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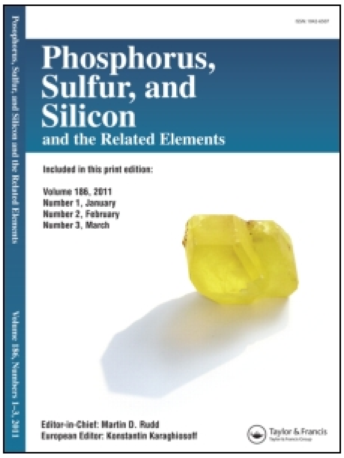

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Contributed Papers

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NEW ASPECTS OF THE SYNTHESES AND MOLECULAR STRUCTURES OF $Me_2SbSeSbMe_2$ AND RELATED COMPOUNDS

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The structures of bis(dimethylstibyl)chalcogenides have been studied by density functional theory calculations and gas electron diffraction.

Keywords: Organoantimony compounds, gas electron diffraction

INTRODUCTION

The observation of unusual colour changes[1] of some members of the series $Me_2SbESbMe_2$ (E = O, S, Se, Te) has prompted us to study the molecular structures using Density Functional Theory (**DFT**) calculations and Gas Electron Diffraction (**GED**).

Synthesis

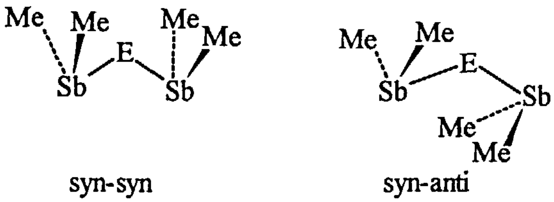
The synthesis of $(Me_2Sb)_2O$ (colourless, ugly smelling liquid, b.p.$_{(5)}$ 57.5-58.5 °C, yield 60 %, ^{1}H-NMR (C_6D_6) 0.840 ppm, MS (EI) m/z

320 (55%) M^+), was carried out by alkaline hydrolysis of Me_2SbBr[2]. The crude product contained 18 % Me_3Sb. It was distilled three times to reach a purity of 99 %. The reaction of $Me_2SbSbMe_2$ with elemental sulphur[3] selenium[4], or tellurium[4], resulted in the formation of $(Me_2Sb)_2E$ (E = S, Se, Te). Novel aspects of the preparative chemistry are the findings that $Me_2SbSeSbMe_2$ reacts with additional selenium until the stoichiometry of a diselenide $Me_2SbSeSeSbMe_2$ is reached. $Me_2SbTeSbMe_2$ is purified by distillation (b.p.$_{(0.0045)}$ 74-78 °C).

DFT and GED study of $(Me_2Sb)_2E$ (E = O, S, Se, Te)

Results of DFT calculations of $(Me_2Sb)_2E$ (E = O, S, Se) and GED data of $(Me_2Sb)_2E$ (E = O, Se) have recently been published[5]. The GED data of $(Me_2Sb)_2S$ were recorded on the Baltzers KDG2 unit at the University of Oslo with a metal inlet system at 94-98°C. Exposures were made with nozzle-to-plate distances of 25 cm (3 plates) and 50 cm (6 plates). Backgrounds were drawn as least-squares adjusted polynomials to the difference between the total experimental and the calculated molecular intensities. The structure refinements were based on a mixture of the *syn-syn* (C_2) and the *syn-anti* conformer (C_{2v}). All the $SbCH_3$ fragments had local C_{3v} symmetry. One C-H bond in each fragment was fixed in *anti* position to Sb-S. The structure of the *syn-syn* conformer is then determined by eight independent parameters (bond distances S-Sb, Sb-C, C-H; interatomic distance Sb···Sb, valence angles <SSbC, <CSbC, <SbCH;

torsion angle <SbSSblp, where lp is the lone electron pair of the antimony atom). The difference between Sb···Sb distances of *syn-anti* and *syn-syn* conformer was fixed at the DTF calculated value. Other structure parameters of *syn-anti* were assumed equal to that of *syn-syn*. Eight independent structure parameters, seven root-mean-square vibrational amplitudes and the mole fraction were refined. The estimated standard deviations were doubled to include uncertainty due to the data correlation and expanded to include a scale uncertainty of 0.1 %. R-factors obtained: 3.9% (50 cm), 16.5% (25 cm), 5.5 % (total).



Structural parameters of $(Me_2Sb)_2S$ and other bis(dimethylantimony) chalcogenides including preliminary data of the tellurium derivative are given in Table I.

TABLE I. Distances [pm] and angles [°] in the structures of $(Me_2Sb)_2E$ (E = O, S, Se, Te)

		syn-syn		syn-anti	
E atom	Sb-E	Sb···Sb	<SbESb	Sb···Sb	<SbXSb
O	198	346	122	360	131
S	241	366	99	382	105
Se	255	380	96	396	102
Te	278	396	91	412	96

Summary

DFT calculations on $(Me_2Sb)_2E$ (E = O, S, Se, Te) indicate that the equilibrium structures are *syn-syn* or near *syn-syn* conformers. The barriers restricting rotation about Sb-E bonds are very low, the equilibrium values for the dihedral angles ϕ(Sb-E-Sb-lp) (lp = direction of a lone pair at Sb) are probably less than 45°. The calculations further indicate the existence of *syn-anti*-conformers some 4 $kJ \cdot mol^{-1}$ above the more stable *syn-syn* conformer. GED data show that both conformers are present in gaseous $(Me_2Sb)_2O$ and $(Me_2Sb)_2S$, while the presence of the *syn-anti* conformer in gaseous $(Me_2Sb)_2Se$ or $(Me_2Sb)_2Te$ is uncertain. The Sb-O-Sb angle is wide compared to the Sb-Se-Sb or Sb-Te-Sb bond angle. It is suggested that the intramolecular repulsion between the antimony atoms is responsible for the wide angle of the oxo derivative.

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