The Molecular Structures of Hexamethyldistannane, (CH₃)₆Sn₂, and Dimethylditellurane, (CH₃)₂Te₂, by Gas Electron Diffraction

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

Experimental

Hexamethyldistannane, Me₃SnSnMe₃, with stated purity of 99% was purchased from Aldrich-Chemie and used without further purification. Dimethylditellurane, MeTeTeMe, was synthesized from Na₂Te₂ and CH₃I as described in ref. [1] and characterized by high resolution mass spectrometry [2].

The gas electron diffraction data of both compounds were recorded on Balzers Eldigraph KDG-2 with nozzle-temperatures of about 25 °C (Me₆Sn₂) and 130 °C (Me₂Te₂).

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 Δs = 1.25 nm⁻¹ (six plates, 50 cm) and from s = 50.00 to 225.00 nm⁻¹ with increment Δs = 2.50 nm⁻¹ (six plates, 25 cm) for Me₆Sn₂ and from s = 35.00 to 145.00 nm⁻¹ with increment Δs = 1.25 nm⁻¹ (six plates, 50 cm) and from s = 70.00 to 200.00 nm⁻¹ (four plates, 25 cm) for Me₂Te₂.

Atomic scattering factors, f'(s)/E, were taken from Schäfer, Yates and Bonham [3]. The molecular intensities were modified by multiplication with s'/|f'₁(s)/I₁(s)|, E = Sn or Te.

Least-squares refinement of the seven structure parameters of Me₂Te₂, three vibrational amplitudes and the mole fraction of TeMe₂, now proceeded satisfactorily to the best values quoted in Table I. Experimental and calculated radial distribution curves, Fig. 1, are in good agreement.

Structure refinements

Structure refinements were based on molecular models of D₃ (Me₆Sn₂) and C₂ (Me₂Te₂) symmetry. In both molecules methyl groups were assumed to have C₃ᵥ symmetry with the threefold axes coinciding with the C–E bonds.

The molecular structure of either compound is then determined by seven parameters, e.g. the E–E, E–C and C–H bond distances, the <EEC and <EHC valence angles and two torsional angles (CEE)C and (ECE)H.

For Me₆Sn₂, least squares refinements of these parameters plus eight root-mean-square vibrational amplitudes (f-values) proceeded satisfactorily to yield the best values listed in Table I. Experimental and calculated radial distribution curves, Fig. 1, are in good agreement.

Similar least-squares refinements of the structure of Me₂Te₂ would at first not proceed properly, and inspection of radial distribution curves showed that experimental curves contained a peak at 313 pm corresponding to the C–D distance in dimethylditellurane, TeMe₂. The presence of TeMe₂, as an impurity was not detected by MS since the mass spectrum of Me₂Te₂ contains a strong peak assigned to TeMe₂⁺ [2].

The mole fraction of TeMe₂ in the gas jet was therefore introduced as an additional parameter, the structure parameters of TeMe₂ were fixed at the values obtained in a recent study in this laboratory [4].

Least-squares refinement of the seven structure parameters of Me₂Te₂, three vibrational amplitudes and the mole fraction of TeMe₂ now proceeded satisfactorily to the best values quoted in Table I. Experimental and calculated radial distribution curves, Fig. 2, are in good agreement. Since the bond distances and valence angles of Me₂Te₂ are consistent with molecular models of D₃ and C₂ symmetry and bond distances Sn–Sn = 277.6(3) pm and Te–Te = 268.6(3) pm, respectively.
have been determined with reasonable accuracy despite the presence of the TeMe₂ 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.

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

<table>
<thead>
<tr>
<th>Bond distances/pm</th>
<th>$r_e$/pm</th>
<th>$\ell$/pm</th>
<th>$r_e$/pm</th>
<th>$\ell$/pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>E–E</td>
<td>277.6(3)</td>
<td>7.0(3)</td>
<td>268.6(3)</td>
<td>5.4(3)</td>
</tr>
<tr>
<td>E–C</td>
<td>216.5(3)</td>
<td>7.6(4)</td>
<td>215.6(5)</td>
<td>[5.5]</td>
</tr>
<tr>
<td>C–H</td>
<td>110.3(4)</td>
<td>9.4(5)</td>
<td>111.1(15)</td>
<td>10(2)</td>
</tr>
</tbody>
</table>

Valence angles/deg

| E–E–E        | 111.9(4) |
| E–E–C        | 98.9(4)  |

Dihedral angles/deg

| $\phi$(CEEC) | 37(8)   |
| $\phi$(EECH) | 27(14)  |

Non-bonded distances/pm

| E–C          | 411(1)  |
| E–H          | 277(1)  |
| C–C          | 348(1)  |

$R^2$(50 cm)

| Me₃SnSnMe₃  | 2.2%    |
| MeTeTeMe    | 4.0%    |

$R^2$(25 cm)

| Me₃SnSnMe₃  | 9.0%    |
| MeTeTeMe    | 6.9%    |

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Fig. 1. Experimental (●) and calculated (—) radial distribution curves for Me₃SnSnMe₃. Below: Difference curve. Artificial damping constant $k = 30$ pm$^2$.

