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## ABSTRACT

### STRUCTURES, INTRAMOLECULAR ROTATION BARRIERS, AND THERMODYNAMIC PROPERTIES OF METHANE AND ETHYLENE CARBONS BONDING TO TWO UNSATURATED GROUPS: ETHYLENE, ACETYLENE, PHENYL AND CARBONYL

by  
**Manish H. Gurbani**

Enthalpy,  $\Delta H_f^\circ_{298}$ , entropy,  $S^\circ_{298}$  and heat capacities  $C_p(T)$  ( $300 \leq T/K \leq 1500$ ) are determined for Methane, bi-phenyl (CCB2H2); Methane, phenyl-vinyl (CCBCDH2); Toluene, 1-formyl (CCBCOH2), Propyne, 3-phenyl (CCBCTH2); 1,4-pentadiene (CCD2H2); Propene, 3-formyl (CCDCOH2); Methane, di-formyl (CCO2H2); Propyne, 3-formyl (CCOCTH2); Methane, di-ethynl (CCT2H2); Ethene, bi-phenyl (CDCB2); 1,4 Butadiene, 3-phenyl (CDCBCD); Ethene, 1-ethynl-1-phenyl (CDCBCT); 1,4 Butadiene, 3-vinyl (CDCD2); 1,4 Butadiene, 2-ethynl (CDCDCT) and Ethene, 1,1-di-ethynl (CDCT2) using density functional B3LYP/6-31G(d) calculation method. Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d) density functional calculation level. Evaluation of data from the isodesmic reactions results in  $\Delta H_f^\circ_{298}$  values for CCB2H2 of 42.41 kcal/mol, CCBCDH2 of 34.7 kcal/mol, CCBCOH2 of -13.35 kcal/mol, CCBCTH2 of 74.7 kcal/mol, CCD2H2 of 27.08 kcal/mol, CCDCOH2 of -20.68 kcal/mol, CCO2H2 of -64.88 kcal/mol, CCOCTH2 of 19.72 kcal/mol, CCT2H2 of 112.43 kcal/mol, CDCB2 of 60.86 kcal/mol, CDCBCD of 53.41 kcal/mol, CDCBCT of 94.96 kcal/mol, CDCD2 of 48.68 kcal/mol, CDCDCT of 85.45 kcal/mol and CDCT2 of 131.68 kcal/mol. Standard entropy ( $S^\circ_{298}$ ) and heat capacity ( $C_p(T)$ 's,  $300 \leq T/K \leq 1500$ ) from vibrational, translational, and external rotational contributions are calculated using the rigid-rotor-harmonic-oscillator approximation

based on the vibration frequencies and structures obtained from the density functional studies. Potential energy as a function of internal rotation barrier is also determined using relaxed and non relaxed calculations using the B3LYP functional. Hindered internal rotational contributions to Entropy and Heat Capacity are calculated by the method of Pitzer and Gwinn. Groups for use in Benson type additivity estimations are determined. Enthalpy, entropy and  $C_p(T)$  properties are determined for C/CB<sub>2</sub>/H<sub>2</sub>, C/CB/CD/H<sub>2</sub>, C/CB/CO/H<sub>2</sub>, C/CB/CT/H<sub>2</sub>, C/CD<sub>2</sub>/H<sub>2</sub>, C/CD/CO/H<sub>2</sub>, C/CO<sub>2</sub>/H<sub>2</sub>, C/CO/CT/H<sub>2</sub>, C/CT<sub>2</sub>/H<sub>2</sub>, CD/CB<sub>2</sub>, CD/CB/CD, CD/CB/CT, CD/CD<sub>2</sub>, CD/CD/CT, CD/CT<sub>2</sub> groups for use in group additivity. Calculations result Group Values for C/CB<sub>2</sub>/H<sub>2</sub> of -1.61 kcal/mol, C/CB/CD/H<sub>2</sub> of -2.16 kcal/mol, C/CB/CO/H<sub>2</sub> of -5.96 kcal/mol, C/CB/CT/H<sub>2</sub> of -1.81 kcal/mol, C/CD<sub>2</sub>/H<sub>2</sub> of -2.62 kcal/mol, C/CD/CO/H<sub>2</sub> of -6.13 kcal/mol, C/CO<sub>2</sub>/H<sub>2</sub> of -6.08 kcal/mol, C/CO/CT/H<sub>2</sub> of -5.38 kcal/mol, C/CT<sub>2</sub>/H<sub>2</sub> of -3.43 kcal/mol, CD/CB<sub>2</sub> of 10 kcal/mol, CD/CB/CD of 11.81 kcal/mol, CD/CB/CT of 11.3 kcal/mol, CD/CD<sub>2</sub> of 12.19, CD/CD/CT of 11.05 kcal/mol, CD/CT<sub>2</sub> of 15.22 kcal/mol.

