions leading to the formation of a supramolecular assembly.

**Keywords:** diorganotellurium diiodide, secondary bonding, intramolecular coordination.

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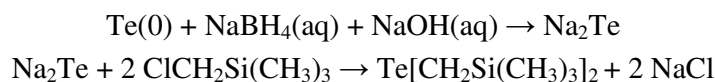
### Introduction

Diorganyl tellurides form a well-known class of compounds.<sup>1</sup> Dialkyl tellurides can be prepared by alkylation of  $\text{Na}_2\text{Te}$  with an alkylhalide.<sup>2</sup> The direct reaction of a dialkyltelluride and iodine yields dialkyltellurium diiodides.<sup>3</sup> In this type of molecules, tellurium atom displays a pseudo-trigonal bipyramidal coordination geometry where the alkyl groups and the tellurium lone-pair occupy the equatorial positions while the iodine atoms lie at the axial positions.<sup>3,4</sup> Furthermore, tellurium usually interacts with neighbouring iodine atoms through secondary bonding interactions, leading to supramolecular associations.<sup>5</sup> It has also been reported that, depending on the nature of the alkyl groups, other secondary interactions may be present.<sup>6</sup>

Herein we report the synthetic details and  $^{13}\text{C}\{^1\text{H}\}$ - and  $^{125}\text{Te}$ -NMR spectroscopic data of  $\text{Te}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$  (**1**) and  $\text{TeI}_2[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$  (**2**). The X-ray single crystal structure analysis of **2** is also reported.

## Results and Discussion

Bis(trimethylsilylmethyl)telluride (**1**) was synthesized in a high yield by treating  $\text{ClCH}_2\text{SiMe}_3$  with  $\text{Na}_2\text{Te}$  prepared from the reduction of elemental tellurium by the aqueous alkaline solution of  $\text{NaBH}_4$ .<sup>7</sup>



### Scheme 1 Synthesis of $\text{Te}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$ .

Compound **1** is an orange liquid, which can be stored at low temperatures for several months. Although elemental tellurium and tellurium oxides are rapidly formed,<sup>7</sup> pure **1** can easily be obtained by removing the precipitations by filtration. A direct reaction of **1** with iodine affords **2**.

$^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **1** exhibits two singlets at -3 ppm ( $\text{CH}_3$ ) and at -16 ppm ( $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2** resembles that of **1** with the high frequency shift of the signals caused by the presence of iodine atoms. Consistently, the  $^{125}\text{Te}$  chemical shift of **2** (660 ppm) also appears significantly to high frequency with respect to that of **1** (26 ppm).

### Crystal structure of **2**

The molecular structure and the numbering of the atoms of **2** is shown in Fig.1. Selected bond distances and bond angles are shown in Table 1.

The coordination environment around the tellurium center is pseudo-trigonal bipyramidal with the two  $-\text{CH}_2\text{Si}(\text{CH}_3)_3$  group and the tellurium lone pair occupying equatorial positions and iodine atoms the axial positions. Consistently, the I-Te-I fragment is not linear [ $\text{I-Te-I} = 175.29(2)^\circ$ ]. The C-Te-C angle is rather small [ $\text{C}(1)\text{-Te}(1)\text{-C}(2)$  is  $99.9(3)^\circ$ ] but agrees with those previously reported for related  $\text{R}_2\text{TeI}_2$  species.<sup>3-6</sup> The Si(1)-C(1)-Te(1)-C(2)-Si(2) fragment is approximately coplanar as the relative torsion angles are close to  $180^\circ$ .

