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Experimental and Theoretical Studies into the
Laser Pyrolytic Formation of Chlorinated
Polycyclic Aromatic Hydrocarbons and
Fullerene Precursors

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Abstract

Fullerenic materials are likely to play an important role in technologies of the future. To ensure that production techniques will be able to keep up with demand, a thorough understanding of their mechanism of formation, which has thus far proved elusive, is required. Hydrocarbon pyrolysis is a potentially viable fullerene production technique, and the pyrolysis of chlorohydrocarbons has also shown promise. However, decomposition of the latter produces toxic and environmentally hazardous chlorinated polycyclic aromatic hydrocarbons, also formed in industrial waste incinerators, as a byproduct. Close study of the high temperature chemistry of chlorohydrocarbons may aid both the mitigation of hazardous byproducts and implementation of more effective fullerene synthesis techniques.

To this end, we have studied the formation mechanisms of dichloromethane degradation products generated *via* Infrared Laser Powered Homogeneous Pyrolysis. This unique technique is well known for having a non-uniform temperature profile, which has a number of attractive features for this work. The most important of these are the absence of complicating surface catalysed reactions, and the potential for allowing annealing reactions necessary for fullerene growth. Time resolved product yields are monitored *via* GC-MS and FTIR, and mechanistic deductions are supported heavily by Density Functional Theory calculations and kinetic arguments.

Results indicate that the initial growth of chlorinated compounds deviate significantly from the radical-based growth found with hydrocarbons. Facile Cl-loss in important radicals and stabilisation of carbenes by chlorine permits novel C₄ and C₆ production channels. Conventional channels involving acetylene addition to aromatic radicals are eventually restored in C₈–C₁₂ formation, although we do suggest some amendments to the mechanism. Bimolecular polycyclic aromatic hydrocarbon addition reactions may also play an important role. Acenaphthylene (C₁₂H₈) congeners also allow for the first studies of the migration of five-membered rings about chlorinated polycyclic aromatic hydrocarbon frameworks, a vital process in fullerene annealing; it is found that the presence of chlorine significantly stabilises transition states, suggesting these reactions are much more facile in heavily chlorinated systems.

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Table of Contents

ABSTRACT	II
ACKNOWLEDGMENTS	III
TABLE OF CONTENTS	IV
TABLE OF FIGURES	VII
TABLE OF TABLES	XII
GLOSSARY	XIII
CHAPTER 1.	1
DICHLOROMETHANE PYROLYSIS: ITS IMPORTANCE AND APPLICATIONS	1
1.1 – SIGNIFICANCE OF DCM COMBUSTION AND PYROLYSIS STUDIES	1
1.1.1 – Low Molecular Weight Products of DCM and Related Chlorohydrocarbons	1
1.1.2 – High Molecular Weight Products of DCM and Related Chlorohydrocarbons	2
1.1.3 – Formation Mechanisms of Fullerenes in Pyrolysis Systems	4
1.2 – THE MECHANISMS OF PAH AND FULLERENE PRECURSOR FORMATION: AN EXPERIMENTAL AND THEORETICAL INVESTIGATION	6
CHAPTER 2.	8
EXPERIMENTAL TECHNIQUES AND COMPUTATIONAL METHODOLOGY	8
2.1 – EXPERIMENTAL TECHNIQUES AND ANALYTICAL PROCEDURES	8
2.1.1 – IR LPHP: History and Development	8
2.1.2 – IR LPHP: Experimental Setup	10
2.1.3 – Experimental Overview: The Vacuum Line	11
2.1.4 – Experimental Overview: The Pyrolysis Cell	13
2.1.5 – Experimental Overview: Modified Pyrolysis Cells for Handling Solid Products	14
2.1.6 – Experimental Overview: Cell Windows	15
2.1.7 – Experimental Overview: The Photosensitiser	16
2.1.8 – Experimental Overview: The CO ₂ Laser	17
2.1.9 – Sample Preparation: Chemicals Used	19
2.1.10 – Sample Preparation: Gaseous Samples	20
2.1.11 – Sample Preparation: Solid Samples	20
2.1.12 – Analytical Procedures: Infrared Spectroscopy	21
2.1.13 – Analytical Procedures: Gas Chromatography and Mass Spectroscopy	23
2.1.14 – Analytical Procedures: GC-MS Product Identification in the Absence of Standards	26
2.2 – QUANTUM CHEMISTRY: THEORY AND APPLICATION	27
2.2.1 – The Hartree-Fock Method I: Quantum Mechanics of Many-Body Systems	27
2.2.2 – The Hartree-Fock Method II: Derivation and Solution of the HF Equations	30
2.2.3 – Capturing Electron Correlation I: Møller-Plesset Perturbation Theory, MPn	33
2.2.4 – Capturing Electron Correlation II: CC and QCI Methods	35
2.2.5 – Capturing Electron Correlation III: Density Functional Theory, DFT	37
2.2.6 – Basis Sets	40
2.2.7 – The PES: Geometry Optimisation and Vibrational Modes	42
2.2.8 – Transition State Theory, TST	45
2.2.9 – Computational Software	47
CHAPTER 3.	48
THE INITIAL STAGES OF DICHLOROMETHANE PYROLYSIS: C₂ AND C₃ PRODUCT FORMATION	48
3.1 – LITERATURE REVIEW OF THE INITIAL DEGRADATION STEPS OF DCM	48
3.1.1 – Review of the Formation of Reactive C ₁ Species from DCM	48
3.1.2 – Review of the Formation of the Initial Products During DCM Degradation	49
3.2 – PREVIOUS IR LPHP STUDIES OF DCM	50
3.2.1 – Review of Initial Products Formed During Neat DCM Pyrolyses Initiated by IR LPHP	50