**STRUCTURES, INTRAMOLECULAR ROTATION BARRIERS, AND  
THERMODYNAMIC PROPERTIES OF METHANE AND ETHYLENE  
CARBONS BONDING TO TWO UNSATURATED GROUPS:  
ETHYLENE, ACETYLENE, PHENYL AND CARBONYL**

by  
**Manish H. Gurbani**

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**APPROVAL PAGE**

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This thesis is dedicated to my family  
for their unending love and encouragement.

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## TABLE OF CONTENTS

| Chapter  | Page |
|--|------|
| 1 INTRODUCTION.....  | 1    |
| 2 STRUCTURES, INTRAMOLECULAR ROTATION BARRIERS, AND THERMODYNAMIC PROPERTIES OF METHANE AND ETHYLENE CARBONS BONDING TO TWO UNSATURATED GROUPS .....             | 4    |
| 2.1 Overview .....   | 4    |
| 2.2 Background .....   | 6    |
| 2.3 Computational Methods .....  | 8    |
| 2.3.1 Selection of Method .....  | 8    |
| 2.3.2 Enthalpies of Formation ( $\Delta H_f^\circ_{298}$ ) .....   | 9    |
| 2.3.3 Entropy ( $S^\circ_{298}$ ) and Heat Capacities ( $C_p(T)$ 's, $300 \leq T/K \leq 1500$ ) Hindered Rotation Contribution to Thermodynamic Parameters ..... | 10   |
| 2.4 Results and Discussion .....   | 11   |
| 2.4.1 Geometries and Vibrational Frequencies .....   | 11   |
| 2.4.2 Enthalpies of Formation ( $\Delta H_f^\circ_{298}$ ) .....   | 50   |
| 2.4.3 Rotational Barriers .....  | 59   |
| 2.4.4 Entropy ( $S^\circ_{298}$ ) and Heat Capacity ( $C_p(T)$ 's ( $300 \leq T/K \leq 1500$ )) .....  | 97   |
| 2.4.5 Group Additivity Values .....  | 116  |
| 2.5 Summary .....  | 121  |
| 3 CONCLUSION .....   | 122  |
| APPENDIX A SPREADSHEET FOR CALCULATING SPECIES ENTHALPIES FROM ISODESMIC REACTIONS AND B3LYP/6-31G(d) ENERGIES .....   | 124  |
| APPENDIX B REFERENCE GROUP VALUES USED TO CALCULATE THE GROUP VALUES OF TARGET GROUPS .....  | 129  |
| REFERENCES .....   | 131  |

