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Preliminary Ion Mobility Mass Spectrometric Studies on Fullerenyl Bisadducts

A thesis submitted in fulfillment of the requirements for the award of the degree

Master by Research

from



University of Wollongong

by

Qing Xiang Zhang

**Supervisor: Assoc. Prof. Paul Keller
Prof. Stephen Pyne**

School of Chemistry

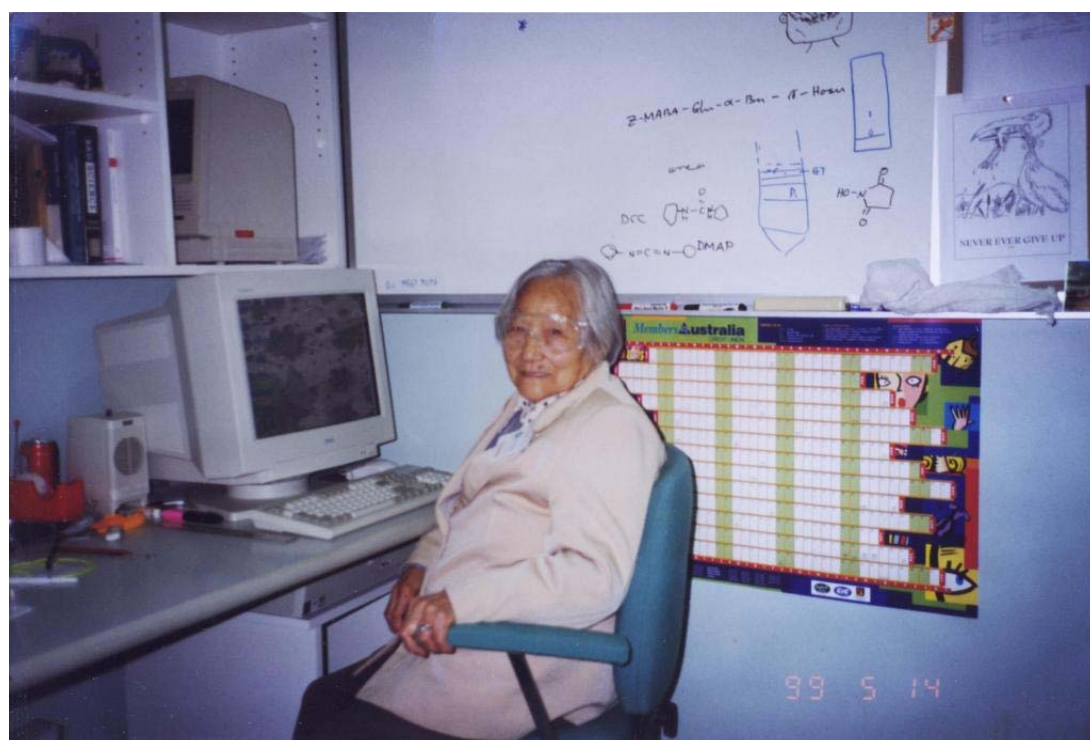
2009

Declaration

I declare that this thesis, submitted in fulfillment of the requirements for the award of the degree of Master by Research, in the School of Chemistry, Faculty of Sciences, University of Wollongong, does not contain any material which has been accepted for the award of any degree or diploma in this or any other academic institution and to my best knowledge and belief contains no material in any previous publication except where due reference has been acknowledged.

Qing Xiang Zhang

November, 2009



in the memory of my dear granny...