3.2.2 –	<i>Radical Trapping in DCM Pyrolyses With Deuterium</i>	52
3.3 –	<i>FURTHER IR LPHP STUDIES OF DCM</i>	53
3.3.1 –	<i>GC-MS Investigations of the Products of DCM Pyrolysis</i>	53
3.3.2 –	<i>GC-MS Investigations of DCM/trans-DCE Co-pyrolyses</i>	55
3.3.3 –	<i>GC-MS Investigations of DCM/TCE Co-pyrolyses</i>	57
3.4 –	<i>CONCLUSIONS DRAWN FROM DCM PYROLYSES AND THE DIRECTION OF THIS WORK</i>	57
CHAPTER 4.		61
THERMAL DECOMPOSITION AND RECOMBINATION OF CHLORINATED C₂ HYDROCARBONS		61
4.1 –	<i>PREVIOUS WORK ON C₂ DECOMPOSITION AND C₄ FORMATION</i>	61
4.1.1 –	<i>Review of the Decomposition of (Non)-Chlorinated C₂ Hydrocarbons</i>	61
4.1.2 –	<i>Review of C₄ Formation I: The Vinyl Radical</i>	65
4.1.3 –	<i>Review of C₄ Formation II: The Chemistry of Acetylene</i>	70
4.2 –	<i>PRELIMINARY EXPERIMENTAL RESULTS ON C₂ DECOMPOSITION AND C₄ GROWTH</i>	74
4.2.1 –	<i>Trans-dichloroethylene (E-C₂H₂Cl₂) Pyrolyses</i>	74
4.2.2 –	<i>Trichloroethylene (C₂HCl₃) pyrolyses</i>	77
4.2.3 –	<i>Pyrolysis of Equal Pressure Trans-DCE and TCE Mixtures</i>	80
4.3 –	<i>RESULTS OF LOW TEMPERATURE STUDIES OF C₂ DECOMPOSITION AND TRAPPING EXPERIMENTS</i>	83
4.3.1 –	<i>Low Temperature Trans-DCE Pyrolyses</i>	83
4.3.2 –	<i>Low Temperature Pyrolysis of Equal Pressure Trans-DCE/TCE Mixtures</i>	85
4.3.3 –	<i>Low Temperature Pyrolysis of Trans-DCE with Acetylene</i>	86
4.3.4 –	<i>Low Temperature Pyrolysis of Chloroacetylene with Acetylene</i>	87
4.3.5 –	<i>Low Temperature Pyrolysis of Trans-DCE with H₂ and D₂</i>	88
4.3.6 –	<i>Low Temperature Pyrolysis of TCE with H₂ and D₂</i>	90
4.4 –	<i>DISCUSSION OF EXPERIMENTAL RESULTS CONCERNING CHLOROETHYLENE DECOMPOSITION AND GROWTH OF C₄ PRODUCTS</i>	91
4.4.1 –	<i>Decomposition of Chlorinated Ethylenes: Radical-based Mechanisms</i>	92
4.4.2 –	<i>Formation of Chlorinated C₄ Products: Mechanisms Based on a Radical Perspective</i>	95
4.4.3 –	<i>Formation of Chlorinated C₄ Products: Deficiencies of the Radical Model</i>	98
4.5 –	<i>EXPERIMENTAL STUDIES OF C₄ PRODUCTS: CONCLUDING REMARKS</i>	104
CHAPTER 5.		106
THEORETICAL TREATMENT OF NON-RADICAL CHLOROETHYLENE/ACETYLENE RECOMBINATION		106
5.1 –	<i>REVIEW OF NON-RADICAL C₄ GROWTH MECHANISMS</i>	106
5.2 –	<i>BENCHMARKING CALCULATIONS RELEVANT TO MOLECULAR C₂ ADDUCTS</i>	109
5.2.1 –	<i>Benchmarking Calculations for Searching C₂ Dimerisation PESs</i>	109
5.2.2 –	<i>Benchmarking High Level G2MS Calculations</i>	111
5.3 –	<i>COMPUTATIONAL RESULTS I: ETHYLENE/ACETYLENE ADDUCTS</i>	112
5.3.1 –	<i>Ethylene/Acetylene Adducts: The initial adduct</i>	112
5.3.2 –	<i>Stabilisation of Ethylene/Acetylene Adducts Process I: A Concerted HCl Elimination/Acetylene Slipping Mechanism</i>	114
5.3.3 –	<i>Stabilisation of Ethylene/Acetylene Adducts Process II: H and Cl Migrations Leading to 1,3-Butadiene Formation</i>	116
5.3.4 –	<i>Stabilisation of Ethylene/Acetylene Adducts Process III: H and Cl Migrations Leading to Methylene cyclopropane Formation</i>	119
5.3.5 –	<i>Stabilisation of Ethylene/Acetylene Adducts Process IV: Formation and Decomposition of Cyclobutene Congeners</i>	122
5.3.6 –	<i>Stabilisation of Ethylene/Acetylene Adducts: A Summary</i>	124
5.4 –	<i>COMPUTATIONAL RESULTS II: ACETYLENE/ACETYLENE RECOMBINATION</i>	124
5.4.1 –	<i>Acetylene/Acetylene Adducts: The initial adduct</i>	125
5.4.2 –	<i>Stabilisation of Acetylene/Acetylene Adducts Process A: H and Cl Migrations Leading to Methylene cyclopropene Formation</i>	127

