The Molecular Structures and Conformational Preferences of Bis(dimethylstibyl)-Sulfane and -Tellurane, E(SbMe₂)₂, E = S or Te, Me = CH₃, by Density Functional Theory Calculations and Gas Electron Diffraction

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Density functional theory calculations on E(SbMe₂)₂, E = S or Te, Me = CH₃, indicate that the equilibrium structures are syn-syn or near syn-syn conformers with overall C₂ or C₂ symmetry. The calculations further indicate the existence of syn-anti conformers about 4 kJ mol⁻¹ (E = S) or 1 kJ mol⁻¹ (E = Te) above the equilibrium structure. Gas electron diffraction data show that both conformers are present in gaseous S(SbMe₂)₂, while the presence of the syn-anti conformer in gaseous Te(SbMe₂)₂ is uncertain. The Sb–S and Sb–Te bond distances are 241.4(4) and 278.1(3) pm, respectively, the valence angles of the syn-syn conformers are <SbSSb = 98.7(5)° and <SbTeSb = 91(2)°.

Introduction

Distibanes have received much attention due to the unusual colour changes observed on melting or dissolution in organic solvents. One of the possible explanations for these colour changes is based on the presence of different conformers and intermolecular interactions between electron lone pairs [1]. A structural investigation of tetramethyl-distibane in the gas phase yielded the Sb–Sb bond distance of 281.8(4) pm, but failed to establish the conformational composition [2]. Recently, UV photoelectron spectra and quantum chemical calculations showed that both gauche and anti conformers are present in the gas phase [3].

Some years ago we determined the molecular structures of the compounds Me₂SbEMe, Me = CH₃; E = S or Se, by gas electron diffraction (GED) [4]. The predominant conformers in the gas phase were characterised by eclipsing – or near eclipsing – of the E–C bonds and the electron lone pair on the Sb atom. In these syn conformers the dihedral angles θ(C–E–Sb–lp) were found to be less than 45°.

More recently we have reported on the molecular structures and conformational preferences of O(SbMe₂)₂ and Se(SbMe₂)₂ determined experimentally by GED and computationally by density functional theory (DFT) calculations, as well as a computational study of S(SbMe₂)₂ [5]. We now complete the series by reporting the results of GED studies of S(SbMe₂)₂ and Te(SbMe₂)₂ as well as a DFT study of the latter.

Computational and Experimental

DFT calculations

The results of DFT calculations on S(SbMe₂)₂ have been described earlier [5]. Similar calculations on Te(SbMe₂)₂ were carried out with the program system Gaussian94 [6] using the BPW91 density functional with the gradient correction of Becke [7a] for exchange and of Perdew and Wang for correlation [7b]. The standard LanL2DZ basis set [8] was applied with d polarisation functions added to all non-hydrogen atoms according to Ref. 9.

The DFT force field was used to calculate root-mean-square (rms) vibrational amplitudes by use of the ASYM40 program [10].

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**Gas electron diffraction**

The synthesis and characterisation of S(SbMe₂)₂ and Te(SbMe₂)₂ have been described elsewhere [11]. GED data were recorded on the Balzers KDG2 unit at the University of Oslo [12] with a metal (brass and steel) inlet system. Experimental conditions are summarised in Table I. The plates were scanned on an Agfa Arcus II scanner and data processed with a program system written by T. G. Strand [13]. Atomic scattering factors were taken from Ref. 14. Backgrounds were drawn as least-squares adjusted polynomials to the difference between experimental total and calculated molecular intensities. Structure refinements were carried out with the program KCED26 written by G. Gundersen, S. Samdal, H. M. Seip and T. G. Strand. The estimated standard deviations computed by the program were multiplied by a factor of two to include uncertainty due to data correlation [15] and expanded to include an estimated scale uncertainty of 0.1%.

Table I. Information about the gas electron diffraction experiment.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nozzle-to-plate distance (cm)</th>
<th>Nozzle temperature (°C)</th>
<th>Number of plates (25 cm/50 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(SbMe₂)₂</td>
<td>25/50</td>
<td>54±5</td>
<td>3/6</td>
</tr>
<tr>
<td>Te(SbMe₂)₂</td>
<td>25/50</td>
<td>96±2</td>
<td>3/3</td>
</tr>
</tbody>
</table>

**Results and Discussion**

**Density functional theory calculations**

Structure optimisation of Te(SbMe₂)₂ under C₂ symmetry converged to a model of C₂v symmetry in which the two dihedral angles φ(Sb–Te–Sb-lp) where lp indicates the supposed direction of the hybrid AO containing the electron lone pair on one of the Sb atoms, were equal to zero. We believe this syn-syn conformer to represent the equilibrium structure. The potential energy curve restricting torsion about Te–Sb bonds is, however, very soft; the lowest torsional mode (of B₁ symmetry) was 17 cm⁻¹. This means that a molecule in the gas phase at the temperature of our GED experiment will undergo large amplitude torsional vibrations, and that the thermal average structure, if not the equilibrium structure, will have effective C₂ symmetry. Bond distances and valence angles of the syn-syn conformer are listed in Table II.

