The Molecular Structures of Hexamethyldistannane, (CH$_3$)$_6$Sn$_2$, and Dimethylditellurane, (CH$_3$)$_2$Te$_2$, by Gas Electron Diffraction

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Gas Electron Diffraction, Hexamethyldistannane, Dimethylditellurane

Gas electron diffraction data of both compounds were recorded on Balzers Eldigraph KDG-2 with nozzle temperatures of about 25 °C (Me$_6$Sn$_2$) and 130 °C (Me$_2$Te$_2$).

Exposures were made with nozzle-to-plate distances of 50 and 25 cm. The plates were photometered and the data processed by standard procedures. The resulting modified molecular intensity curves extended from $s = 20.00$ to 147.50 nm$^{-1}$ with increment $\Delta s = 1.25$ nm$^{-1}$ (six plates, 50 cm) and from $s = 50.00$ to 225.00 nm$^{-1}$ with increment $\Delta s = 2.50$ nm$^{-1}$ (six plates, 25 cm) for Me$_6$Sn$_2$ and from $s = 35.00$ to 145.00 nm$^{-1}$ with increment $\Delta s = 1.25$ nm$^{-1}$ (six plates, 50 cm) and from $s = 70.00$ to 200.00 nm$^{-1}$ (four plates, 25 cm) for Me$_2$Te$_2$.

Atomic scattering factors, $f'(s)$, were taken from Schäfer, Yates and Bonham [3]. The molecular intensities were modified by multiplication with $s/|f_E'(s)|/|f_C'(s)|$, $E =$ Sn or Te.

The present study was undertaken to provide reference values for Sn–Sn and Te–Te single bonds in simple, gaseous molecules.

Experimental

Hexamethyldistannane, Me$_3$SnSnMe$_3$, with stated purity of 99% was purchased from Aldrich-Chemie and used without further purification. Dimethylditellurane, MeTeTeMe, was synthesized from Na$_2$Te$_2$ and CH$_3$I as described in ref. [1] and characterized by high resolution mass spectrometry [2].

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The molecular structure of either compound is characterized by high resolution mass spectrometry [2].

Structure refinements

Structure refinements were based on molecular models of D$_3$ (Me$_6$Sn$_2$) and C$_2$ (Me$_2$Te$_2$) symmetry. In both molecules methyl groups were assumed to have C$_3v$ symmetry with the threefold axes coinciding with the C–E bonds.

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The molecular structures of hexamethyldistannane
\[ \text{Me}_3\text{SnSnMe}_3 \]
and dimethylditellurane
\[ \text{MeTeTeMe} \]

### Table I. Bond distances, valence angles, dihedral angles and root-mean-square amplitudes of vibration (\( \ell \)) of hexamethyldistannane and dimethylditellurane

<table>
<thead>
<tr>
<th></th>
<th>Me(_3)SnSnMe(_3) (E = Sn)</th>
<th>MeTeTeMe (E = Te)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond distances/pm</td>
<td>( r_j/\text{pm} )</td>
<td>( \ell/\text{pm} )</td>
</tr>
<tr>
<td>E--E</td>
<td>277.6(3)</td>
<td>7.0(3)</td>
</tr>
<tr>
<td>E--C</td>
<td>216.5(3)</td>
<td>7.6(4)</td>
</tr>
<tr>
<td>C--H</td>
<td>110.3(4)</td>
<td>9.4(5)</td>
</tr>
<tr>
<td>Valence angles/deg</td>
<td>(&lt;\text{EEC}&gt; )</td>
<td>111.9(4)</td>
</tr>
<tr>
<td></td>
<td>(&lt;\text{ECH}&gt; )</td>
<td>111.8(7)</td>
</tr>
<tr>
<td>Dihedral angles/deg</td>
<td>( \phi(\text{CEEC}) )</td>
<td>37(8)</td>
</tr>
<tr>
<td></td>
<td>( \phi(\text{EECH}) )</td>
<td>27(14)</td>
</tr>
<tr>
<td>Non-bonded distances/pm</td>
<td>( E--C )</td>
<td>411(1)</td>
</tr>
<tr>
<td></td>
<td>( E--H )</td>
<td>277(1)</td>
</tr>
<tr>
<td></td>
<td>( C--C^b )</td>
<td>348(1)</td>
</tr>
<tr>
<td></td>
<td>( C--C^c )</td>
<td>446(6)</td>
</tr>
<tr>
<td></td>
<td>( C--C^d )</td>
<td>532(12)</td>
</tr>
<tr>
<td></td>
<td>( C--C^e )</td>
<td>581(6)</td>
</tr>
<tr>
<td>R(^2) (50 cm)</td>
<td>2.2%</td>
<td>4.0%</td>
</tr>
<tr>
<td>R(^2) (25 cm)</td>
<td>9.0%</td>
<td>6.9%</td>
</tr>
</tbody>
</table>