5.4.3 –	<i>Stabilisation of Acetylene/Acetylene Adducts Process B: Cyclisation to Cyclobutadiene and Further Rearrangement</i>	130
5.4.4 –	<i>Competition for the Direct Acetylene/Acetylene Adducts: Concerted Recombination/HCl Elimination Transition States</i>	132
5.4.5 –	<i>Non-radical Acetylene/Acetylene Reactions: A Summary</i>	134
5.4.6 –	<i>G2-MS Tests of the Accuracy of DFT Energies of Acetylene Adducts</i>	135
5.5 –	DISCUSSION OF RADICAL AND NON-RADICAL ROUTES IN C₄ GROWTH	136
5.5.1 –	<i>Description of Qualitative Trends of C₄ Growth With Acetylene Adducts</i>	137
5.5.2 –	<i>Kinetic Analysis of C₄ Growth With Radical and Acetylene Adduct Routes</i>	139
5.5.3 –	<i>The Electronic Structure of Acetylene Adduct Formation</i>	143
5.6 –	ON THE FORMATION OF C₄ PRODUCTS IN CHLORINATED SYSTEMS: CONCLUSIONS	147
CHAPTER 6.		149
6.1 –	PREVIOUS WORK INTO THE FORMATION OF AROMATIC RINGS IN HIGH TEMPERATURE SYSTEMS	149
6.1.1 –	<i>Mechanisms of Aromatic Formation in Non-Chlorinated Systems</i>	149
6.1.2 –	<i>Radical Mechanisms to Aromatic Formation in Chlorinated Systems</i>	153
6.1.3 –	<i>Thermochemistry of Potentially Important C₄ and C₆ Intermediates</i>	154
6.2 –	EXPERIMENTAL STUDIES INTO CHLORINATED BENZENE FORMATION	158
6.2.1 –	<i>Probing Benzene Formation: Experimental Details</i>	158
6.2.2 –	<i>Aromatic Formation in Chlorinated Ethylene Systems</i>	159
6.2.3 –	<i>Aromatic Formation in C₄Cl₆ and C₄Cl₄-based Pyrolyses</i>	161
6.2.4 –	<i>Discussion of Experimental Results of Aromatic Growth in DCE and TCE Soot</i>	163
6.3 –	THEORETICAL STUDIES INTO CHLORINATED BENZENE FORMATION	166
6.3.1 –	<i>Benchmarking Calculations</i>	166
6.3.2 –	<i>System A, C₄Cl₃ + C₂Cl₂</i>	168
6.3.3 –	<i>System B, C₄Cl₅ + C₂Cl₂</i>	173
6.3.4 –	<i>System C, C₄Cl₄ + C₂Cl₂</i>	178
6.3.5 –	<i>System D, C₄H₂Cl₂ + C₂HCl</i>	182
6.4 –	KINETIC MODEL OF AROMATIC FORMATION IN CHLORINATED SYSTEMS	186
6.5 –	DISCUSSION AND CONCLUDING REMARKS	191
CHAPTER 7		195
THE FIRST FUSED RINGS: PRODUCTION OF PHENYLACETYLENES AND NAPHTHALENES		195
7.1 –	LITERATURE REVIEW OF THE C₈ AND C₁₀ FORMATION PATHWAYS IN HIGH TEMPERATURE SYSTEMS	195
7.1.1 –	<i>Review of High Temperature Non-Chloro-C₈ and C₁₀ Product Formation</i>	195
7.1.2 –	<i>Review of High Temperature Chloro-C₈ and C₁₀ Product Formation</i>	201
7.2 –	EXPERIMENTAL INVESTIGATIONS REGARDING CHLORINATED NAPHTHALENE FORMATION	202
7.2.1 –	<i>C₈H_{8-x}Cl_x, C₈H_{6-x}Cl_x and C₁₀H_{8-x}Cl_x formation in Chlorinated Ethylene Systems</i>	202
7.2.2 –	<i>C₈H_{8-x}Cl_x, C₈H_{6-x}Cl_x and C₁₀H_{8-x}Cl_x formation in TriCB/Ethylene systems</i>	204
7.3 –	COMPUTATIONAL STUDIES OF CHLORINATED C₈ AND C₁₀ FORMATION	205
7.3.1 –	<i>The triCB/TCE and DCE HACA Channels</i>	206
7.3.2 –	<i>Testing the Feasibility of the HACA Growth Schemes</i>	211
7.4 –	PROBABILISTIC KINETIC MODELS OF CHLORINATED C₈ AND C₁₀ FORMATION	215
7.4.1 –	<i>The Amended Bittner-Howard HACA mechanism</i>	216
7.4.2 –	<i>The Development and Implementation of Probabilistic Reaction Trees</i>	216
7.5 –	TRICB CO-PYROLYSES: FURTHER MODEL AMENDMENTS AND CONFIRMATION OF THE HACA MECHANISM	222
7.5.1 –	<i>Non-Gaussian Curve Fitting and the Similarity Index</i>	222
7.5.2 –	<i>Total Yield Prediction with Amended Bittner-Howard HACA Sequences</i>	223
7.5.3 –	<i>Final Model Refinements: Inclusion of C₄Cl₄ additions</i>	224
7.5.4 –	<i>Phenylacetylene Yields in TriCB-doped DCE and TCE IR LPHP Systems</i>	226
7.5.5 –	<i>Naphthalene Yields in TriCB-doped DCE and TCE IR LPHP Systems</i>	226

7.5.6 –	Additional C_{10} Isomer Yields in TriCB-doped DCE and TCE IR LPHP Systems	227
7.6 –	CHLOROETHYLENE-ONLY PYROLYSES: THE EFFICACY OF THE HACA AND C_4Cl_4-ADDITION MECHANISM IN A GENERAL SYSTEM	228
7.6.1 –	Phenylacetylene Yields in DCE and TCE IR LPHP Systems	229
7.6.2 –	Naphthalene Yields in DCE and TCE IR LPHP Systems	230
7.6.3 –	Additional C_{10} Isomer Yields in DCE and TCE IR LPHP Systems	232
7.7 –	C_8 AND C_{10} FORMATION FROM CHLORINATED PRECURSORS - CONCLUSIONS	232
CHAPTER 8		234
IMPORTANT MODELS IN PAH/FULLERENE GROWTH: PROTOTYPES BASED ON C_{12} SPECIES		234
8.1 –	LITERATURE REVIEW OF C_{12} FORMATION IN HIGH TEMPERATURE SYSTEMS	234
8.1.1 –	Ring-contraction Initiated Isomerisation of CP-PAHs	234
8.1.2 –	PAH Recombination Models of Growth	236
8.1.3 –	3C Bay Closure Acetylene Addition Models of Growth	238
8.1.4 –	4C Bay Closure Acetylene Addition Models of Growth	240
8.2 –	THE CHEMISTRY OF HEPTACHLOROACENAPHTHYLENE: 5-MEMBERED RING SHIFTS AND 3C BAY ACETYLENE ADDITIONS	241
8.2.1 –	Experimental Results: Chlorinated Acenaphthylenes, Cl-ACN	241
8.2.2 –	Discussion of Experimental Results: Cl-ACN	243
8.2.3 –	Theoretical Studies Concerning CP-shift Isomerisation Reactions in Cl-ACNs	245
8.2.4 –	3C Bay Acetylene Addition in Cl-ACN Formation	250
8.3 –	THE CHEMISTRY OF HEXACHLOROBIPHENYL: PAH DIMERISATION AND 4C BAY ACETYLENE ADDITIONS	253
8.3.1 –	Experimental Results: Chlorinated Biphenyls	253
8.3.2 –	PAH Dimerisation: Analysis of (Hexachloro-)biphenyl Formation	254
8.3.3 –	Preliminary Evidence for 4C Bay Acetylene Additions	261
8.4 –	PROTOTYPICAL STEPS IN PAH/FULLERENE FORMATION - CONCLUSIONS	262
CHAPTER 9		264
CONCLUSIONS AND FUTURE WORK		264
CHAPTER A2. EXPERIMENTAL TECHNIQUES AND COMPUTATIONAL METHODOLOGY		267
A2.1 –	Derivation of the Hartree-Fock Equations	269
A2.2 –	Iterative Solution of the Hartree-Fock-Roothaan Equations	272
A2.3 –	Time-Independent Rayleigh-Schrödinger Perturbation Theory	274
A2.4 –	Derivation of the Kohn-Sham Equations of Density Functional Theory	275
CHAPTER A6. THE FIRST AROMATIC RINGS: PYROLYTIC FORMATION OF THE CHLOROBENZENES		276
CHAPTER A7. THE FIRST FUSED RINGS: PRODUCTION OF PHENYLACETYLENES AND NAPHTHALENES		289
CHAPTER A8. IMPORTANT MODELS IN PAH/FULLERENE GROWTH: PROTOTYPES BASED ON C_{12} SPECIES	306	
REFERENCES		309