Fig. 2. Experimental (●) and calculated (—) radial distribution curves for MeTeTeMe. Peaks representing distances in the TeMe₂ impurity are indicated by stipled bars. Below: Difference curve. Artificial damping constant $k = 50$ pm$^2$. 

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*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; $e R = [\sum W(I_{obs} - I_{calc})^2]/\Sigma W(I_{obs})^{1/2}$. 

have been determined with reasonable accuracy despite the presence of the TeMe₂ 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.
**Discussion**

**Molecular shapes**

The gas electron diffraction data of Me$_3$SnSnMe$_3$ and MeTeTeMe are in good agreement with molecular models of D$_3$ and C$_2$ symmetry, respectively.

The estimated standard deviations of the dihedral angles $\varphi$(CCEE) 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 Sn$_2$H$_6$ 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 (D$_3d$) with a rotational barrier of 0.39 kcal mol$^{-1}$ [5]. The experimentally determined barrier to internal rotation about the Sn-C bond in H$_3$SnCH$_3$ [6] is 0.65 kcal mol$^{-1}$ (calculated [5] 0.57 kcal mol$^{-1}$). It seems likely, therefore, that both rotational barriers in Me$_3$SnSnMe$_3$ 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 ($\varphi = 0^\circ$) and staggered ($60^\circ$) conformations.

The best value of the dihedral angle $\varphi$(CTeTeC) in MeTeTeMe is close to the more accurately determined dihedral angles in Me$_2$Se$_2$ [7], Me$_2$S$_2$ [8] and Me$_2$O$_2$ [9]; 85(4)$^\circ$, 84(1)$^\circ$ and 119(4)$^\circ$, respectively.

**E–E bond distances**

The observed E–E bond distances in gaseous Me$_3$Sn–SnMe$_3$, Me$_3$Sb–SbMe$_3$ [10], MeTe–TeMe and I$_2$ [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:

- a-Sn has a diamond structure with Sn–Sn bonds about 3 pm greater than in Me$_3$SnSnMe$_3$ [13]. Similarly, the Ge–Ge bond in a-Ge [13], 245.0 pm, is about 5 pm greater than in gaseous H$_3$GeGeH$_3$ [14], 240.3(3) pm, and the Si–Si bond in a-Si [13], 235.2 pm, is about 2 pm longer than in gaseous H$_3$SiSiH$_3$ [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 H$_3$SnSnH$_3$ [5], the energy required to extend the Sn–Sn bond by 3 pm is less than 0.10 kcal mol$^{-1}$.

In crystalline I$_2$ [13] 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 I$_2$. The coordination number of the atoms in a-Te [17], a-Sb [12] and $\beta$-Sn [12] is six; in a-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 a-Sb each atom participates in three covalent and three secondary bonds, the latter are 53 pm longer than the normal bond in gaseous Me$_2$SbSbMe$_2$; finally, in $\beta$-Sn each atom participates in four normal and two secondary bonds which are 40 pm longer than the normal bond in Me$_3$SnSnMe$_3$. Formation of the secondary bonds is in every case accompanied by elongation of the normal bonds, in crystalline I$_2$ by 4 pm, in a-Te by 15 pm, in a-Sb by 9 pm and in $\beta$-Sn by 25 pm.

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<table>
<thead>
<tr>
<th>Gas phase</th>
<th>Me$_3$Sn–SnMe$_3$</th>
<th>Me$_3$Sb–SbMe$_3$</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>$\beta$-Sn</td>
<td>281.0 pm (4 $\times$)</td>
<td>290.8 pm (3 $\times$)</td>
<td>283.5 pm (2 $\times$)</td>
<td>271.5 pm (1 $\times$)</td>
</tr>
<tr>
<td>Solid phase</td>
<td>a-Sb</td>
<td>a-Sb</td>
<td>a-Te</td>
<td></td>
</tr>
<tr>
<td>302.2 pm (4 $\times$)</td>
<td>335.5 pm (3 $\times$)</td>
<td>349.1 pm (4 $\times$)</td>
<td>353 pm (2 $\times$)</td>
<td></td>
</tr>
</tbody>
</table>

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

Table II. E–E single bond distances, $E = Sn$, Sb, Te or I in simple gaseous molecules Me$_3$E–EMe$_3$, Me = CH$_3$, and in the crystalline elements [13].