CONTENTS

Synopsis vi
List of figures xiii
List of tables xviii
List of abbreviations xxi

CHAPTER 1 INTRODUCTION 1
1.1 Scope of the present work 13
References 15

CHAPTER 2 EXPERIMENTAL AND COMPUTATIONAL PROCEDURES 21
2.1 Experiments 21
  2.1.1 Matrix isolation infrared spectroscopy 21
  2.1.2 Matrix effects 23
    2.1.2.1 Rotation of analyte in matrix cage 25
    2.1.2.2 Multiple trapping site effects 26
    2.1.2.3 Aggregation 28
    2.1.2.4 Lifting of degeneracy of vibrational levels 30
  2.1.3 Matrix isolation infrared setup 31
    2.1.3.1 Sample introduction system 33
  2.1.4 Experimental procedure 35
2.2 Computations 36
  2.2.1 Geometry optimization and frequency calculation 36
  2.2.2 Stabilization energy calculation of complexes 38
  2.2.3 Atoms-in-molecules (AIM) methodology 40
  2.2.4 Natural bond orbital (NBO) analysis 41
  2.2.5 Calculation of dipole moment 44
References 45
<table>
<thead>
<tr>
<th>CHAPTER 3</th>
<th>STUDIES OF NON-PLANAR TRANS-STILBENE</th>
<th>49</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>49</td>
</tr>
<tr>
<td>3.2</td>
<td>Experimental details</td>
<td>53</td>
</tr>
<tr>
<td>3.3</td>
<td>Computational details</td>
<td>54</td>
</tr>
<tr>
<td>3.4</td>
<td>Results</td>
<td>54</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Experimental</td>
<td>54</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Computational</td>
<td>59</td>
</tr>
<tr>
<td>3.5</td>
<td>Discussion</td>
<td>60</td>
</tr>
<tr>
<td>3.6</td>
<td>Conclusion</td>
<td>66</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>68</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 4</th>
<th>STUDIES ON THE CONFORMATIONS OF DIMETHYL CARBONATE AND ITS COMPLEXES WITH WATER</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>70</td>
</tr>
<tr>
<td>4.2</td>
<td>Experimental details</td>
<td>72</td>
</tr>
<tr>
<td>4.3</td>
<td>Computational details</td>
<td>73</td>
</tr>
<tr>
<td>4.4</td>
<td>Results – Conformations of DMC</td>
<td>75</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Experimental</td>
<td>75</td>
</tr>
<tr>
<td>4.4.2</td>
<td>Computational</td>
<td>79</td>
</tr>
<tr>
<td>4.5</td>
<td>Discussions – Conformations of DMC</td>
<td>79</td>
</tr>
<tr>
<td>4.5.1</td>
<td>Vibrational assignments</td>
<td>79</td>
</tr>
<tr>
<td>4.5.2</td>
<td>Natural bond orbital analysis</td>
<td>85</td>
</tr>
<tr>
<td>4.5.3</td>
<td>Comparison of DMC with Dimethoxymehtane (DMM) and methylformate</td>
<td>90</td>
</tr>
<tr>
<td>4.5.4</td>
<td>Dipole moment</td>
<td>93</td>
</tr>
<tr>
<td>4.6</td>
<td>Results – DMC-H₂O complex</td>
<td>94</td>
</tr>
<tr>
<td>4.6.1</td>
<td>Experimental</td>
<td>94</td>
</tr>
<tr>
<td>4.6.2</td>
<td>Computational</td>
<td>94</td>
</tr>
<tr>
<td>4.7</td>
<td>Discussions – DMC-H₂O complex</td>
<td>99</td>
</tr>
<tr>
<td>4.7.1</td>
<td>Vibrational assignments</td>
<td>99</td>
</tr>
<tr>
<td>4.7.1.1</td>
<td>Features of the DMC submolecule in the DMC-H₂O complex</td>
<td>102</td>
</tr>
</tbody>
</table>
4.7.1.1 C=O stretch ($\nu_3$) 102
4.7.1.2 CH$_3$ symmetric deformation ($\nu_{19}$) 102
4.7.1.3 O-C-O antisymmetric stretch ($\nu_{20}$) 102
4.7.1.4 CH$_3$ O stretch ($\nu_{22}$) 103
4.7.1.5 CO$_2$ symmetric stretch ($\nu_8$) 103
4.7.1.6 CO$_3$ out-of-plane deformation ($\nu_{28}$) 103
4.7.1.2 Features of the H$_2$O submolecule in the DMC-H$_2$O complex
4.7.1.2.1 H$_2$O symmetric stretch ($\nu_1$) 103
4.7.1.2.2 H$_2$O antisymmetric stretch ($\nu_3$) 104
4.7.1.2.3 H$_2$O bending ($\nu_2$) 104
4.7.2 AIM analysis 104
4.8 Conclusion 105

References 107

CHAPTER 5 STUDIES ON CONFORMATION OF DIETHYL CARBONATE AND ITS COMPLEXES WITH WATER 109
5.1 Introduction 109
5.2 Experimental details 109
5.3 Computational details 110
5.4 Results – Conformations of DEC 111
5.4.1 Experimental 111
5.4.2 Computational 118
5.5 Discussion – Conformations of DEC 124
5.5.1 Vibrational assignments 124
5.5.2 Dipole moment 129
5.5.3 Comparison of conformations of DEC with Diethoxymethane (DEM) 129
5.5.4 Natural bond orbital analysis 131
5.6 Results – DEC-H$_2$O complex 132
5.6.1 Experimental 132
5.6.2 Computational 136
CHAPTER 6  STUDIES ON THE CONFORMATIONS OF DIPHENYL CARBONATE  152

6.1  Introduction  152
6.2  Experimental details  155
6.3  Computational details  156
6.4  Results  156
6.4.1  Experimental  156
6.4.2  Computational  156
6.5  Discussion  165
6.5.1  Vibrational assignments  165
6.5.2  Comparison of DPC with DMC  168
6.5.3  Natural bond orbital analysis  169
6.6  Conclusion  172

References  174

CHAPTER 7  AB INITIO STUDY ON THE CONFORMATIONS OF DIMETHOXY SILANONE AND ITS COMPARISON WITH DIMETHYL CARBONATE AND TRIMETHYL PHOSPHATE  176

7.1  Introduction  176
7.2  Computational details  177
7.3  Results and discussion  178
7.3.1  Natural bond orbital analysis  183