## LIST OF TABLES

| <b>Table</b> |   | <b>Page</b> |
|--------------|---|-------------|
| 2.1          | Structure Parameters for CCB2H2 .....   | 12          |
| 2.2          | Structure Parameters for CCBCDH2 .....  | 14          |
| 2.3          | Structure Parameters for CCBCOH2 .....  | 16          |
| 2.4          | Structure Parameters for CCBCTH2 .....  | 18          |
| 2.5          | Structure Parameters for CCD2H2 .....   | 20          |
| 2.6          | Structure Parameters for CCDCOH2 .....  | 22          |
| 2.7          | Structure Parameters for CCO2H2 .....   | 24          |
| 2.8          | Structure Parameters for CCOCTH2 .....  | 26          |
| 2.9          | Structure Parameters for CCT2H2 .....   | 28          |
| 2.10         | Structure Parameters for CDCB2 .....    | 30          |
| 2.11         | Structure Parameters for CDCBCD .....   | 32          |
| 2.12         | Structure Parameters for CDCBCT .....   | 34          |
| 2.13         | Structure Parameters for CDCD2 .....    | 36          |
| 2.14         | Structure Parameters for CDCDCT .....   | 38          |
| 2.15         | Structure Parameters for CDCT2 .....    | 40          |
| 2.16         | Vibration Frequencies for CCB2H2 .....  | 43          |
| 2.17         | Vibration Frequencies for CCBCDH2 ..... | 44          |
| 2.18         | Vibration Frequencies for CCBCOH2 ..... | 44          |
| 2.19         | Vibration Frequencies for CCBCTH2 ..... | 45          |
| 2.20         | Vibration Frequencies for CCD2H2 .....  | 45          |
| 2.21         | Vibration Frequencies for CCDCOH2 ..... | 46          |

**LIST OF TABLES**  
(Continued)

| <b>Table</b> |   | <b>Page</b> |
|--------------|---|-------------|
| 2.22         | Vibration Frequencies for CCO <sub>2</sub> H <sub>2</sub> .....   | 46          |
| 2.23         | Vibration Frequencies for CCOCTH <sub>2</sub> .....   | 46          |
| 2.24         | Vibration Frequencies for CCT <sub>2</sub> H <sub>2</sub> .....   | 47          |
| 2.25         | Vibration Frequencies for CDCB <sub>2</sub> .....   | 47          |
| 2.26         | Vibration Frequencies for CDCBCD .....  | 48          |
| 2.27         | Vibration Frequencies for CDCBCT .....  | 48          |
| 2.28         | Vibration Frequencies for CDCD <sub>2</sub> .....   | 49          |
| 2.29         | Vibration Frequencies for CDCDCT .....  | 49          |
| 2.30         | Vibration Frequencies for CDCT <sub>2</sub> .....   | 50          |
| 2.31         | Total Energies at 298 K .....   | 51          |
| 2.32         | Calculated Enthalpies at 298K .....   | 58          |
| 2.33         | Total Energies at 298 K and $\Delta H_f^\circ_{298}$ for Reference Species in the<br>Reaction Schemes ..... | 58          |
| 2.34         | Moments of Inertia of Internal Rotors, Rotational Barrier & Foldness.                                       | 62          |
| 2.35         | Total Energy and Internal Rotation Barriers for CCB <sub>2</sub> H <sub>2</sub> .....                       | 63          |
| 2.36         | Total Energy and Internal Rotation Barriers for CCBCDH <sub>2</sub> .....                                   | 66          |
| 2.37         | Total Energy and Internal Rotation Barriers for CCBCOH <sub>2</sub> .....                                   | 69          |
| 2.38         | Total Energy and Internal Rotation Barriers for CCBCTH <sub>2</sub> .....                                   | 72          |
| 2.39         | Total Energy and Internal Rotation Barriers for CCD <sub>2</sub> H <sub>2</sub> .....                       | 74          |
| 2.40         | Total Energy and Internal Rotation Barriers for CCDCOH <sub>2</sub> .....                                   | 77          |
| 2.41         | Total Energy and Internal Rotation Barriers for CCO <sub>2</sub> H <sub>2</sub> .....                       | 80          |

