



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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March, 2001

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.

I would like to add an indebted gratitude to Dr Mark Buntine for his advice, and Annette Chigros, Professor Bill Jensen and Jean Todd for taking the time out to proofread scripts from my thesis. I would also like to thank Jeff Borkent and Craig Patten for their last minute computational help.

Further, I would like to thank the Australian Research Council for the financial assistance provided during the first year of my candidature.

Hugs and thanks go to my parents, Dr Ben Woolven, and his family, for their tolerance, patience, and support over the years that I have been studying at university.

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)

TABLE OF CONTENTS

Declaration	i
Acknowledgments	ii
Abstract	iii
Publications	iv
Table of Contents	v

Chapter 1: Introduction

1.1 The History and Uses of Tin and its Compounds	1
1.2 The Chemistry of Tin	3
1.3 Organotin(IV) Compounds	4
<i>(i) Tetraorganotin Compounds</i>	4
<i>(ii) Organotin Halide Compounds</i>	6
1.4 The Aim of the Project	8
1.5 References	11

Chapter 2: The Experimentation of *Ab Initio* Molecular Orbital Calculations Using Different Basis Sets on Small Organotin Compounds

2.1 Introduction	14
2.1.1 Previous Computational Methodologies for Organotin Compounds	15
<i>(i) Methyltin triiodide</i>	15
<i>(ii) Tin(IV) hydride and Tetramethyltin</i>	16
<i>(iii) Pentacarbonylmolybdenum(0)-stanylene</i>	17
<i>(iv) Tetraorganotin derivatives: $\text{Sn}(\text{CH}_3)\text{Cl}_{4-n}$ ($n=0-4$)</i>	18
2.2 Experimental	19
2.3 Results and Discussion	20

<i>(i) Tetramethyltin</i>	20
<i>(ii) Methyltin trichloride</i>	21
<i>(iii) Trimethyltin chloride</i>	23
2.4 Conclusion	24
2.5 Appendix	26
2.6 References	27

Chapter 3: Determination of Hypervalency and the Comparative Studies of Monoorganotin Trichloride Compounds Between the Solid State and Gaseous Phase

3.1 Introduction	30
3.2 Experimental	30
3.3 Results and Discussion	31
<i>(i) (2-Methoxy-5-methylphenyl)tin trichloride</i>	31
<i>(ii) (2,6-Dimethoxyphenyl)tin trichloride</i>	34
<i>(iii) γ-Chloropropyltin trichloride</i>	36
3.4 Conclusion	37
3.5 Appendix	39
3.6 References	40

Chapter 4: Comparative Studies of Diorganotin Dichloride Compounds Between the Solid State and Gaseous Phase

4.1 Introduction	41
4.2 Experimental	43
4.3 Results and Discussion	43
<i>(i) Dimethyltin dichloride</i>	44

(ii) Diethyltin dichloride	46
(iii) Diisopropyltin dichloride	47
(iv) Dibutyltin dichloride	49
(v) Diterbutyltin dichloride	50
(vi) Diphenyltin dichloride	51
(vii) Dicyclohexyltin dichloride	53
(viii) Bis(biphenyl-2-yl)tin dichloride	55
(ix) Methylphenyltin dichloride	56
(x) 5,5-Dichloro-10,11-dihydrodibenzo-[b,f]stannepine	58
(xi) Comparative Study - Crystal Packing Effects and/or Hypervalent Interactions?	59
4.4 Conclusion	65
4.5 Appendix	66
4.6 References	68

Chapter 5: Comparative Studies of Triorganotin Chloride Compounds Between the Solid State and Gaseous Phase

5.1 Introduction	70
5.2 Experimental	70
5.3 Results and Discussion	70
(i) Triphenyltin chloride	70
(ii) Tribenzyltin chloride	72
(iii) Tris(bis(tri-methylsilyl)methyl)tin chloride	73
(iv) Tris(4-tert-butylphenyl)tin chloride	74
5.4 Conclusion	74
5.5 Appendix	76

5.6	References	77
 Chapter 6: Determination of Hypervalency and Comparative Studies of Tetraorganotin Compounds of the form $R_3R'Sn$ Between the Solid State and Gaseous Phase 		
6.1	Introduction	78
6.2	Experimental	78
6.3	Results and Discussion	79
	(i) <i>(Z)</i> -2-Methyl-3-triphenylstannyl-pent-3-en-2-ol	79
	(ii) <i>(Z)</i> -3,4,4-Trimethyl-1-(triphenylstannyl)-1-penten-3-ol	82
	(iii) <i>(Z)</i> -1-[2-(Triphenylstannyl)vinyl]-1-cycloheptanol and	
	(iv) <i>(Z)</i> -1-[2-(Tri- <i>p</i> -tolylstannyl)vinyl]-1-cycloheptanol	85
	(v) (2-Carbomethoxy-1,4-cyclohexadien-1-yl)trimethyltin	89
	(vi) [2-(4,4-Dimethyl-2-oxazoliny)-3-thienyl]tri(<i>p</i> -tolyl)tin	91
	(vii) <i>C,N</i> -(3-(2-Pyridyl)-2-thienyl)-tri- <i>p</i> -tolyl-tin	93
	(viii) [Bis(2-methoxy-3- <i>tert</i> -butyl-5-methylphenyl)methyl]-triphenyltin	96
	(ix) (8-(Dimethylamino)-1-naphthyl)-triphenyl-tin	97
	(x) General Considerations	99
6.4	Conclusion	99
6.5	Appendix	101
6.6	References	103

Chapter 7: Conclusion

7.1	Summary and Conclusion	104
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