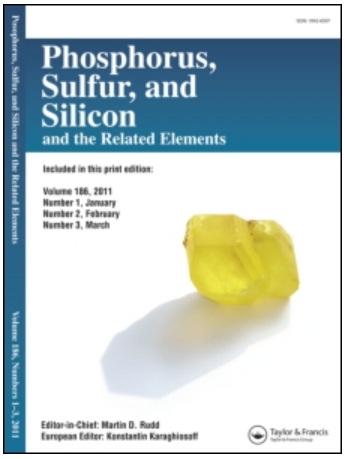

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A Comparison between Crystallographic and Theoretical Structures for Three Hypervalent $RSnCl_3$ Compounds

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Three compounds of the general formula $RSnCl_3$, where R contains an additional potential donor atom (*i.e.* O or Cl), have been subjected to *ab initio* geometry optimisation calculations. The interatomic parameters of the optimised geometries (calculated using Hartree-Fock (HF) theory, Density Functional Theory (DFT) and hybrid HF/DFT (B3LYP) theories, each employing the LanL2DZ basis set) are compared with previously determined crystallographic results. The study shows that Sn...O hypervalent interactions persist in the theoretical gas phase structures emphasising the chemical importance of such interactions. By contrast, intramolecular Sn...Cl interactions seen in the solid state do not persist in the theoretical structures suggesting that these may arise as a result of crystal packing effects.

Keywords: tin; hypervalency; *ab initio* calculations

INTRODUCTION

Recent investigations have shown that the use of a combination of crystallographic and theoretical methods provides great insight into the influence of intermolecular forces, *i.e.* crystal packing effects, on molecular geometry in organotin systems.[1-3] Differences in coordination geometries as well as non-systematic variations in Sn-ligand parameters have been ascribed to crystal packing effects.[1-3] These studies have been recently extended to include an examination of

hypervalent Sn···donor atom interactions in tetraorganotin compounds.[4] The focus of the later study was to determine whether such hypervalent interactions arose as a result of crystal packing effects or that they indeed represent real interactions. The conclusion of this study is that as the hypervalent interactions persisted in the gas phase structures, they are of real chemical significance. The present report represents an extension of the earlier work in which hypervalent interactions in three $RSnCl_3$ structures are investigated using *ab initio* geometry optimisations and the derived interatomic parameters are compared with literature experimental structures.

EXPERIMENTAL

Computational Methods

All geometry optimisations were performed using the GAUSSIAN 94 suite of programs[5] run on Silicon Graphics Indigo^{2}xZ Workstation and Silicon Graphics Power Challenge computers. All calculations were performed using i) Hartree-Fock SCF theory, ii) Density Functional Theory and, iii) a hybrid HF/DFT theory (B3LYP). The LanL2DZ basis set[5] was used for all calculations and includes the Dunning/Huzinaga double zeta descriptor[6] for all first-row elements and replaces the core electrons of sulfur (up to 2*p*), chlorine (up to 2*p*), and tin (up to 4*p*) with the effective core potentials (ECPs) of Hay and Wadt.[7]

RESULTS AND DISCUSSION

(2-Methoxy-5-methylphenyl)trichlorostannane

The structure of (2-Methoxy-5-methylphenyl)trichlorostannane features a tetrahedrally coordinated tin centre defined by the chloride atoms and the *ipso*-carbon atom of the disubstituted phenyl group. Selected interatomic parameters, gleaned from the original publication,[8] are reproduced in Table 1. Distortions from the ideal geometry arise from the non-symmetrical ligand donor set, intermolecular Sn···Cl interactions and the presence of an intramolecular Sn···O(1) contact, *i.e.* an

TABLE I Geometric Parameters (Å, deg) for (2-methoxy-5-methylphenyl) trichlorostannane