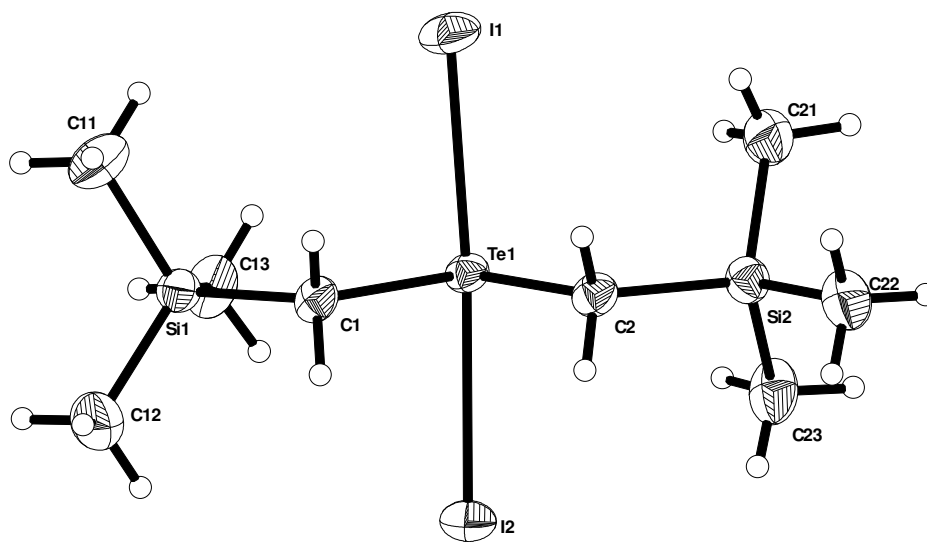
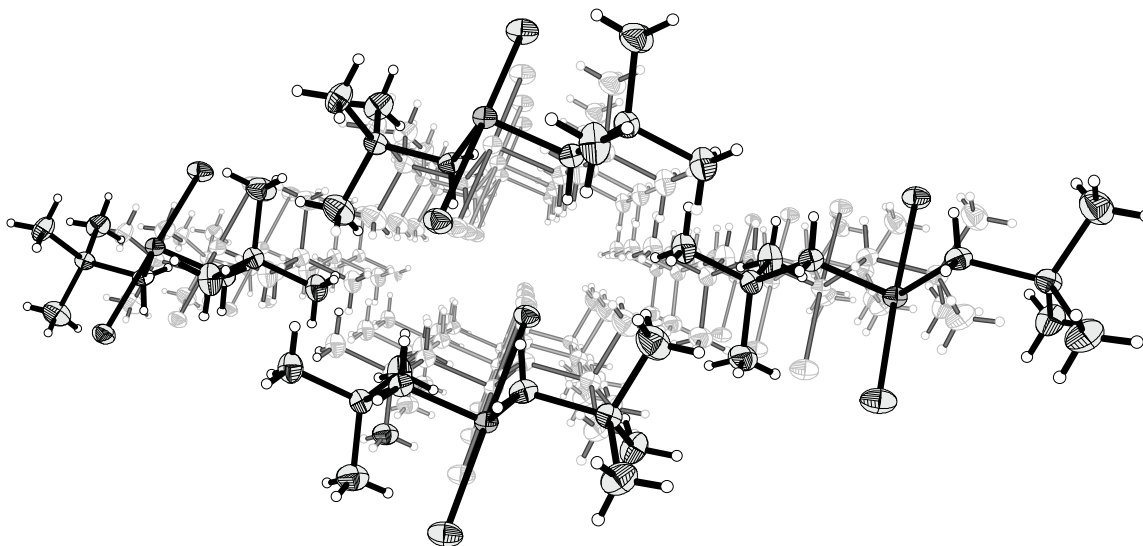


Fig. 1 Molecular structure of **2**.

**Table 1** Selected bond distances (Å) and angles (°) of **2**

|                       |           |
|-----------------------|-----------|
| Te(1)-C(1)            | 2.129(6)  |
| Te(1)-C(2)            | 2.132(7)  |
| Te(1)-I(1)            | 2.890(1)  |
| Te(1)-I(2)            | 2.949 (1) |
|                       |           |
| C(1)-Te(1)-C(2)       | 99.9(3)   |
| I(1)-Te(1)-I(2)       | 175.29(2) |
| Si(1)-C(1)-Te(1)      | 113.1(3)  |
| Si(2)-C(2)-Te(1)      | 113.1(3)  |
|                       |           |
| C(2)-Te(1)-C(1)-Si(1) | -178.5(3) |
| C(1)-Te(1)-C(2)-Si(2) | 178.8(3)  |

The crystal packing of **2** is shown in Fig.2. Weak intermolecular Te...I and I...I secondary bonding interactions between neighboring molecules link the structure into a supramolecular network. The Te...I intermolecular contacts are 4.229(1) Å<sup>10</sup> and I...I intermolecular contacts span a range of 4.185(2) – 4.246(1) Å.<sup>11</sup> These contacts are significantly longer than what has been reported for a number of related species.<sup>5</sup>

**Fig. 2** The packing of the molecules of **2**.

## Experimental Section

### General

Chloromethyltrimethylsilane (Aldrich), tellurium (powder, Johnson Matthey Chemicals), NaBH<sub>4</sub> (Riedel de Haen), NaOH (Merck), CH<sub>3</sub>OH (Lab-Scan), MgSO<sub>4</sub> (Fisher Scientific), diethyl ether (Lab-Scan), *n*-hexane (Lab-Scan), THF (Lab-Scan), CH<sub>2</sub>Cl<sub>2</sub> (Lab-Scan), iodine (Aldrich) were commercially available and were used without further purification.

