ADELAIDE UNIVERSITY
AUSTRALIA

Department of Chemistry

Systematic Studies of Organotin Compounds Using *Ab Initio* Molecular Orbital Calculations

A Master of Science Thesis Submitted by
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ADDENDUM

Page 8,	para. 2, line 3:	replace 'tribenzyl' with 'triphenyl'
Page 8,	para. 2, line 6:	replace 'trimethyl' with 'tribenzyl'
Page 20,	para. 5, line 1:	...molecule shows **that** the molecule...
Page 21,	para. 1, line 1:	...elongations may be **the** result...
Page 21,	para. 5, line 5:	...trichloride exists **as** a C2b...
Page 24,	para. 4, line 2:	replace 'crystallographically' with 'X-ray diffraction'
Page 31,	para. 3, line 3:	...packing **nor** due **to** basis sets.
Page 32,	para. 3, line 4:	replace phrase beginning 'The lengths...' with 'The lengths of Sn-Cl(2) and Sn-Cl(3) are expected to be the same as these atoms exist in similar chemical environments,...'
Page 43,	para. 5, line 1:	replace 'see below molecule **8**' with 'see molecule **8** below'
Page 45,	para. 4, line 3:	replace 'crystallographic' with 'X-ray crystallographic'
Page 55,	para. 5, line 1:	...structure it **has** in the...

DECLARATION

This thesis contains no material that has been submitted previously for a degree or diploma in any university and to the best of my knowledge contains no material published or written by another person, except where due reference is made.

I consent to this thesis being made available for photocopying and loan.

Signed:

Date: 29 March 2001.

ACKNOWLEDGMENTS

This thesis represents the summary of four years effort of part-time research at the University of Adelaide. It was somewhat a struggle at times to undertake research as it was combined with studies in Law. Nevertheless, I believe that completing a Master of Science dissertation has made me a stronger, and more experienced person in more ways than one.

I would sincerely like to thank my laboratory colleagues: David Clarke, Dr Michael Cox, Dr Ismael Ibrahim, Douglas Smyth and Jean Todd for the memories of postgraduate life that they have left me with.

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I would finally like to thank my supervisor Dr Edward R.T. Tiekink for the support, help, and patience over the years I have been in the group.

ABSTRACT

In this thesis, various organotin(IV) compounds were studied using *ab initio* molecular orbital calculations. This is because there has been a lack of information relating to the structural status of such compounds in the gas phase.

Chapter 2 deals with the determination of the most appropriate level of theory to be used on organotin compounds. Three levels of theory, Hartree Fock (HF) [with the basis sets Lanl2dz, 3-21G**, and 3-21G** with polarisation functions], Density Functional Theory (DFT), and a hybrid of these two levels, B3LYP, were tested on three small organotin compounds.

The HF level of theory was determined to be the most appropriate model to be used for future investigations as it generated parameters for angles and bonds that were most similar to structures determined by electron diffraction studies, and relatively unexaggerated values for energy differences between the two states.

Chapters 3 and 6 describe the study of monoorganotin trichloride and tetraorganotin compounds of type $R_3R'Sn$, respectively. There is debate as to whether these compounds can undergo intramolecular hypervalent interactions in the solid state. Studies were carried out in the gaseous phase using *ab initio* molecular orbital calculations to determine whether close intramolecular interactions found in the solid state persisted in the theoretical (gas phase) structures.

Chapters 4 and 5 deal with diorganotin dichloride and triorganotin chloride compounds, respectively. There has been dispute in the literature as to whether these compounds can also undergo intermolecular hypervalent interactions in the solid state. It is debatable whether the distortions from regular geometries seen in the solid state were sufficient to indicate hypervalency and therefore, were sometimes attributed to crystal packing effects. Analysis using *ab initio* molecular orbital calculations on these compounds showed that both hypervalency and crystal packing effects caused the distortions observed in these compounds.

PUBLICATIONS

1. Buntine, M.A.; Hall, V.J.; Kosovel, F.J.; Tiekink, E.R.T.; *J. Phys. Chem. A.* **102** (1998) 2472-2482. (Research from Chapter 2)

2. Buntine, M.A.; Kosovel, F.J.; Tiekink, E.R.T.; *Phosphorus, Sulfur, and Silicon.* **150-151** (1999) 261-270. (Research from Chapter 3)

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