**LIST OF TABLES**  
(Continued)

| <b>Table</b> |   | <b>Page</b> |
|--------------|---|-------------|
| 2.42         | Total Energy and Internal Rotation Barriers for CCOCTH2.....  | 83          |
| 2.43         | Total Energy and Internal Rotation Barriers for CDCB2.....  | 85          |
| 2.44         | Total Energy and Internal Rotation Barriers for CDCBCD .....  | 88          |
| 2.45         | Total Energy and Internal Rotation Barriers for CDCBCT.....   | 90          |
| 2.46         | Total Energy and Internal Rotation Barriers for CDCD2.....  | 92          |
| 2.47         | Total Energy and Internal Rotation Barriers for CDCDCT.....   | 95          |
| 2.48         | Number of Internal Rotors, Symmetry and Moments of Inertia used<br>in the estimation of contributions to Entropy and Heat Capacity..... | 98          |
| 2.49         | Translation, Vibration and External Rotation contributions to Entropy<br>and Heat Capacity for CCB2H2 at different temperatures .....   | 99          |
| 2.50         | Translation, Vibration and External Rotation contributions to Entropy<br>and Heat Capacity for CCBCDH2 at different temperatures.....   | 100         |
| 2.51         | Translation, Vibration and External Rotation contributions to Entropy<br>and Heat Capacity for CCBCOH2 at different temperatures.....   | 101         |
| 2.52         | Translation, Vibration and External Rotation contributions to Entropy<br>and Heat Capacity for CCBCTH2 at different temperatures.....   | 102         |
| 2.53         | Translation, Vibration and External Rotation contributions to Entropy<br>and Heat Capacity for CCD2H2 at different temperatures.....    | 103         |
| 2.54         | Translation, Vibration and External Rotation contributions to Entropy<br>and Heat Capacity for CCDCOH2 at different temperatures .....  | 104         |
| 2.55         | Translation, Vibration and External Rotation contributions to Entropy<br>and Heat Capacity for CCOCTH2 at different temperatures.....   | 105         |
| 2.56         | Translation, Vibration and External Rotation contributions to Entropy<br>and Heat Capacity for CCT2H2 at different temperatures .....   | 106         |
| 2.57         | Translation, Vibration and External Rotation contributions to Entropy<br>and Heat Capacity for CDCBCT at different temperatures.....    | 107         |

**LIST OF TABLES**  
**(Continued)**

| <b>Table</b> |   | <b>Page</b> |
|--------------|---|-------------|
| 2.58         | Translation, Vibration and External Rotation contributions to Entropy and Heat Capacity for CDCDCT at different temperatures..... | 108         |
| 2.59         | Translation, Vibration and External Rotation contributions to Entropy and Heat Capacity for CDCT2 at different temperatures ..... | 109         |
| 2.60         | Translation, Vibration and External Rotation contributions to Entropy and Heat Capacity for CCO2H2 at different temperatures..... | 110         |
| 2.61         | Translation, Vibration and External Rotation contributions to Entropy and Heat Capacity for CDCB2 at different temperatures ..... | 111         |
| 2.62         | Translation, Vibration and External Rotation contributions to Entropy and Heat Capacity for CDCBCD at different temperatures..... | 112         |
| 2.63         | Translation, Vibration and External Rotation contributions to Entropy and Heat Capacity for CDCD2 at different temperatures.....  | 113         |
| 2.64         | Internal Rotor Contributions to Entropy and Heat Capacity for Each Species .....  | 114         |
| 2.65         | Ideal Gas-phase Thermodynamic Properties .....  | 115         |
| 2.66         | Groups (for Group Additivity) and Structure Parameters for Species...   | 118         |
| 2.67         | Group Values .....  | 120         |