Table of Contents

| | |
|---|------|
| Certification | i |
| Table of Contents | iii |
| List of Figures | vii |
| List of Schemes | viii |
| List of Tables | x |
| List of Abbreviations | xi |
| Acknowledgements | xv |
| Abstract | xvi |
| Chapter 1: Introduction | 1 |
| 1.1 Fullerene | 2 |
| 1.1.1 Discovery | 2 |
| 1.1.2 Structure | 3 |
| 1.1.3 Physical and Chemical Properties | 6 |
| 1.1.4 Applications | 6 |
| 1.1.4.1 Prospective Biological Applications | 6 |
| 1.1.4.2 Potential Applications in Material Science and Technology | 8 |
| 1.2 Chemical Properties of C ₆₀ | 10 |
| 1.2.1 Reduction | 10 |
| 1.2.2 Nucleophilic Addition | 13 |
| 1.2.3 Cycloaddition | 16 |
| 1.2.4 Radical Addition | 17 |
| 1.2.5 Oxidation and Reactions with Electrophiles | 18 |
| 1.3 Regioisomerism, Stereoisomerism and Chiral Functionalised | |

| | |
|---|-----------|
| Fullerenyl Bisadducts | 18 |
| 1.3.1 Regioisomerism | 19 |
| 1.3.2 Stereoisomerism | 21 |
| 1.3.3 Chirality | 23 |
| 1.4 Bingel Reaction | 24 |
| 1.5 Chemical Realisation of Methanofullerenyl Bisadducts of Desired Regioselectivity | 27 |
| 1.6 Electrochemically Induced Isomerisation of Tetraethyl Bismethano[60]fullerenyl Malonates | 30 |
| 1.7 Ion Mobility Mass Spectroscopy (IMMS) | 33 |
| 1.7.1 Introduction of IMMS | 33 |
| 1.7.2 Development of IMMS | 33 |
| 1.7.3 Principle of Ion Mobility Spectroscopy (IMS) | 34 |
| 1.8 Project Aims | 36 |
| Chapter 2: Results and Discussion | 39 |
| 2.1 Tartaric Acid Derived Tethered Bismethano[60]fullerenyl Adducts | 41 |
| 2.1.1 Reduction of Dimethyl 2,2-dimethyl-1,3-dioxolane-4,5 -dicarboxylate (37) | 41 |
| 2.1.2 Formation of the Tartaric Bismalonate Tether (+)-(4 <i>R</i> ,5 <i>R</i>)-bis{[(ethoxycarbonyl)acetoxy]methyl}-2,2- dimethyl-1,3-dioxolane (36) | 43 |
| 2.1.3 Tethered Functionalisation of [60]fullerene by (36) to Form Bismethano[60]fullerenyl Adducts under Bingel Reaction Condition | 44 |
| 2.2 1,4-Benzenedimethanol Tethered Bismethano[60]fullerenyl Adducts | 46 |
| 2.2.1 Formation of the 1,4-benzenedimethanol Tethered Bismalonate, 1,4-bis{[(ethoxycarbonyl)acetoxy]methyl} | |

| | |
|--|------------|
| benzene (34) | 46 |
| 2.2.2 Tethered Functionalisation of [60]fullerene by (36) to Form Bismethano[60]fullerenyl Adducts under Bingel Reaction Conditions | 46 |
| 2.3 1,3-Benzenedimethanol Tethered Bismethano[60]fullerenyl Adducts | 48 |
| 2.3.1 Formation of the 1,3-benzenedimethanol Tethered Bismalonate 1,3-bis{[(ethoxycarbonyl)acetoxy]methyl} benzene (35) | 48 |
| 2.3.2 Tethered Functionalisation of [60]fullerene by (35) to Form Bismethano[60]fullerenyl adducts under Bingel Reaction Conditions | 49 |
| 2.4 Generation of Tetraethyl Bismethano[60]fullerenyl Tetracarboxylate | 50 |
| 2.5 Semi-empirical Calculations of Heat of Formation of Regioisomeric Bisadducts | 53 |
| 2.6 Study on Tethered and Non-tethered Methano[60]fullerenyl Bisadducts | 60 |
| 2.7 Mass Spectrometry (MS) and Ion Mobility Mass Spectrometric (IMMS) Studies | 61 |
| 2.7.1 ESIMS Studies | 61 |
| 2.7.2 IMMS Studies | 63 |
| Chapter 3: Conclusions | 71 |
| Chapter 4: Experimental | 75 |
| Chapter 5: References | 87 |
| Appendix I: Summary of Reactions | 97 |
| Appendix II: NMR Spectra | 103 |

| | |
|----------------------------------|------------|
| Appendix III: IR Spectra | 131 |
| Appendix IV: Mass Spectra | 141 |