Parameter	X-ray	HF	Hybrid HF/DFT (B3LYP)	DFT (BLYP)
Sn—Cl(1)	2.316(2)	2.377	2.402	2.423
Sn—Cl(2)	2.317(11)	2.358	2.389	2.412
Sn—Cl(3)	2.276(11)	2.358	2.390	2.412
Sn—C(1)	2.100(11)	2.072	2.090	2.109
Sn···O	2.820(3)	2.630	2.763	2.879
C(1)—C(2)	1.391(14)	1.394	1.407	1.421
C(2)—C(3)	1.389(19)	1.382	1.402	1.417
C(3)—C(4)	1.410(14)	1.402	1.409	1.419
C(4)—C(5)	1.383(17)	1.395	1.413	1.424
C(5)—C(6)	1.398(18)	1.406	1.416	1.427
C(1)—C(6)	1.390(12)	1.388	1.403	1.415
C(2)—O(1)	1.356(11)	1.385	1.399	1.413
C(7)—O(1)	1.462(11)	1.443	1.460	1.480
C(5)—C(8)	1.572(16)	1.515	1.518	1.529
Cl(1)—Sn—Cl(2)	101.9(5)	103.8	104.7	105.2
Cl(1)—Sn—Cl(3)	105.8(5)	103.8	104.8	105.2
Cl(1)—Sn—C(1)	108.7(2)	106.5	106.0	105.9
Cl(2)—Sn—Cl(3)	104.4(4)	107.1	107.3	107.3
Cl(2)—Sn—C(1)	116.6(1,6)	117.0	116.6	116.0
Cl(3)—Sn—C(1)	117.8(1,5)	117.0	116.2	116.1

hypervalent interaction. Specially notable is the Sn···O(1) contact of 2.820(3) Å, a distance that is well within the sum of the van der Waals radii for these atoms of 3.7 Å[9] and which corresponds to a Pauling bond order of 0.07.[10] In order to ascertain whether the Sn···O(1) contact arises as a result of crystal packing effects, *i.e.* the desire to maximise the spherical nature of the molecule, rather than due to an inherent chemical reason, the molecule was subjected to geometry

optimisation calculations. The experimentally determined structure, *i.e.* X-ray structure, was used as the starting point for calculations which were performed at three levels of theory employing the LanL2DZ basis set.

The optimised structure for (2-methoxy-5-methylphenyl) trichlorostannane is shown in Figure 1 and calculated interatomic parameters are collected in Table I.

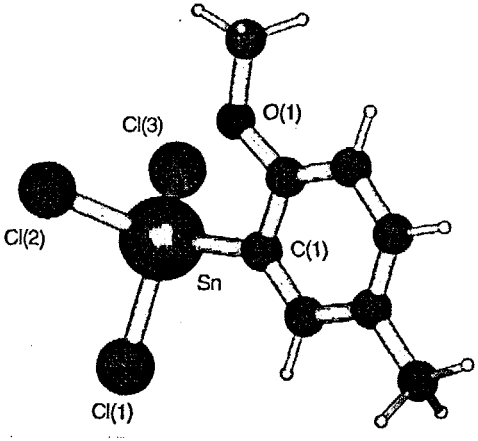

FIGURE 1 Molecular geometry for (2-methoxy-5-methylphenyl) trichlorostannane

Consistent with previous work, it can be seen from Table I that the results obtained with HF give the closest match to the experimentally determined structure with, generally, an elongation of the Sn-ligand parameters. The elongation of the distances has been shown to be due, in part, to the theoretical model employed.[1] It should be stated, however, that the overall geometries are similar regardless of the level of theory. Therefore, the results obtained are not due to limitations associated with the computational approach. The gas phase structure is more symmetrical that the solid state structure with the Sn—Cl(2) and Sn—Cl(3) bond distances being equal as would be expected from chemical considerations. Further, the Sn—Cl(1) distance, *i.e.* opposite to the O(1) atom, is longer (2.377 Å; HF) consistent with the presence

of a hypervalent Sn···O(1) interaction. Indeed, contrary to the expansions observed in most interatomic separations, the hypervalent interaction increases in magnitude in the optimised structure; the bond order was calculated to be 0.13.

(2,6-dimethoxyphenyl) trichlorostannane

The X-ray structure of (2,6-dimethoxyphenyl)trichlorostannane shows the presence of a intramolecular Sn···O interactions involving both methoxy substituents; Table II.[11] The tin atom geometry is distorted tetrahedral with a C_3Cl donor set. The Sn···O(1) and Sn···O(2) distances are 3.20(1) Å and 2.85(1) Å, respectively which correspond to bond orders of 0.02 and 0.06, respectively. In the optimised structure, illustrated in Figure 2 (HF), the stronger of these interactions is maintained but the weaker is not. Thus, the Sn···O(1) and Sn···O(2) distances expand and contract to 3.283 Å and 2.765 Å, respectively (bond orders: 0.02 and 0.08, respectively for HF). The Sn—Cl(1) and Sn—Cl(3) distances are equal to each other in the optimised structure and these distances are marginally longer than the Sn—Cl(2) distance which occupies a position approximately opposite to the Sn—O(2) vector. Similar to that described above, the ligand donor set is more symmetrical in the gas phase structure.