## LIST OF FIGURES

| Figure |  | Page |
|--------|--|------|
| 2.1    | B3LYP/6-31G(d) optimized geometry of CCB2H2.....   | 13   |
| 2.2    | B3LYP/6-31G(d) optimized geometry of CCBCDH2 .....   | 15   |
| 2.3    | B3LYP/6-31G(d) optimized geometry of CCBCOH2 .....   | 17   |
| 2.4    | B3LYP/6-31G(d) optimized geometry of CCBCTH2.....  | 19   |
| 2.5    | B3LYP/6-31G(d) optimized geometry of CCD2H2.....   | 21   |
| 2.6    | B3LYP/6-31G(d) optimized geometry of CCDCOH2 .....   | 23   |
| 2.7    | B3LYP/6-31G(d) optimized geometry of CCO2H2.....   | 25   |
| 2.8    | B3LYP/6-31G(d) optimized geometry of CCOCTH2.....  | 27   |
| 2.9    | B3LYP/6-31G(d) optimized geometry of CCT2H2 .....  | 29   |
| 2.10   | B3LYP/6-31G(d) optimized geometry of CDCB2.....  | 31   |
| 2.11   | B3LYP/6-31G(d) optimized geometry of CDCBCD .....  | 33   |
| 2.12   | B3LYP/6-31G(d) optimized geometry of CDCBCT.....   | 35   |
| 2.13   | B3LYP/6-31G(d) optimized geometry of CDCD2.....  | 37   |
| 2.14   | B3LYP/6-31G(d) optimized geometry of CDCDCT.....   | 39   |
| 2.15   | B3LYP/6-31G(d) optimized geometry of CDCT2 .....   | 41   |
| 2.16   | Potential Barriers for Internal Rotation about CB-CCBH2 bond<br>(Dihedral 9876) of CCB2H2.....   | 64   |
| 2.17   | Potential Barriers for Internal Rotation about CB-CCBH2 bond<br>(Dihedral 8761) of CCB2H2.....   | 65   |
| 2.18   | Potential Barriers for Internal Rotation about CB-CCDH2 bond<br>(Dihedral 9876) of CCBCDH2 ..... | 67   |
| 2.19   | Potential Barriers for Internal Rotation about CD-CCBH2 bond<br>(Dihedral 8761) of CCBCDH2 ..... | 68   |



**LIST OF FIGURES**  
**(Continued)**

| <b>Figure</b> |  | <b>Page</b> |
|---------------|--|-------------|
| 2.20          | Potential Barriers for Internal Rotation about CO-CCBH <sub>2</sub> bond<br>(Dihedral 5123) of CCBCOH <sub>2</sub> .....             | 70          |
| 2.21          | Potential Barriers for Internal Rotation about CB-CCOH <sub>2</sub> bond<br>(Dihedral 9876) of CCBCOH <sub>2</sub> .....             | 71          |
| 2.22          | Potential Barriers for Internal Rotation about CB-CCTH <sub>2</sub> bond<br>(Dihedral 8761) of CCBCTH <sub>2</sub> .....             | 72          |
| 2.23          | Potential Barriers for Internal Rotation about CD-CCDH <sub>2</sub> bond<br>(Dihedral 9514) of CCD <sub>2</sub> H <sub>2</sub> ..... | 75          |
| 2.24          | Potential Barriers for Internal Rotation about CD-CCDH <sub>2</sub> bond<br>(Dihedral 9514) of CCD <sub>2</sub> H <sub>2</sub> ..... | 76          |
| 2.25          | Potential Barriers for Internal Rotation about CO-CCDH <sub>2</sub> bond<br>(Dihedral 10712) of CCDCOH <sub>2</sub> .....            | 78          |
| 2.26          | Potential Barriers for Internal Rotation about CD-CCOH <sub>2</sub> bond<br>(Dihedral 7126) of CCDCOH <sub>2</sub> .....             | 79          |
| 2.27          | Potential Barriers for Internal Rotation about CO-CCOH <sub>2</sub> bond<br>(Dihedral 4312) of CCO <sub>2</sub> H <sub>2</sub> ..... | 81          |
| 2.28          | Potential Barriers for Internal Rotation about CO-CCOH <sub>2</sub> bond<br>(Dihedral 5213) of CCO <sub>2</sub> H <sub>2</sub> ..... | 82          |
| 2.29          | Potential Barriers for Internal Rotation about CO-CCTH <sub>2</sub> bond<br>(Dihedral 5124) of CCOCTH <sub>2</sub> .....             | 84          |
| 2.30          | Potential Barriers for Internal Rotation about CB-CDCB bond<br>(Dihedral 171621) of CDCB <sub>2</sub> .....                          | 86          |
| 2.31          | Potential Barriers for Internal Rotation about CB-CDCB bond<br>(Dihedral 6521) of CDCB <sub>2</sub> .....                            | 87          |
| 2.32          | Potential Barriers for Internal Rotation about CD-CBCD bond<br>(Dihedral 6512) of CDCBCD .....                                       | 89          |
| 2.33          | Potential Barriers for Internal Rotation about CD-CBCT bond<br>(Dihedral 5412) of CDCBCT .....                                       | 91          |