List of Figures

| | | |
|--------------|--|----|
| Figure 1.1: | Structural similarities among the Montreal Biosphère, C ₆₀ and a common football | 3 |
| Figure 1.2: | C ₆₀ structural characters presented in the Kelulé formulas | 4 |
| Figure 1.3: | C ₆₀ Spectra (IR, ¹³ C-NMR and UV-Vis) | 5 |
| Figure 1.4: | Partial Hückel molecular orbital diagram of C ₆₀ | 11 |
| Figure 1.5: | Reduction of C ₆₀ in CH ₃ CN/toluene at -10°C detected by cyclic voltammetry and differential pulse voltammetry | 11 |
| Figure 1.6: | The circulatory stepwise reduction of C ₆₀ using TBAClO ₄ in acetonitrile | 12 |
| Figure 1.7: | Positional notation for C ₆₀ bismethano-adducts | 20 |
| Figure 1.8: | Schlegel and schematic diagrams of typical the C ₅ -symmetrical methanofulleryl bisadducts and the C ₂ -symmetrical methanofulleryl bisadducts | 21 |
| Figure 1.9: | Stereoisomerism illustrated by the <i>cis</i> -2 and <i>cis</i> -3 methanofullerenyl bisadducts | 23 |
| Figure 1.10: | The ^f C and ^f A numberings schemes lead to a pair of enantiomers of the <i>cis</i> -3 methanofullerenyl bisadduct | 24 |
| Figure 1.11: | A general scheme of tethered double functionalisation of C ₆₀ | 30 |
| Figure 1.12: | A schematic ambient-pressure IMMS | 36 |
| Figure 2.1: | The structures of the tethered bismalonates (34) , (35) and (36) | 41 |
| Figure 2.2: | IMMS spectra of tethered bisadducts, +ve ion mode | 64 |
| Figure 2.3: | IMMS spectra of tethered bisadducts, -ve ion mode | 65 |
| Figure 2.4: | IMMS spectra of non-tethered bisadducts, +ve ion mode | 66 |
| Figure 2.5: | IMMS spectra of non-tethered bisadducts, -ve mode | 67 |

List of Schemes

| | | |
|--------------|---|----|
| Scheme 1.1: | Treatment of electrochemically generated C_{60}^{2-} with MeI gives rise to a mixture of 1,2- and 1,4-dimethyl dihydro[60]fullerenes (5) and (6) in a ratio of 1.4:1 | 12 |
| Scheme 1.2: | Formation of the Pd-complex (8) through quenching the electrochemically generated C_{60}^{2-} by a phosphine ligand (7) | 13 |
| Scheme 1.3: | Direct reduction of C_{60} by the electron-donor TDAE | 13 |
| Scheme 1.4: | Addition of C_{60} by various nucleophilic organolithium and Grignard compounds | 14 |
| Scheme 1.5: | Diethyl methano[60]fullerenyl diester synthesised through cyclopropanation by deprotonated diethyl bromomalonate | 15 |
| Scheme 1.6: | Nucleophilic additions by methyl 2-chloroacetylacetate, ω -bromoacetophenone and desylchloride under Bingel conditions | 15 |
| Scheme 1.7: | Diazomethane, a typical 1,3-dipole as an example of [3+2]cycloaddition to C_{60} | 17 |
| Scheme 1.8: | Radical addition to C_{60} | 18 |
| Scheme 1.9: | Double Bingel reaction of C_{60} with diethyl malonate and regioselective double cyclopropanation with <i>m</i> - and <i>p</i> -benzenedimethanol derived tethered bis- <i>N</i> -(diphenyl methylene)glycinate esters under Bingel reaction conditions | 28 |
| Scheme 1.10: | The two-step mechanism of bisfunctionalisation of C_{60} by a tethered malonate ester | 29 |
| Scheme 1.11: | Mixed regioisomers of tetraethyl bismethano[60]fullerenyl malonates resulted from double cycloaddition to C_{60} with diethyl malonate | 31 |