γ-chloropropyltrichlorostannane

By contrast to the systems described above, the structure of γ-chloropropyltrichlorostannane is reported to contain a hypervalent Sn···Cl interaction.[12] The distorted tetrahedral geometry about the tin atom is defined by three chloride atoms and the carbon atom of the *n*-propyl chain. The Cl(4) atom, at the 3-position of the chain, approaches the Sn atom at a distance of 3.279(4) Å compared with 3.9 Å being the sum of the van der Waals radii for Sn and Cl.[9] Consistent with the X-ray study, the Sn—Cl(1) and Sn—Cl(2) distances are approximately equal with the Sn—Cl(3) distance being longer than these in the optimised structure shown in Figure 3; see Table III for geometric parameters. Small deviations from mirror symmetry arise as the *n*-propyl group does not possess this symmetry. However, in the optimised structures the Sn···Cl separations are longer than that found in the solid state. Given the retention of the hypervalent interactions in the two structures

described above, it is argued on this basis that the Sn···Cl contact does not represent a significant hypervalent interaction.

TABLE II Geometric Parameters (Å, deg) for (2,6-dimethoxyphenyl)trichlorostannane

Parameter	X-ray	HF	Hybrid HF/DFT (B3LYP)	DFT (BLYP)
Sn—Cl(1)	2.311(4)	2.366	2.396	2.419
Sn—Cl(2)	2.293(5)	2.361	2.390	2.411
Sn—Cl(3)	2.303(3)	2.366	2.396	2.419
Sn—C(1)	2.082(10)	2.068	2.090	2.111
Sn···O(1)	3.20(1)	3.283	3.322	3.322
Sn···O(2)	2.85(1)	2.765	2.798	2.873
C(1)—C(2)	1.38(2)	1.393	1.408	1.422
C(2)—C(3)	1.431(19)	1.400	1.415	1.427
C(3)—C(4)	1.40(3)	1.393	1.406	1.416
C(4)—C(5)	1.40(3)	1.396	1.408	1.417
C(5)—C(6)	1.402(19)	1.391	1.406	1.419
C(1)—C(6)	1.40(2)	1.394	1.408	1.422
C(2)—O(1)	1.347(18)	1.361	1.384	1.402
C(7)—O(1)	1.444(19)	1.440	1.460	1.481
C(6)—O(2)	1.346(19)	1.371	1.392	1.408
C(8)—O(2)	1.45(2)	1.442	1.459	1.480
Cl(1)—Sn—Cl(2)	102.8(1)	102.2	102.7	102.8
Cl(1)—Sn—Cl(3)	104.2(1)	107.3	108.1	108.3
Cl(1)—Sn—C(1)	113.2(3)	113.4	113.0	112.6
Cl(2)—Sn—Cl(3)	101.3(1)	102.2	102.6	102.8
Cl(2)—Sn—C(1)	118.4(4)	117.1	116.4	116.9
Cl(3)—Sn—C(1)	115.1(3)	113.4	113.0	112.5