*Synthesis of  $\text{Te}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$  (**1**).*<sup>7</sup>

A suspension of tellurium powder (0.642 g; 5.032 mmol) and  $\text{NaBH}_4$  (0.479 g; 12.661) in 10 ml of 20% aqueous  $\text{NaOH}$  was refluxed under a nitrogen atmosphere for 3 h, giving during the first 30 minutes an intense violet colour solution which subsequently turned into a pale yellow solution of  $\text{Na}_2\text{Te}$ . The deaerated solution of  $\text{ClCH}_2\text{Si}(\text{CH}_3)_3$  (1.244 g; 10.143 mmol) in 10 ml of methanol was added to the reaction mixture and refluxed for 20 h. The alcohol was distilled off and the residual solution was extracted with three 7.5 ml portions of diethyl ether (or n-hexane). The combined extracts were washed with water and dried over  $\text{MgSO}_4$ , and the solvent was removed upon vacuum distillation, giving a pale orange liquid **1** (1.42 g; 94 %).  $\delta\text{C}$  -3.460 (s,  $\text{SiMe}_3$ ), -15.795 (s,  $\text{CH}_2$ );  $\delta\text{Te}$  25.673 (s).

*Synthesis of  $\text{TeI}_2[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$  (**2**).*

Iodine (0.082 g; 0.32 mmol) was dissolved in 10 ml of THF in an argon atmosphere and **1** (0.099 g; 0.33 mmol) was added dropwise into the resulting solution. The reaction mixture was stirred for one hour and sequentially concentrated by evaporation of the solvent. The raw product was filtered and recrystallized from  $\text{CH}_2\text{Cl}_2$  giving red needles of **2**.  $\delta\text{C}$  0.662 (s,  $\text{SiMe}_3$ ), 25.826 (s,  $\text{CH}_2$ );  $\delta\text{Te}$  25.673 (s).

*NMR spectroscopy*

$^{13}\text{C}\{^1\text{H}\}$  and  $^{125}\text{Te}$ -NMR spectra were recorded on a Bruker DPX400 spectrometer operating at 100.61, and 126.28 MHz, respectively. The respective spectral widths were 20.16 and 126.58 kHz. The pulse widths were 4.00 and 10.00  $\mu\text{s}$ , respectively.  $^{13}\text{C}\{^1\text{H}\}$  pulse delay was 3.00 s and that for  $^{125}\text{Te}$  was 1.60 s.  $^{13}\text{C}\{^1\text{H}\}$  accumulations contained ca. 50000 transients and those of  $^{125}\text{Te}$  30000 transients. Tetramethylsilane was used as an internal standard and a saturated solution of  $\text{Ph}_2\text{Te}_2$  in  $\text{CDCl}_3$  was used as external standard for  $^{125}\text{Te}$ . Chemical shifts (ppm) are reported relative to  $\text{Me}_4\text{Si}$ , and to neat  $\text{Me}_2\text{Te}$  [ $\delta(\text{Me}_2\text{Te}) = \delta(\text{Ph}_2\text{Te}_2) + 422$ ].<sup>11</sup>

*X-ray crystallography*

Diffraction data of **2** were collected on a Nonius Kappa-CCD diffractometer using graphite monochromated  $\text{Mo-K}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ; 55 kV, 25 mA). Crystallographic data of **2** are given in Table 2. The structure was solved by direct methods using SIR-92<sup>12</sup> and refined using SHELXL-97.<sup>13</sup> 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 methyl groups ( $\text{C-H} = 0.98 \text{ \AA}$ ) and in the  $\text{CH}_2$  groups ( $\text{C-H} = 0.99 \text{ \AA}$ ). The scattering factors for the neutral atoms were those incorporated with the programs.

**Table 2** Details of the structure determination of **2**

| <b>2</b>   |  |
|--|--|
| Empirical formula  | C <sub>8</sub> H <sub>22</sub> I <sub>2</sub> Si <sub>2</sub> Te |
| Relative molecular mass  | 555.84   |
| Crystal system   | Triclinic  |
| Space group  | $P\bar{1}$   |
| $a$ (Å)  | 7.233(2)   |
| $b$ (Å)  | 9.870(2)   |
| $c$ (Å)  | 12.813(3)  |
| $\alpha$ (°)   | 106.96(3)  |
| $\beta$ (°)  | 94.41(3)   |
| $\gamma$ (°)   | 92.25(3)   |
| $V$ (Å <sup>3</sup> )  | 870.5(3)   |
| $Z$  | 2  |
| F(000)   | 512  |
| $D_{\text{calc.}}$ (g cm <sup>-3</sup> )                             | 2.121  |
| $\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )                           | 5.364  |
| Crystal size (mm)  | 0.50 x 0.50 x 0.10   |
| $\theta$ range (°)   | 1.67 - 26.00   |
| N. reflections collected   | 13573  |
| N. unique reflections  | 3376   |
| N. observed reflections  | 2745   |
| N. parameters/restraints   | 124/0  |
| $R_{\text{int}}$   | 0.0694   |
| $R_1$  | 0.0546   |
| $wR_2$   | 0.1366   |
| $R_1$ (all data)   | 0.0680   |
| $wR_2$ (all data)  | 0.1577   |
| Goodness-of-fit on $F^2$   | 1.093  |
| Max/min heights in final dif. Fourier synthesis (e Å <sup>-3</sup> ) | 2.182, - 3.329   |

### Acknowledgements

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