| | | |
|--------------|---|----|
| Scheme 1.12: | Electrochemically induced “walk-on-the-sphere” rearrangement of two addends to give mixtures of regioisomers with the approximate distributions in percentages. | 32 |
| Scheme 2.1: | Reduction of dimethyl 2,2-dimethyl-1,3-dioxolane -4,5-dicarboxylate (37) by lithium aluminium hydride to generate the diol (38) | 42 |
| Scheme 2.2: | Mechanism of reduction of the diester (37) by LiAlH ₄ to form the diol (38) | 43 |
| Scheme 2.3: | Synthesis of the tartaric bismalonate tether (36) | 44 |
| Scheme 2.4: | Mechanism of diesterification of the diol (38) by (39) to form the tartaric bismalonate tether (36) | 44 |
| Scheme 2.5: | Synthesis of tartaric acid derived tethered bismethano[60]fullerenyl adducts (40) and (41) under Bingel reaction conditions | 45 |
| Scheme 2.6: | Synthesis of the 1,4-benzenedimethanol tethered bismalonate (34) | 46 |
| Scheme 2.7: | Synthesis of 1,4-benzenedimethanol tethered bismethano[60]fullerenyl adducts (43) and (44) under Bingel reaction condition | 47 |
| Scheme 2.8: | Synthesis of the 1,3-benzenedimethanol tethered bismalonate (35) | 48 |
| Scheme 2.9: | Synthesis of 1,3-benzenedimethanol tethered bismethano[60]fullerenyl adduct (46) | 49 |
| Scheme 2.10: | Transesterification of bisadducts by ethanol | 52 |
| Scheme 2.11: | Methanol adduct of a tethered bisadduct in methanol solvent. | 62 |

List of Tables

| | | |
|------------|---|----|
| Table 1.1: | Summary of symmetry operations and stereoisomerism corresponding to regioisomeric assignments for fullereryl bisadducts | 22 |
| Table 1.2: | Methanofullerenes formed under Bingel reaction conditions by addition/elimination mechanism | 25 |
| Table 1.3: | Bingel cycloaddition with malonic esters | 26 |
| Table 1.4: | Addition reactions of <i>N</i> -(diphenylmethylene)glycinate esters to C ₆₀ | 27 |
| Table 2.1 | 1,4-Benzenedimethanol tethered bisadducts | 53 |
| Table 2.2: | 1,3-Benzenedimethanol tethered bisadducts | 55 |
| Table 2.3: | Tartaric acid derived bismethano[60]fullereryl tethered bisadducts | 57 |
| Table 2.4: | Tetraethyl bismethano[60]fullereryl tetracarboxylates | 59 |
| Table 2.5: | Mass spectrometry studies on tethered and non-tethered bisadducts | 62 |
| Table 2.6: | ESI (-ve) results of methanol adducted tethered bisadducts | 63 |
| Table 2.7: | Ion mobility mass spectrometry studies on tethered and non-tethered bisadducts | 63 |

List of Abbreviations

| | |
|---------------------|---|
| °C | degree celsius |
| ¹³ C-NMR | carbon nuclear magnetic resonance |
| ¹ H-NMR | proton nuclear magnetic resonance |
| 2-D | two dimensional |
| 3-D | three dimensional |
| Ac | acetate |
| Ar | aromatic |
| Bu | butyl group |
| C | coulomb |
| C | carbon |
| cm | centimeter |
| CPE | coulometrically controlled potential electrolysis |
| d | doublet |
| DBU | 1,8-diazabicyclo[5.4.0]undec-7-ene |
| dd | doublet of doublets |
| DNA | deoxyribonucleic acid |
| dt | doublet of triplets |
| E | electronic field strength |
| equiv. | equivalence |
| ESI | electrospray ionisation |
| ESR | electron spin resonance |
| Et | ethyl |
| eV | electron volt |
| g | gram |
| g·cm ⁻³ | gram per cubic centimeter |