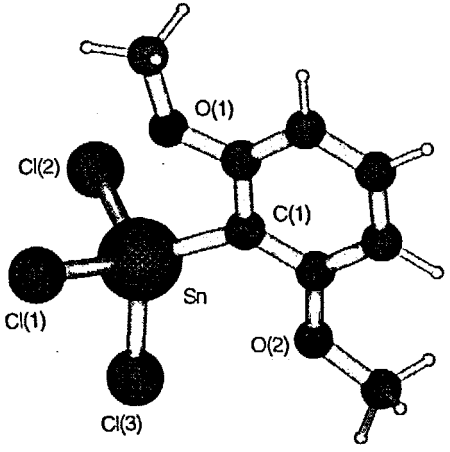

FIGURE 2 Molecular geometry for (2,6-dimethoxyphenyl)-trichlorostannane

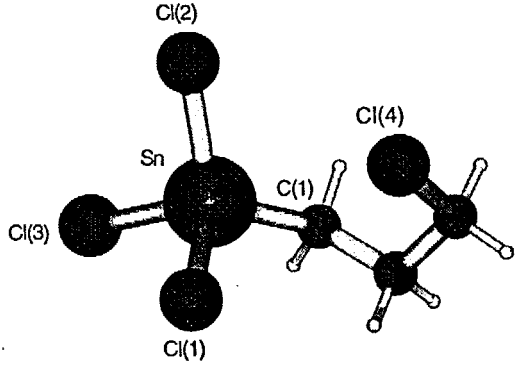

FIGURE 3 Molecular geometry for γ-chloropropyltrichlorostannane

TABLE III Geometric Parameters (Å, deg) for γ-chloropropyltrichlorostannane

Parameter	X-ray	HF	Hybrid HF/DFT (B3LYP)	DFT (BLYP)
Sn—Cl(1)	2.314(4)	2.358	2.393	2.416
Sn—Cl(2)	2.320(4)	2.353	2.388	2.412
Sn—Cl(3)	2.336(4)	2.372	2.404	2.428
Sn—C(1)	2.144(13)	2.124	2.140	2.163
Sn···Cl(4)	3.279(4)	3.429	3.348	3.407
C(1)—C(2)	1.516(15)	1.542	1.554	1.554
C(2)—C(3)	1.554(19)	1.522	1.527	1.537
C(3)—Cl(4)	1.845(15)	1.878	1.898	1.923
Cl(1)—Sn—Cl(2)	104.9(2)	109.9	110.7	110.9
Cl(1)—Sn—Cl(3)	99.9(3)	104.4	104.5	104.7
Cl(1)—Sn—C(1)	115.3(6)	113.9	113.4	113.4
Cl(2)—Sn—Cl(3)	100.8(2)	103.6	103.3	103.4
Cl(2)—Sn—C(1)	120.7(7)	118.5	119.6	119.6
Cl(3)—Sn—C(1)	112.4(5)	104.8	103.3	102.7

Energy Considerations

The differences in energy between the experimental (single-point calculation) and optimised geometries for the three levels of theory are collected in Table IV. Energy differences are greatest for the calculations performed using the B3LYP and BLYP levels of theory, consistent with earlier studies.[1-3] Nevertheless, energy differences calculated using HF are also exaggerated owing to limitations of the theory and errors associated with the experimental structures.[1-3] For example, it has been shown that the treatment of hydrogen atoms in the refinement of the X-ray data (modelled to account for electron distribution) may account for up to one third of the energy difference between an experimental structure and its calculated optimised structure.

TABLE IV Calculated energies (hartrees, kJ mol^{-1}) for (2-methoxy-5-methylphenyl) trichlorostannane (**1**), (2,6-dimethoxyphenyl)trichlorostannane (**2**) and γ-chloropropyltrichlorostannane (**3**)

	1	2	3
Single point			
HF (hartrees)	-430.3044	-505.1338	-179.1664
B3LYP (hartrees)	-433.6216	-508.8185	-181.0991
BLYP (hartrees)	-433.3023	-508.4943	-180.8306
Optimised geometry			
HF (hartrees)	-430.4507	-505.2767	-179.2682
B3LYP (hartrees)	-433.7905	-508.9865	-181.2150
BLYP (hartrees)	-433.4889	-508 .6824	-180.9569
Δ (kJ mol^{-1})			
HF	384.1	375.2	267.3
B3LYP	443.5	441.1	304.3
BLYP	489.9	493.8	331.6

CONCLUSIONS

The results obtained in this study match closely those found in a related study of hypervalent interactions in tetraorganotin systems.[4] Hypervalent Sn···O interactions found in the solid state are retained in the theoretical structures and indeed, relative to the primary coordination geometry, are strengthened. These results indicate persistence of hypervalent interactions of this type and indicate their true chemical significance. In contrast, a Sn···Cl interaction found in the solid state of γ-chloropropyltrichlorostannane does not persist in the gas phase structure suggesting that this interaction should not be regarded as significant. So, whereas Sn···O interactions are retained in the theoretical structures, it is suggested that the Sn···Cl contact arises as a result of

crystal packing considerations rather than as a result of a *bona fide* bonding interaction. The observation of symmetrisation in molecular geometry and the closer match of geometric parameters calculated using HF to experimental structures found in the present work also matches previous reports.[1-4]

ACKNOWLEDGMENTS

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