\(^a\) Estimated standard deviations in parentheses in units of the last digit. Non-refined amplitudes of vibration in square brackets; \(^b\) within a Me\(_3\)Sn fragment; \(^c\) assumed equal; \(^d\) mole fraction; \(^e\) \( R = [\Sigma W(I_{\text{obs}} - I_{\text{calc}})^2 / \Sigma W(I_{\text{obs}})]^{1/2} \).

have been determined with reasonable accuracy despite the presence of the TeMe\(_2\) impurity, we did not think it worth while to record data with a pure sample.

The \( R \)-factors, Table I, show that the 25 cm plates of both compounds are of poor quality. This, in our experience, is often the case for compounds containing fifth period elements.

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**Fig. 1.** Experimental (●) and calculated (—) radial distribution curves for Me\(_3\)SnSnMe\(_3\). Below: Difference curve. Artificial damping constant \( k = 30 \text{ pm}^2 \).

**Fig. 2.** Experimental (●) and calculated (—) radial distribution curves for MeTeTeMe. Peaks representing distances in the TeMe\(_2\) impurity are indicated by stippled bars. Below: Difference curve. Artificial damping constant \( k = 50 \text{ pm}^2 \).
Discussion

Molecular shapes

The gas electron diffraction data of Me₃SnSnMe₃ and MeTeTeMe are in good agreement with molecular models of D₃ and C₂ symmetry, respectively.

The estimated standard deviations of the dihedral angles $\varphi$(CEE) and $\varphi$(EECH), $E = Sn$ or Te, are so large that they may be regarded as undetermined. The reason for this is probably the small scattering powers of C and H compared to Sn or Te atoms.

Self consistent field molecular orbital calculations on Sn₂H₆ with effective core potentials and a double zeta basis for the valence electrons followed by second-order MP calculations of correlation energies, indicate that the equilibrium geometry is staggered (D₃d) with a rotational barrier of 0.39 kcal mol⁻¹ [5]. The experimentally determined barrier to internal rotation about the Sn-C bond in H₃SnCH₃ [6] is 0.65 kcal mol⁻¹ (calculated [5] 0.57 kcal mol⁻¹). It seems likely, therefore, that both rotational barriers in Me₃SnSnMe₃ are of the order of the thermal energy available during our experiment, RT = 0.60 kcal mol⁻¹. Under these circumstances it is not surprising that the best thermal average values for $\varphi$(CSnSnC) and $\varphi$(SnSnCH) fall near the middle of the range between eclipsed ($\varphi = 0°$) and staggered (60°) conformations.

The best value of the dihedral angle $\varphi$(CTeTeC) in MeTeTeMe is close to the more accurately determined dihedral angles in Me₂Se₂ [7], Me₂S₂ [8] and Me₂O₂ [9]; 85(4)°, 84(1)° and 119(4)°, respectively.