| | |
|------------|--|
| h | hour |
| HIV | human immunodeficiency virus |
| HIV-1 | type one of Human immunodeficiency virus |
| HIVP | HIV-1 protease |
| HOMO | highest occupied molecular orbital |
| HPLC | high performance liquid chromatography |
| Hz | Hertz |
| IMMS | ion mobility mass spectrometry |
| IMS | ion mobility spectrometry |
| IPR | isolated pentagon rule |
| IR | infrared |
| <i>J</i> | coupling constant (Hz) |
| K | degree Kelvin |
| kJ | kilojoule |
| kV | kilovolt |
| L | liter |
| LUMO | lowest unoccupied molecular orbital |
| LUMO + 1 | second lowest unoccupied molecular orbital |
| m | multiplet |
| <i>m</i> | <i>meta</i> |
| m/s | meter per second |
| <i>m/z</i> | mass to charge ratio |
| mbar | millibar |
| MCPBA | <i>m</i> -chloroperoxybenzoic acid |
| Me | methyl |
| mg | milligram |
| MHz | megahertz |
| ml | milliliter |

| | |
|------------------|--|
| mmol | millimole |
| mol | mole |
| Mpa | Megapascal |
| MS | mass spectrometry |
| ms | millisecond |
| nm | nanometer |
| NMR | nuclear magnetic resonance |
| ns | nanosecond |
| <i>o</i> | <i>ortho</i> |
| <i>p</i> | <i>para</i> |
| P | pressure |
| PBMC | peripheral blood mononuclear cells |
| pm | picometre |
| ppm | part per million |
| q | ion charge |
| Ref. | reference |
| RG | reactive group |
| rt | room temperature |
| s | second |
| s | singlet |
| SAM | self-assembled monolayers |
| T | absolute temperature |
| t | triplet |
| <i>t</i> | tertiary |
| TBA ⁺ | tetra- <i>n</i> -butyl ammonium cation |
| t _d | drift time |
| TDAE | tetrakis(dimethylamino)ethylene |
| <i>tert</i> | tertiary |

| | |
|---------------|--|
| THF | tetrahydrofuran |
| TMS | tetramethylsilane |
| TOF | time of flight |
| TOFMS | time-of-flight mass spectrometer |
| Torr | millimeter of mercury |
| UV | ultraviolet |
| UV-Vis | ultraviolet-visible |
| V | volt |
| V_d | drift velocity |
| δ_c | chemical shift on ^{13}C -NMR spectra |
| μs | microsecond |

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Abstract

In this study, four selected regioisomeric tetraethyl bismethano[60]fullerenyl tetracarboxylates (*trans-4, e, cis-2* and *cis-3* symmetry patterns) were prepared through the chemical methods reported in the literature with satisfactory yields and purities. They were subsequently analysed by ion mobility mass spectrometry (IMMS) to examine the potential of this method to resolve fullerenyl bisadduct regioisomers of the same molecular weights based on their different cross-sectional areas. This study was also of interest to see if these regioisomeric compounds would undergo a “walk-on-the-sphere” rearrangement under the reductive conditions of – ve ion mode ESIMS.

The tethered bisadducts **(40)**, **(41)**, **(43)**, **(44)** and **(46)** were chemically prepared according to Nierengarten’s report giving the desired products with satisfactory yields and purities. Transesterification of these tethered bisadducts with distilled and dry methanol generated the non-tethered bisadducts **(47)** – **(50)**.

The employment of IMMS in this study was to enable a comparison of the cross-sectional areas of the tethered and non-tethered [60]fullerenyl bisadducts, providing some structural information that might be useful for further studies of fullerenyl derivatives of complicated structures in the future. The size of the cross-sectional area of a fullerenyl derivative was directly reflected by the length of the drift time required to travel through the drift tube of the spectrometer, in both the + ve and – ve ion modes. In the case of this study, all of the four non-tethered bisadducts **(47)** – **(50)** may have experienced an incomplete “walk-on-the-sphere” rearrangement under the reductive conditions of their – ve ion IMMS studies. Further improvements of experimental conditions might be necessary in order to enhance the occurrence of such rearrangements in future studies.