**LIST OF FIGURES**  
**(Continued)**

| <b>Figure</b> |   | <b>Page</b> |
|---------------|---|-------------|
| 2.34          | Potential Barriers for Internal Rotation about CD-CDCD bond<br>(Dihedral 111012) of CDCD2 ..... | 93          |
| 2.35          | Potential Barriers for Internal Rotation about CD-CDCD bond<br>(Dihedral 6512) of CDCD2 .....   | 94          |
| 2.36          | Potential Barriers for Internal Rotation about CD-CDCT bond<br>(Dihedral 4321) of CDCDCT .....  | 96          |

## CHAPTER 1

### INTRODUCTION

The importance of reliable and conveniently accessible thermochemical data (Enthalpies of Formation, Entropies, and Heat Capacities) is universally accepted among both scientists and engineers. This work is an attempt to provide thermochemical data for certain selected Hydrocarbons and Oxygenated Hydrocarbons, which are important intermediates in pyrolysis and thermal combustion processes. The species are also important in soot formation and low-pressure vapor deposition processes.<sup>1</sup>

The pyrolysis of light hydrocarbons such as methane, ethylene, acetylene or benzene is an important technical process. Chemical vapor deposition (CVD) or chemical vapor infiltration (CVI) are commonly used techniques to deposit materials with a large variety of functional and structural properties.<sup>2-5</sup> Depending on temperature, pressure and other conditions, the reaction may either lead to soot or, if the reaction co-ordinates are properly tuned, to products like improved carbon fibres, and other useful materials.<sup>6</sup>

However, despite the technical and industrial importance of CVD and CVI processes, comparatively little is known about the underlying chemical reactions that promote the formation of one material or the other.<sup>1</sup> The reaction system consists of virtually thousands of different elementary steps, all of which can be important at the high temperatures commonly employed in this field of material science.<sup>1</sup> Detailed information about the possible reaction mechanisms is, however, mandatory for a better understanding and a systematic improvement of existing synthetic strategies. Ultimately,

this knowledge may lead to the accelerated development of materials with desired properties. Furthermore, important information about the reverse process, i.e. carbon gasification reactions, may also be obtained.

It has been suggested that PACHs are precursors to soot in hydrocarbon flames.<sup>7-9</sup> and one area of uncertainty in these polycyclic aromatic systems concerns the fundamental thermodynamic properties and the kinetic behavior of PCAH formation and destruction, specifically as the temperature of varied pyrolysis, synthesis and combustion processes covers a wide range. An example of the limited level of understanding is that the influence of temperature, size, degree of ring condensation, etc. on individual PCAH stability is not quantitatively known or modeled. This is primarily due to the lack of requisite thermochemical properties of PCAHs.<sup>10</sup> It is, however, the molecules and intermediate stable species, which are an important part of the formation and synthesis processes, (precursors) that are a target of this study. We need to know the thermochemical properties of these species before we can model the formation and destruction of the polycyclics accurately.

Thermochemical property data on these precursor molecules are needed for evaluation of reaction paths and kinetic processes, including stability of intermediate adducts and prediction of final products. Thermochemical properties are also needed for use in kinetic modeling and in equilibrium codes. There is very little or no data on thermochemical properties of these species in the literature.<sup>22,33,34,35,36</sup> This thesis is an attempt to estimate fundamental thermochemical property data on a series of molecules which contain important chemical moieties – sp<sup>3</sup> carbon structures (--CH<sub>2</sub>--) bonded to

two highly unsaturated groups and  $sp^2$  carbons ( $>C=CH_2$ ) bonded to two unsaturated groups. The unsaturated groups bonding to the Methane and Ethylene are Ethylene, Acetylene, Phenyl and Carbonyl.