E–E bond distances

The observed E–E bond distances in gaseous Me₃Sn–SnMe₃, Me₃Sb–SbMe₃ [10], MeTe–TeMe and I₂ [11] (Table II) are in good agreement with the values calculated by doubling the normal single bond radii listed in ref. [12]; 280 pm, 282 pm, 270 pm and 266 pm, respectively. They are, however, significantly shorter than the single bonds encountered in the solid elements:

$α$-Sn has a diamond structure with Sn–Sn bonds about 3 pm greater than in Me₃SnSnMe₃ [13]. Similarly, the Ge–Ge bond in $α$-Ge [13], 245.0 pm, is about 5 pm greater than in gaseous H₃GeGeH₃ [14], 240.3(3) pm, and the Si–Si bond in $α$-Si [13], 235.2 pm, is about 2 pm longer than in gaseous H₃SiSiH₃ [15], 233.1(3) pm. We assume the elongation to be due to weak repulsion between the four metal atoms bonded to a fifth: Using the force constant $f_{Sn-Sn}$ obtained by normal coordinate analysis of H₃SnSnH₃ [5], the energy required to extend the Sn–Sn bond by 3 pm is less than 0.10 kcal mol⁻¹.

In crystalline I₂ each I atom participates in one normal bond at 271.5 pm and two secondary bonds [16] at 350 and 356 pm, the latter are 80 to 90 pm greater than the normal, covalent bond in gaseous I₂. The coordination number of the atoms in $α$-Te [17], $α$-Sb [12] and $β$-Sn [12] is six; in $α$-Te each atom participates in two normal and four secondary bonds, the latter are 80 pm longer than the normal bond in gaseous MeTeTeMe; in $α$-Sb each atom participates in three covalent and three secondary bonds, the latter are 53 pm longer than the normal bond in gaseous Me₂SbSbMe₂; finally, in $β$-Sn each atom participates in four normal and two secondary bonds which are 40 pm longer than the normal bond in Me₃SnSnMe₃. Formation of the secondary bonds is in every case accompanied by elongation of the normal bonds, in crystalline I₂ by 4 pm, in $α$-Te by 15 pm, in $α$-Sb by 9 pm and in $β$-Sn by 25 pm.

We are grateful to the Norwegian Research Council for Science and the Humanities (NAVF) and the VISTA program for general support and to the NAVF for a scholarship to Andreas Hammel.

<table>
<thead>
<tr>
<th>Gas phase</th>
<th>Me₃Sn–SnMe₃</th>
<th>Me₃Sb–SbMe₃</th>
<th>MeTe–TeMe</th>
<th>I–I</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Sn</td>
<td>277.6(3) pm</td>
<td>281.8(2) pm</td>
<td>268.6(3) pm</td>
<td>267.7(3) pm</td>
</tr>
<tr>
<td>β-Sn</td>
<td>281.0 pm (4 x)</td>
<td>290.8 pm (3 x)</td>
<td>283.5 pm (2 x)</td>
<td>271.5 pm (1 x)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solid phase</th>
<th>Me₃Sn–SnMe₃</th>
<th>Me₃Sb–SbMe₃</th>
<th>MeTe–TeMe</th>
<th>I–I</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Sn</td>
<td>281.0 pm (4 x)</td>
<td>290.8 pm (3 x)</td>
<td>283.5 pm (2 x)</td>
<td>271.5 pm (1 x)</td>
</tr>
<tr>
<td>β-Sn</td>
<td>302.2 pm (4 x)</td>
<td>335.5 pm (3 x)</td>
<td>349.1 pm (4 x)</td>
<td>353 pm (2 x)</td>
</tr>
</tbody>
</table>

Table II. E–E single bond distances, $E = Sn$, Sb, Te or I in simple gaseous molecules Me₃E–EMe₃, Me = CH₃, and in the crystalline elements [13].

* This work; † ref. [10]; ‡ ref. [11].