Table of Figures

Figure 1.1: (Left to right) fullerenes C_{60} , C_{70} , and C_{540} demonstrating the pentagonal ring	3
Figure 1.2: The Pentagon Road mechanism of fullerene formation.....	5
Figure 1.3: The Fullerene Road mechanism of fullerene formation	6
Figure 2.1: Overview of an IR LPHP setup.....	11

Figure 2.2: Photograph and schematic of the pertinent features of the vacuum line.....	12
Figure 2.3: A typical pyrolysis cell utilised for handling gaseous products	14
Figure 2.4: A typical pyrolysis cell utilised for handling solid products.....	15
Figure 2.5: IR spectrum of gaseous SF ₆	17
Figure 2.6: The M-80 Electroxx free running CW CO ₂ laser used in this work	18
Figure 2.7: Pertinent energy transitions involved in the CO ₂ laser	19
Figure 2.8: Concentrations of dichloroethylenes as calculated using absorption coefficients derived from DFT calculations and as measured (see text).....	24
Figure 2.9: (left to right) – The spin and orbital arrangements representing the RHF, UHF, and ROHF wavefunctions	32
Figure 2.10: Pertinent features of a PES linking chemical concepts to molecular geometry	42
Figure 2.11: Pertinent features of the IRC-based representation of the PES	43
Figure 3.1: Concentrations of IR detectable products in a typical DCM pyrolysis	51
Figure 3.2: Dominant initial reactions during DCM pyrolysis	52
Figure 3.3: IR Spectrum of the CD ₂ Cl ₂ + H ₂ System, Post-pyrolysis (CD ₂ Cl ₂ ▲, CDHCl ₂ ◊, C ₂ DCl ₂ Δ, C ₂ D ₂ Cl ₂ ◻, C ₂ H ₂ ●, C ₂ DH◦, C ₂ D ₂ *)	52
Figure 3.4: Chromatogram of DCM pyrolysis products (20 Torr DCM, aperture 3, 3 × 8 s exposures)....	54
Figure 3.5: Chromatogram of DCM/trans-DCE co-pyrolysis products (20 Torr each of DCM and DCE, aperture 3, 2 × 8 s exposures).....	56
Figure 3.6: Chromatogram of DCM/TCE co-pyrolysis products (20 Torr each of DCM and TCE, aperture 3, 2 × 8 s exposures).....	58
Figure 4.1: Pertinent reactions available to the C ₂ H ₃ + C ₂ H ₂ system	68
Figure 4.2: IR yields of C ₂ and C ₄ products from aperture 6 trans-DCE pyrolyses.....	75
Figure 4.3: GC yields of C ₂ and C ₄ products from aperture 3 trans-DCE pyrolyses (8 s each)	75
Figure 4.4: Chromatogram of major products formed during trans-C ₂ H ₂ Cl ₂ pyrolysis; ~20 Torr reagent, 5 × 8 s pyrolysis at aperture 3.....	76
Figure 4.5: IR yields of C ₂ and C ₄ products from aperture 3 TCE pyrolyses.....	78
Figure 4.6: Chromatogram of major products formed during C ₂ HCl ₃ pyrolysis; ~20 Torr reagent, 2 × 8 s pyrolysis at aperture 3.....	79
Figure 4.7: GC yields of C ₂ and C ₄ products from aperture 3 TCE pyrolyses (8 s each)	80
Figure 4.8: Maximum IR yields of C ₂ and C ₄ products from aperture 3 DCE/TCE pyrolyses.....	81
Figure 4.9: GC yields of C ₂ and C ₄ products from aperture 3 DCE/TCE pyrolyses (8 s each)	82
Figure 4.10: GC yields of C ₄ products as a function of starting material.....	82
Figure 4.11: IR yields of C ₂ and C ₄ products formed during low temperature trans-DCE pyrolyses	84
Figure 4.12: IR yields of C ₂ and C ₄ products low temperature DCE/TCE pyrolyses.....	86
Figure 4.13: Time-resolved chromatographic peak areas of DCE/C ₂ H ₂ co-pyrolysis products, (time proceeds left to right of a product cluster)	87
Figure 4.14: The products C ₂ HCl/C ₂ H ₂ pyrolysis; the over-pressure of C ₂ H ₂ is added between recording the third and fourth spectra	88
Figure 4.15: Hydrogenated products of 10 Torr DCE and 3 Torr D ₂	89
Figure 4.16: Deuterated products of 10 Torr DCE and 3 Torr D ₂	89
Figure 4.17: Hydrogenated products of 12 Torr TCE and 3 Torr D ₂	91
Figure 4.18: Deuterated products of 12 Torr TCE and 3 Torr D ₂	91
Figure 4.19: Radical-initiated formation routes of chlorovinylacetylene congeners.....	96
Figure 4.20: Radical-initiated formation routes of chlorodiacetylene congeners.....	97
Figure 4.21: Partial chromatogram of C ₄ HCl ₃ isomers formed during DCE/TCE pyrolyses.....	103
Figure 5.1: Reactions (5.a) - (5.f) from Table 5.1; bond lengths in Å from DFT-opt	111
Figure 5.2: Geometries of initial adduct formation transition states, TS1a-h, and their products 1a-h; all bond lengths in Å, energies in Table 5.3	113
Figure 5.3: The electrostatic potential energy surface of TS1c.....	114
Figure 5.4: Schematic detailing the processes considered in the stabilisation of adducts 1a-h.....	115
Figure 5.5: Geometries of α,α-HCl elimination transition states, TS2a-h, and their products 2a-h; all bond lengths in Å, energies in Table 5.4	116
Figure 5.6: Geometries of H-migration transition states, TS3a-h, and their products 3a-h; all bond lengths in Å, energies in Table 5.5.....	117
Figure 5.7: Geometries of Cl-migration transition states, TS4a-h, and their products 4a-h; all bond lengths in Å, energies in Table 5.5.....	118