<table>
<thead>
<tr>
<th>Compound</th>
<th>S(SbMe₂)₂</th>
<th>Te(SbMe₂)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GED</td>
<td>DFT</td>
</tr>
<tr>
<td>Intermolecular distances</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb–E</td>
<td>241.4(4)</td>
<td>248.9</td>
</tr>
<tr>
<td>Sb–C</td>
<td>213.2(3)</td>
<td>220.0</td>
</tr>
<tr>
<td>C–H (mean)</td>
<td>109.6(5)</td>
<td>110.0</td>
</tr>
<tr>
<td>E–C</td>
<td>329.5(16)</td>
<td>346.2</td>
</tr>
<tr>
<td>Sb–H (mean)</td>
<td>2731(2)</td>
<td>276.5</td>
</tr>
<tr>
<td>Valence angles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>φ(Sb–E–Sb–lp)</td>
<td>±33(4)</td>
<td>±45(12)</td>
</tr>
<tr>
<td>φ(Sb–C–Sb–lp)</td>
<td>±10(3)</td>
<td>±10(3)</td>
</tr>
<tr>
<td>φ(Sb–C–C–lp)</td>
<td>±368(2)</td>
<td>±365(2)</td>
</tr>
<tr>
<td>φ(Sb–H–H–lp)</td>
<td>±16(2)</td>
<td>±16(2)</td>
</tr>
</tbody>
</table>

Table II. Structure parameters of E(SbMe₂)₂, E = S or Te, Me = CH₃, obtained by gas electron diffraction (GED) or density functional theory (DFT) calculations. Interatomic distances (rₑ or rₑ*) and root-mean-square vibrational amplitudes (l) in pm, angles in degrees. Relative energies of conformers in kJ mol⁻¹.

The DFT calculations also indicate the existence of a local minimum on the potential energy surface, corresponding to a second, less stable conformer 0.9 kJ mol⁻¹ above the equilibrium (Fig. 1). In this syn-anti conformer the two dihedral angles are 0° and 180°, respectively, and the overall symmetry is Cᵥ. Rotation of one SbMe₂ fragment from syn to anti increases the valence angle <SbTeSb from 94.8° to 99.8°, presumably because of increased Sb...Me repulsions. Bond distances and the other valence angles are virtually unaffected;
all changes are less than 1 pm or 1°, respectively. DFT calculations on Te(SbMe2)2 thus yield results very similar to those previously obtained for the S and Se analogs [5].

The DFT force fields of the syn-syn conformers of the sulfane [5] and the tellurane were used to calculate r.m.s. vibrational amplitudes, l, at the temperatures of the GED experiments (Table II). The limited computational resources at our disposal did not allow us to calculate vibrational amplitudes for the less stable syn-anti conformers.

Structure refinements based on the GED data

Structure refinements of S(SbMe2)2 and Te(SbMe2)2 were based on a mixture of the near syn-syn and the syn-anti conformers shown in Fig. 1. The mole fractions were refined. All SbCH3 fragments were assumed to exhibit local C3v symmetry, and methyl group orientations were fixed in such a way that one C–H bond is anti relative to the Sb–E bond. The structure of the syn-syn conformer is then determined by eight independent parameters. We chose the C–H, Sb–C and Sb–E bond distances, the valence angles <ESbC, <CSbC and <SbCH, and the magnitude of the dihedral angles q. Since we believe that the valence angle <SbESb is determined by Sb···Sb repulsion rather than by electronic effects, the nonbonded Sb···Sb distance, rather than the angle was selected as the eighth independent variable.

The difference between the Sb···Sb distances in the two conformers was fixed at the DFT calculated value, other structure parameters of the two conformers were assumed equal. (And indeed, the final esd.s of these parameters listed in Table II show that the experimental uncertainties are much larger than the calculated differences.)
The mole fractions of the two conformers and the eight independent structure parameters of each compound were refined by least-squares calculations on the intensity data along with seven amplitude parameters for the sulfane and three for the tellurane. The values thus obtained are listed in Table II.

