



*Thesis titled:*

**Different Mass Spectrometers, Widely Differing  
Purposes.**

**From Structure Elucidation Tool to Gas Phase  
Ion-Molecule Reactions.**

Submitted for the Degree of Doctor of Philosophy (PhD)

by

**Micheal (Mike) John Maclean**

BSc (Hons) MRACI CChem

GradDipForsSc (DNA Tech) MAIBiol

of the

**Department of Chemistry**

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*For my special little mate*

*Maksim Vuk Maclean*

28/11/2005 -

“Dad ‘gave-it-a-go’, so should you”

XOXOXO

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In order to get such amount of work done we are constantly reliant on our equipment, machines and chemicals to be in pristine working order and available when needed. When these things break down, when some things are hard to obtain and need to be replicated or constructed, or even alternatives are the best solutions, we are ever so reliant on our technical staff and support. I thank the number of people that I have had help me on the way to get my work done and overcome some of the technical difficulties I have faced. I have met some great people in these areas, mainly at the university, however some from abroad as well. Thank you all very much, your services are invaluable.



## **PREFACE**

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Also through the time frame of this work I have been to and seen some wonderful places both home and abroad. Along with these travels I have encountered and challenged my taste buds and culinary interests. Some of the wonderful experiences I have had include: International Conferences, Dinners, Lunches, Weddings, Birthdays, Wine Tastings, House Warmings and Scotch Tastings. Some truly wonderful experiences.

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## DECLARATION

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution to Micheal J. Maclean and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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**Micheal (Mike) John Maclean**

BSc (Hons) MRACI CChem

GradDipForsSc (DNA Tech) MAIBiol

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## ABSTRACT

This thesis is comprised of two parts with all the work carried out centred around the use of two mass spectrometers with vastly differing capabilities and with the experimental results obtained supported or refuted with the aid of theoretical quantum chemical calculations.

For the last two decades our research group has been interested in cumulenes and hetero-cumulenes, some detected and some not as yet in their interstellar environs. The work discussed in the first part of this thesis is a continuation of some of that work and a comparison with the new work undertaken within. Our interest is predominantly orientated towards the neutral systems and their rearrangements. Our work on interstellar molecules is of interest because some of the systems investigated here and in the past, along with their precursor molecules are already known interstellar molecules and some have been implicated as possible precursors for the building blocks of life and some as possible antibiotics.

The first part of this thesis uses a combination of mass spectrometric techniques using a VG ZAB 2HF mass spectrometer (mainly charge reversal mass spectrometry) and/or theoretical quantum calculations to investigate the structures and energetics of the neutral tetra-atomic and hetero-cumulenic systems CCCN, CCCSi, CCCP, H<sub>2</sub>CCCN, and ONCS (a possible primordial antibiotic).

The second part of this thesis involves the modification of a Finnigan LCQ ion trap mass spectrometer in order to perform gas phase ion-molecule reactions between selectively generated carbanions and carbon disulfide.

The investigation carried out in the second part of this thesis is a revisit on our earlier group research on the gas phase *ipso* (Smiles) rearrangement. It was proposed that the adducts formed between the carbanions and CS<sub>2</sub> undergo Smiles type rearrangements *via ipso* intermediates upon collision induced dissociation CID.