Figure 5.8: Geometries of H- and Cl-migration transition states, TS5a-h and TS6a-h respectively, and their products 5a-h and 6a-h; bond lengths in Å, energies in Table 5.6	120
Figure 5.9: Geometries of α,α - (TS7a-h) and α,β -HCl (TS8a-h) elimination reactions from methylenecyclopropanes 5a-h, 6a-h, and their products 7a-h; bond lengths in Å, energies in Table 5.7... 121	
Figure 5.10: Geometries of cyclobutene formation routes, TS9a-h, and their products 9a-h; bond lengths in Å, energies in Table 5.8.....	122
Figure 5.11: DFT-SPE energies of cyclobutene congener formation and decomposition on a $C_4H_3Cl_3$ PES	123
Figure 5.12: PES (DFT-SPE level energies) of the major ethylene-acetylene adduct rearrangement reactions on a $C_4H_3Cl_3$ PES	125
Figure 5.13: Geometries of initial adduct formation transition states, TS1m-t, and their products 1m-t; all bond lengths in Å, energies in Table 5.10	126
Figure 5.14: Schematic detailing the processes considered in the stabilisation of adducts 1m-t.....	126
Figure 5.15: Geometries of H- and Cl-migration transition states, TS2m-t and TS3m-t respectively, and their products 2m-t, 3m-t; bond lengths in Å, energies in Table 5.11	128
Figure 5.16: Electrostatic potential energy maps of ethylene/acetylene adducts 1m and 1t.....	129
Figure 5.17: Geometries of H- and Cl-migration transition states, TS4m-t and TS5m-t respectively, and their products 4m-t, 5m-t; bond lengths in Å, energies in Table 5.12	130
Figure 5.18: Geometries of cyclobutadiene formation cyclisations from 1m-t, TS6m-t, and their products 6m-t; bond lengths in Å, energies in Table 5.13.....	131
Figure 5.19: Geometries of cyclobutadiene decomposition steps leading to vinylacetylene congeners; energies provided in Table 5.15	133
Figure 5.20: Geometries of direct concerted recombination/HCl elimination transition states TS10m-t and diacetylene products, 10m-t; energies given in Table 5.16.....	134
Figure 5.21: DFT-SPE PES of the major acetylene adduct rearrangement reactions for $C_4H_2Cl_2$	135
Figure 5.22: Decomposition routes and energies of trichlorocyclobutadiene	138
Figure 5.23: Experimental and theoretical yields of pertinent C_2 and C_4 products formed in low temperature DCE pyrolyses.....	142
Figure 5.24: (left to right) Frontier orbitals of the Diels-Alder cyclisation of ethylene with 1,3-butadiene, dimerisation of C_2HCl , and C_2HCl dimerisation reconsidered with a bent C_2HCl moiety	144
Figure 5.25: Valence bond diagram of C_4H_6/C_2H_4 Diels-Alder cyclisation.....	145
Figure 5.26: Valence bond diagram acetylene dimerisation.....	145
Figure 5.27: HOMO orbitals along the IRC of C_2H_2 (top) and C_2Cl_2 (bottom) dimerisation; carbene p_z orbital circled in orange.....	146
Figure 5.28: The role of E_{ST} and product stability on acetylene dimerisation kinetics and thermodynamics	147
Figure 6.1: <i>i</i> - and <i>n</i> - isomers of potential phenyl and benzene forming radicals C_4H_3 and C_4H_5	151
Figure 6.2: Energies/ kJ mol^{-1} of pertinent C_6H_6 rearrangements	155
Figure 6.3: Important intermediates in the isomerisation of fulvene to benzene	156
Figure 6.4: Experimental $C_6H_{6-x}Cl_x$ yields as a function of the initial fraction of DCE present; also shown are the yields expected via C_2HCl and C_2Cl_2 trimerisation reactions.....	159
Figure 6.5: $C_6H_3Cl_3$ to C_6Cl_6 isomers formed during aperture 5 DCE and TCE pyrolyses.....	160
Figure 6.6: IR spectrum of TCE soots; hxCB \diamond , perchloro-1,5-hexadien-3-yne \bullet	161
Figure 6.7: (top to bottom) Separable products of aperture 2 C_4Cl_6 and C_4Cl_6 /TCE pyrolysis soot	162
Figure 6.8: (top to bottom) $C_6H_2Cl_4$ products of C_4Cl_6/C_2H_2 and C_4Cl_6/C_2H_2 soot.....	163
Figure 6.9: DFT-opt PES of the reaction of C_4Cl_3 isomers with C_2Cl_2 (relative to $C_4Cl_4 + Cl + C_2Cl_2$)..	169
Figure 6.10: DFT-opt PES of the reaction of C_4Cl_5 isomers with C_2Cl_2 (relative to $C_4Cl_6 + Cl + C_2Cl_2$)	174
Figure 6.11: Energy profile at the AM1 level of the C_2Cl_2 rotation about the C-C bond in 4B from 0 – 400° (carbons in varying dihedral marked in red for minima).....	176
Figure 6.12: DFT-SPE PES of the reaction of C_4Cl_4 with C_2Cl_2 (relative to $C_4Cl_4 + C_2Cl_2$).....	179
Figure 6.13: DFT-SPE PES of the acetylene recombination-like reaction of Z-1,2- $C_4H_2Cl_2$ with C_2HCl (relative to Z-1,2- $C_4H_2Cl_2 + C_2HCl$).....	183
Figure 6.14: DFT-SPE PES of the Diels-Alder cycloaddition reactions of Z-1,2- $C_4H_2Cl_2$ with C_2HCl (relative to Z-1,2- $C_4H_2Cl_2 + C_2HCl$).....	184
Figure 6.15: Frontier orbitals of Z-1,2- $C_4H_2Cl_2$, C_2HCl , and bent C_2HCl mimicking TS13D, a Diels-Alder cyclisation step on the $C_6H_3Cl_3$ PES.....	185