Calculated and observed intensity curves are compared in Fig. 2, calculated and observed radial distribution (RD) curves in Fig. 3. We consider the agreement satisfactory.

**Final Remarks**

A previous GED study of molecules Me₂SbE Me, E = S or Se, showed that the predominant species in the gas phase was a syn conformer with \( \varphi(C-E-Sb-lp) \) less than 45° [4]. It is therefore gratifying that DFT calculations on E(SbMe₂)₂, E = O, S, Se or Te indicate that the equilibrium structures are syn-syn conformers with dihedral angles in the same range and overall C₂ symmetry, or C₂ᵥ symmetry if the equilibrium value of \( \varphi = 0° \). The potentials restricting internal rotation about Sb–E bonds are, however, very soft. The calculations suggest that the thermal energy available at room temperature, RT = 2.4 kJ mol⁻¹, is five to ten times larger than the energy required to change the dihedral angles by 20°.

The thermal-average dihedral angles in the syn-syn conformers obtained by gas electron diffraction, \( \varphi(Sb–E–Sb–lp) = 28(4)°(E = O), 33(4)°(S), 26(3)°(Se) \) or 45(12)°(Te) are consistent with the large amplitude torsional motion suggested by the DFT calculations.

The DFT calculations also indicate the existence of syn-anti conformers of the oxane, sulfane and selenane with energies some 4 kJ mol⁻¹ above the more stable syn-syn conformers (Table III). The energy difference between the conformers of the tellurane is calculated to be significantly smaller.

Table III. Sb–E bond distances, \( \varphi(SbESb) \) valence angles, nonbonded Sb–Sb distances, and mole fraction of the syn-anti conformer of E(SbMe₂)₂, E = O, S, Se or Te, found by GED, relative energy of the syn-anti conformer by DFT calculations.

<table>
<thead>
<tr>
<th>E</th>
<th>O</th>
<th>S</th>
<th>Se</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb–E (pm)</td>
<td>197.6(14)</td>
<td>241.4(4)</td>
<td>255.1(5)</td>
<td>278.1(3)</td>
</tr>
<tr>
<td>( \varphi(SbESb) ) (°)</td>
<td>122.3(16)</td>
<td>98.7(5)</td>
<td>96.3(11)</td>
<td>91(2)</td>
</tr>
<tr>
<td>Sb–Sb (pm)</td>
<td>346(2)</td>
<td>366(2)</td>
<td>380(6)</td>
<td>396(5)</td>
</tr>
<tr>
<td>X</td>
<td>0.51(7)</td>
<td>0.48(4)</td>
<td>0.27(18)</td>
<td>0.19(32)</td>
</tr>
<tr>
<td>( \Delta E ) (kJ mol⁻¹)</td>
<td>4.6</td>
<td>3.9</td>
<td>3.7</td>
<td>0.9</td>
</tr>
</tbody>
</table>

a Ref. [5]; b in the syn-syn conformer.

This is not an unexpected result, but it should also be pointed out that the calculations on the tellurane have been carried out with a different set of basis functions. The GED refinements indicate the presence of syn-anti conformers with mole fractions of 51(7)% if E = O and 48(4)% if E = S. The presence of the high energy conformers of the selenane and tellurane is uncertain.

Comparison of computed and experimental bond distances (Table I) shows that DFT calculations consistently overestimate E–Sb and Sb–C bond distances by some five to eight pm. The Sb–

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**Fig. 3.** Experimental (dots) and calculated (line) radial distribution curves of S(SbMe₂)₂ and Te(SbMe₂)₂. Below: Difference curves. Artificial damping constant \( k = 25 \text{ pm}² \).
S bond distance is indistinguishable from that in Me₂SbSMe, 241.4(8) pm. The Sb–Te bond distance, the first to be determined in a gaseous molecule, is 278.1(3) pm as compared to an estimate of 275 pm from the Modified Schomaker-Stevenson Rule [16].

The valence angle \(<\text{SbOSb}\) of the syn-syn conformer, 122.3(16)° by GED and 119.0° by DFT, is larger than tetrahedral. This larger than VSEPR-predicted angle is presumably determined by across-angle repulsion between the Sb atoms [5].

The \(<\text{SbESb}\) angles in the heavier analogs are all smaller than tetrahedral and decrease as the group is descended.

Acknowledgements

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