Figure 6.16: Measured and theoretical yields of C_6Cl_5 isomers as a function of temperature formed via the C_4Cl_3 radical model.....	188
Figure 6.17: Measured and theoretical yields of C_6Cl_6 isomers as a function of temperature formed via the C_4Cl_5 radical model.....	189
Figure 6.18: Measured and theoretical yields of C_6Cl_6 isomers as a function of temperature formed via the C_4Cl_4 non-radical model	190
Figure 6.19: Theoretical yields of $C_6H_3Cl_3$ isomers as a function of temperature formed via the $C_4H_2Cl_2/C_2HCl$ non-radical model.....	190
Figure 6.20: Influence of Cl, F, and CH_3 substitution on the Diels-Alder transition state; note there are multiple ways to arrange 1 or 2 substituents around the groups labelled X in the structure inset.....	193
Figure 7.1: (top to bottom) Experimental $C_8H_{6-x}Cl_x$ and $C_{10}H_{8-x}Cl_x$ yields as a function of the fraction of DCE in the starting material; also shown are theoretical yields	203
Figure 7.2: Yields of phenylacetylene and naphthalene homologues as a function of starting material ...	205
Figure 7.3: DFT-opt PES of Bittner-Howard addition of C_2HCl to 2,4,5-trichlorophenyl radicals.....	207
Figure 7.4: DFT-opt PES of Frenklach addition of C_2HCl to 2,4,5-trichlorophenyl radicals.....	208
Figure 7.5: DFT-opt PES of [4.2.0]-bicyclic-based addition of C_2HCl to 2,4,5-trichlorophenyl radicals.....	209
Figure 7.6: $hxCN$ products formed during aperture 6 1,2,3-triCB/TCE pyrolyses.....	212
Figure 7.7: The modified Bittner-Howard route; internal H-abstraction occurs prior to ring closure.....	216
Figure 7.8: Schematic of the addition of an acetylene unit to 1,2,3-triCB-based radicals	217
Figure 7.9: Probability tree fragment depicting the chances of forming the reactive phenyl radicals necessary for naphthalene growth.....	218
Figure 7.10: Probability tree fragment depicting the chances of adding certain acetylene fragments to phenyl radicals, and their probabilities of survival to form naphthalene.....	220
Figure 7.11: Probability tree fragment depicting the chances of certain cyclisation routes when H and Cl are present on the ortho-carbon.....	222
Figure 7.12: Total predicted yields of naphthalenes based on an HACA-only mechanism	224
Figure 7.13: PES representing the mechanism of C_4Cl_4 addition to phenyl radicals	225
Figure 7.14: (left to right) $C_8H_2Cl_4$ isomers observed (black line) and predicted (red boxes) during 1,2,3- and 1,2,4-triCB-doped TCE pyrolyses respectively.....	226
Figure 7.15: (top to bottom) $C_{10}H_4Cl_4$ isomers observed (black line) and predicted (red boxes) during 1,2,3- and 1,2,4-triCB-doped DCE pyrolyses respectively.....	227
Figure 7.16: (left to right) $C_{10}H_2Cl_6$ isomers observed (black line) and predicted (red boxes) during 1,2,3- and 1,2,4-triCB-doped TCE pyrolyses respectively.....	228
Figure 7.17: (left to right) Non-naphthalenic $C_{10}H_2Cl_6$ isomers observed (black line) and predicted (red boxes) during 1,2,3- and 1,2,4-triCB-doped TCE pyrolyses respectively	229
Figure 7.18: $C_{10}H_4Cl_4$ isomers observed (black line) and predicted (red boxes) during 1:0 DCE:TCE pyrolyses.....	231
Figure 7.19: $C_{10}H_3Cl_5$ isomers observed (black line) and predicted (red boxes) during 0.75:0.25 DCE:TCE pyrolyses.....	231
Figure 7.20: $C_{10}H_2Cl_6$ isomers observed (black line) and predicted (red boxes) during 0.5:0.5 DCE:TCE pyrolyses.....	231
Figure 8.1: 5-membered ring migrations in CP-PAHs	236
Figure 8.2: (top to bottom) 3C and 4C bay addition and 5C bay closure examples in PAH recombination	237
Figure 8.3: Proposed mechanisms of ACN formation via $C_{12}H_9$ intermediates.....	239
Figure 8.4: (top to bottom) Cl-ACN yields in mixed ratio DCE/TCE and triCB-doped DCE or TCE co-pyrolyses respectively.....	242
Figure 8.5: SIM chromatograms of tetACN- and heptaACN isomers as functions of reagent triCB isomer and aperture size (temperature)	243
Figure 8.6: 5-membered ring automerisation reaction in ACN; energies are in kJ mol^{-1} and calculated with the DFT/uB3LYP/6-31G*, [DFT/uB3LYP/6-311G(d,p)]/DFT/uB3LYP/6-31G*, and <DFT/uB3LYP/6-311G(d,p)> levels of theory; bond lengths in Å.....	245
Figure 8.7: Isomerisation and automerisation routes available to $C_{12}HCl_7$ isomers.....	246
Figure 8.8: 5-membered ring isomerisation reactions in $C_{12}HCl_7$ isomers, as calculated at the DFT/B3LYP/6-31G* and [DFT/uB3LYP/6-311G(d,p)]/DFT/uB3LYP/6-31G* levels of theory; bond lengths in Å, energy in kJ mol^{-1}	247

Figure 8.9: (top to bottom) acephenanthrylene ↔ fluoranthene and acepyrene ↔ benzo[ghi]fluoranthene isomerisation energies/ kJ mol^{-1} and calculated with the DFT/uB3LYP/6-31G*, [DFT/uB3LYP/6-311G(d,p)]/DFT/uB3LYP/6-31G*, and <DFT/uB3LYP/6-311G(d,p)> levels of theory; bond lengths in Å	248
Figure 8.10: (left to right) – 1,2,4-triCB + C_2HCl_3 , 1,2,3-triCB + C_2HCl_3 , aperture 2. Solid line is experimental data; predicted thermally equilibrated $\text{C}_{12}\text{HCl}_7$ isomers shown in red	250
Figure 8.11: Simple HACA pathways to $\text{C}_{12}\text{HCl}_7$ isomers based on C_2Cl_2 additions to hxCNs	251
Figure 8.12: (left to right) – 1,2,4-triCB + C_2HCl_3 , 1,2,3-triCB + C_2HCl_3 , aperture 6. Solid line is experimental data; predicted $\text{C}_{12}\text{HCl}_7$ isomers shown in red	252
Figure 8.13: Competing mechanisms of ring closure during $\text{C}_{12}\text{HCl}_7$ formation	252
Figure 8.14: Hexachlorobiphenyl products of aperture 2 pyrolyses of 1,2,3-trichlorobenzene (black lines are experimental data, red theoretical)	255
Figure 8.15: Experimental (black line) and theoretical (red line) yields of hexachlorobiphenyl isomers in equimolar 1,2,3-and 1,2,4-triCB pyrolysis at aperture 2	256
Figure 8.16: Experimental yields of o-dichlorobenzene pyrolysis; our re-derived theoretical results based on kinetic-based models are shown in red	257
Figure 8.17: Transition states of H-abstraction from o-dichlorobenzene and 1,2,3-trichlorobenzene	258
Figure 8.18: Probabilities of H-abstraction from di- and monochlorobenzene	261
Figure A6.1: Geometries and labels of rearrangement products of the i- C_4Cl_3 + C_2Cl_2 reaction; LUMO and spin-density maps of pertinent products also included	277
Figure A6.2: Geometries and labels of rearrangement products of the n- C_4Cl_3 + C_2Cl_2 reaction; LUMO and spin-density maps of pertinent products also included	278
Figure A6.3: Geometries and labels of rearrangement products of the i- C_4Cl_5 + C_2Cl_2 reaction; LUMO and spin-density maps of pertinent products also included	279
Figure A6.4: Geometries and labels of rearrangement products of the n- C_4Cl_5 + C_2Cl_2 reaction; LUMO and spin-density maps of pertinent products also included	280
Figure A6.5: Geometries and labels of rearrangement products of the C_4Cl_4 + C_2Cl_2 reaction; C_2Cl_2 bridges the C_4Cl_4 ethynyl group	282
Figure A6.6: Geometries and labels of rearrangement products of the C_4Cl_4 + C_2Cl_2 reaction; the C_4Cl_4 ethynyl group bridges C_2Cl_2	283
Figure A6.7: Geometries and labels of rearrangement products of C_4Cl_4 + C_2Cl_2 from TS6C	283
Figure A6.8: Geometries and labels of rearrangement products of Z- $\text{C}_4\text{H}_2\text{Cl}_2$ + C_2HCl via acetylene bridging molecular adducts	284
Figure A6.9: Geometries and labels of rearrangement products of Z- $\text{C}_4\text{H}_2\text{Cl}_2$ + C_2HCl via Diels-Alder cyclisation	285
Figure A7.1: PES of 1-chloroethynyl-2,3,4-trichlorobenzene with C_2Cl_2 following molecular acetylene recombination pathways	289
Figure A7.2: Probability tree depicting $\text{C}_2\text{HCl}/\text{C}_2\text{Cl}_2$ addition to pentachlorophenyl radicals	290
Figure A7.3: Probability tree depicting $\text{C}_2\text{HCl}/\text{C}_2\text{Cl}_2$ addition to 2,3,5,6-tetrachlorophenyl radicals	291
Figure A7.4: Probability tree depicting $\text{C}_2\text{HCl}/\text{C}_2\text{Cl}_2$ addition to 2,3,4,5-tetrachlorophenyl radicals (C_2Cl_2 adds first)	292
Figure A7.5: Probability tree depicting $\text{C}_2\text{HCl}/\text{C}_2\text{Cl}_2$ addition to 2,3,4,5-tetrachlorophenyl radicals (C_2HCl adds first)	293
Figure A7.6: Probability tree depicting $\text{C}_2\text{HCl}/\text{C}_2\text{Cl}_2$ addition to 2,3,4,6-tetrachlorophenyl radicals (C_2Cl_2 adds first)	294
Figure A7.7: Probability tree depicting $\text{C}_2\text{HCl}/\text{C}_2\text{Cl}_2$ addition to 2,3,4,6-tetrachlorophenyl radicals (C_2HCl adds first)	295
Figure A7.8: Probability tree depicting $\text{C}_2\text{HCl}/\text{C}_2\text{Cl}_2$ addition to 2,3,6-trichlorophenyl radicals (C_2Cl_2 adds first)	296
Figure A7.9: Probability tree depicting $\text{C}_2\text{HCl}/\text{C}_2\text{Cl}_2$ addition to 2,3,6-trichlorophenyl radicals (C_2HCl adds first)	297
Figure A7.10: Probability tree depicting $\text{C}_2\text{HCl}/\text{C}_2\text{Cl}_2$ addition to 2,3,5-trichlorophenyl radicals (C_2Cl_2 adds first)	298
Figure A7.11: Probability tree depicting $\text{C}_2\text{HCl}/\text{C}_2\text{Cl}_2$ addition to 2,3,5-trichlorophenyl radicals (C_2HCl adds first)	299
Figure A7.12: Probability tree depicting $\text{C}_2\text{HCl}/\text{C}_2\text{Cl}_2$ addition to 2,4,5-trichlorophenyl radicals (C_2Cl_2 adds first)	300

Figure A7.13: Probability tree depicting C_2HCl/C_2Cl_2 addition to 2,4,5-trichlorophenyl radicals (C_2HCl adds first).....	301
Figure A7.14: Probability tree depicting C_2HCl/C_2Cl_2 addition to 3,4,5-tetrachlorophenyl radicals.....	302
Figure A7.15: Probability tree depicting C_2HCl/C_2Cl_2 addition to 2,3,4-trichlorophenyl radicals (C_2Cl_2 adds first).....	303
Figure A7.16: Probability tree depicting C_2HCl/C_2Cl_2 addition to 2,3,4-trichlorophenyl radicals (C_2HCl adds first).....	304
Figure A7.17: Probability tree depicting C_2HCl/C_2Cl_2 addition to 2,4,6-tetrachlorophenyl radicals.....	305
Figure A8.1: $C_{14}H_{10-x}Cl_x$ formation in aperture 6 TCE-doped triCB pyrolyses	306
Figure A8.2: Penta- and Hexachlorobiphenyl products formed during aperture 2 pyrolyses of 1,2,3- and 1,2,3/1,2,4-triCB.....	307
Figure A8.3: Probability tree of reactions available to the 1,2,3- + 1,2,4-triCB system.....	308

Table of Tables

Table 2.1: Assignments of infrared active vibrational modes of SF_6	16
Table 2.2: Aperture sizes of the CO_2 laser employed in this work	18
Table 2.3: Assignment and strengths of IR modes used in obtaining concentration	22
Table 3.1: Activation energies of α,β -HCl elimination processes (3.e) - (3.h)	50
Table 4.1: Dissociation energies/ $kJ\ mol^{-1}$ for Cl loss from pertinent chloroethylenes.....	65
Table 4.2: Energy/ $kJ\ mol^{-1}$ estimates of the $C_2H_3 + C_2H_2$ addition reaction.....	67
Table 4.3: Energy/ $kJ\ mol^{-1}$ estimates of the barrier to acetylene formation from C_2H_3	69
Table 4.4: Dissociation energy/ $kJ\ mol^{-1}$ estimates of Cl-loss in $CX=CY-Cl$ leading to acetylenes + Cl	70
Table 5.1: Energy barriers/ $kJ\ mol^{-1}$ of relevant benchmark reactions	110
Table 5.2: G2MS energy barriers/ $kJ\ mol^{-1}$ of relevant benchmark reactions.....	112
Table 5.3: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of selected ethylene/acetylene reactions for adduct formation	113
Table 5.4: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of selected ethylene/acetylene α,α -HCl elimination reactions	116
Table 5.5: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of selected ethylene/acetylene H- and Cl migration reactions leading to 1,3-butadiene congener formation.....	117
Table 5.6: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of selected ethylene/acetylene H- and Cl migration reactions leading to methylenecyclopropane congener formation.....	120
Table 5.7: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of α,α - (TS7a-h) and α,β -HCl (TS8a-h) elimination from methylenecyclopropanes 5a-h and 6a-h; butatriene congeners 7a-h also included	121
Table 5.8: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of selected ethylene/acetylene cyclobutene formation routes, TS9.....	122
Table 5.9: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of selected ethylene-acetylene cyclobutene decomposition routes; see Figure 5.11.....	123
Table 5.10: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of selected acetylene/acetylene reactions for adduct formation	126
Table 5.11: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of selected acetylene/acetylene H- and Cl-migration reactions leading to methylenecyclopropene congener formation	128
Table 5.12: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of selected H- and Cl-migrations from methylenecyclopropene congeners leading to vinylacetylenes.....	130
Table 5.13: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of selected cyclobutadiene formation cyclisations from 1m-t.....	131
Table 5.14: Energies of all possible H/Cl-migrations from cyclobutadiene congener 6n.....	131
Table 5.15: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of lowest energy cyclobutadiene, 6m-t, decomposition routes.....	132
Table 5.16: Energies/ $kJ\ mol^{-1}$ [DFT-SPE (DFT-opt)] of direct concerted recombination/HCl elimination routes, TS10m-t	134
Table 5.17: DFT-SPE, G2-MS, and CCSD(T) SPE values (employing B3LYP/6-31G* ZPECs) of $2C_2Cl_2$ dimerisation and rearrangement.....	136

Table 5.18: Predicted C ₄ congeners (via acetylene dimerisation) in various ethylene pyrolysis systems..	137
Table 6.1: Benchmark calculations of reaction steps pertinent to the study of chlorobenzene formation .	167
Table 6.2: Absolute energies/ hartree and endothermicity/ kJ mol ⁻¹ , of i- and n-C ₄ Cl ₃ at various levels of theory; <S ² > also provided	171
Table 8.1: Theoretical and experimental relative yields of dichlorobenzene isomer yields formed during chlorobenzene pyrolysis	261
Table A2.1: Unambiguous assignments of products formed in our chromatograms; all retention times (r.t) in minutes, RRI are relative retention indices, and R ² is the coefficient of determination.	267
Table A6.1: Energies of all pertinent stationary points on the C ₄ Cl ₃ + C ₂ Cl ₂ + Cl ₂ PES; all values in kJ mol ⁻¹ and relative to C ₄ Cl ₄ + C ₂ Cl ₂ + Cl	276
Table A6.2: Energies of all pertinent stationary points on the C ₄ Cl ₃ + C ₂ Cl ₂ + Cl ₂ PES; all values in kJ mol ⁻¹ and relative to C ₄ Cl ₆ + C ₂ Cl ₂ + Cl	281
Table A6.3: Energies of all pertinent stationary points on the C ₄ Cl ₄ + C ₂ Cl ₂ PES; all values in kJ mol ⁻¹ and relative to C ₄ Cl ₄ + C ₂ Cl ₂	281
Table A6.4: Energies of all pertinent stationary points on the Z-C ₄ H ₂ Cl ₂ + C ₂ HCl PES; all values in kJ mol ⁻¹ and relative to Z-C ₄ H ₂ Cl ₂ + C ₂ HCl	286
Table A6.5: Kinetic parameters, derived with CTST, of all pertinent reactions discussed in Chapter 6 ...	287
Table A7.1: Cl, 4Cl, and 3Cl parameters giving the probability of reaction via a penta-, tetra-, or triCB based phenyl radical	289
Table A7.2: Other fixed parameters employed in probabilistic modelling	289
Table A8.1: Areas of HxCN isomers from chromatograms of products formed during triCB + C ₂ HCl ₃ pyrolyses at aperture 6	306

Glossary

-ACN [§]	Acenaphthylene
-CB [§]	-Chlorinated Benzene
CC	Coupled Cluster
CI	Configuration Interaction
-CN [§]	-Chlorinated Naphthalene
CP-PAH	Cyclopenta-fused Polycyclic Aromatic Hydrocarbon
(C)TST	(Conventional) Transition State Theory
DCE	Dichloroethylene, C ₂ H ₂ Cl ₂
DCM	Dichloromethane, CH ₂ Cl ₂
DFT	Density Functional Theory
FC	Frozen Core
FCI	Full Configuration Interaction
GC	Gas Chromatography
GGA	Generalised Gradient Approximation
GTO	Gaussian-Type Orbital
HACA	Hydrogen Abstraction C ₂ H ₂ (acetylene) Addition
HLC	High Level Correction
IR LPHP	Infrared Laser Powered Homogeneous Pyrolysis
IRC	Intrinsic Reaction Coordinate
LCAO-(MO)	Linear Combination of Atomic Orbitals (Molecular Orbital)
L(S)DA	Local (Spin) Density Approximation
MO	Molecular Orbital
MS	Mass Spectrometry
MWI	Municipal Waste Incinerator
PAH	Polycyclic Aromatic Hydrocarbon

PCDD	Polychlorinated Dibenzodioxins
PCDF	Polychlorinated Dibenzofurans
PCN	Polychlorinated Naphthalene
PDE	Partial Differential Equation
PES	Potential Energy Surface
QCI	Quadratic Configuration Interaction
RHF	Restricted Hartree-Fock
ROHF	Restricted-Open Hartree-Fock
RRI	Relative Retention Index
SCF	Self Consistent Field
SI	Similarity Index
SIM	Selected Ion Mode
SPE	Single Point Energy
STO	Slater-Type Orbital
TCE	Trichloroethylene, C ₂ HCl ₃
TIC	Total Ion Chromatogram
UHF	Unrestricted Hartree-Fock
ZPE(C)	Zero Point Energy (Correction)
ϕ -	Phenyl (C ₆ H ₅) moiety

*The following abbreviations are used for computational methods** throughout this work*

CCSD(T)	CCSD(T)/6-31G(d)//DFT/B3LYP/6-31G*
DFT-opt	DFT/B3LYP/6-31G* geometry optimisation
DFT-SPE	DFT/B3LYP/6-31+G*//DFT/B3LYP/6-31G*
MP2-SPE	MP2/6-31+G*// DFT/B3LYP/6-31G*
MP4(SDTQ)	MP4(SDTQ)/6-31G(d)//DFT/B3LYP/6-31G*
QCISD(T)	QCISD(T)/6-31G(d)//DFT/B3LYP/6-31G*
ROMP2	ROMP2/6-31G(d)//DFT/B3LYP/6-31G*

§ Prefixes mono-, di-, tri-, tet-, penta-, hx-, hepta-, and octa- are commonly employed throughout this work; e.g. hxCB is shorthand for hexachlorobenzene

** All methods employ ZPECs from the DFT/B3LYP/6-31G* level of theory