During the past decade molecular electronic structure theory has evolved to the stage where it can provide critical information on structures, energetics and other properties that are difficult to obtain experimentally or are not accessible at all.<sup>1</sup> Especially with the progress in density functional theory (DFT) along with development of efficient algorithms and computer programs, molecular modeling has reached a reliability that allows for a description of molecular processes often with chemical accuracy. In this work the method is to use ab initio and moderate level Density Functional Computational chemistry on target molecules where enthalpy values can be determined to within a 1 to 2 kcal/mole.<sup>16</sup> Once the enthalpy of the target molecule is known, the target group is determined from known molecular values and the remaining known groups. Group values for use in group additivity have been calculated in order to construct (estimate) the thermochemical properties of larger molecule systems, where computational chemistry is not sufficiently accurate.

## CHAPTER 2

### **STRUCTURES, INTRAMOLECULAR ROTATION BARRIERS, AND THERMODYNAMIC PROPERTIES OF METHANE AND ETHYLENE CARBONS BONDING TO TWO UNSATURATED GROUPS: ETHYLENE, ACETYLENE, PHENYL AND CARBONYL**

#### **2.1 Overview**

Unsaturated Hydrocarbons and Oxygenated Hydrocarbons are important intermediates in pyrolysis, in combustion, in commercial thermal processes including soot formation as well as in low-pressure vapor deposition processes. Thermochemical property data on these species are important to understanding their stability, reaction paths and kinetics. Enthalpy,  $\Delta H_f^{\circ}_{298}$ , entropy,  $S^{\circ}_{298}$ ; and Heat Capacities,  $C_p(T)$  ( $300 \leq T/K \leq 1500$ ); are determined for Methane, bi-phenyl (CCB2H2); Methane, phenyl-vinyl (CCBCDH2); Toluene, 1-formyl (CCBCOH2), Propyne, 3-phenyl (CCBCTH2); 1,4-pentadiene (CCD2H2); Propene, 3-formyl (CCDCOH2); Methane, di-formyl (CCO2H2); Propyne, 3-formyl (CCOCTH2); Methane, di-ethynl (CCT2H2); Ethene, bi-phenyl (CDCB2); 1,4 Butadiene, 3-phenyl (CDCBCD); Ethene, 1-ethynl-1-phenyl (CDCBCT); 1,4 Butadiene, 3-vinyl (CDCD2); 1,4 Butadiene, 2-ethynl (CDCDCT) and Ethene, 1,1-di-ethynl (CDCT2) using density functional calculation methods – moderate level computational chemistry.

Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d) density functional calculation level. Vibration frequencies are scaled for zero point energies and for thermal corrections. Enthalpies of formation ( $\Delta H_f^{\circ}_{298}$ ) are determined using the  $\Delta H^{\circ}_{rxn,298}$  with known enthalpies of other reactants and products in isodesmic reactions. Standard entropy ( $S^{\circ}_{298}$ ) and heat capacity ( $C_p(T)$ ,  $300 \leq T/K \leq 1500$ )

from vibration, translation, and external rotational contributions are calculated using the rigid-rotor-harmonic-oscillator approximation based on the vibration frequencies and structures obtained from the density functional studies. Potential energy as a function of internal rotation barrier is determined using relaxed and non relaxed calculations using the B3LYP functional. Evaluation of data from the reactions results in  $\Delta H_f^{\circ}_{298}$  values for CCB<sub>2</sub>H<sub>2</sub> of 42.41 kcal/mol, CCBCDH<sub>2</sub> of 34.7 kcal/mol, CCBCOH<sub>2</sub> of -13.35 kcal/mol, CCBCTH<sub>2</sub> of 74.7 kcal/mol, CCD<sub>2</sub>H<sub>2</sub> of 27.08 kcal/mol, CCDCOH<sub>2</sub> of -20.68 kcal/mol, CCO<sub>2</sub>H<sub>2</sub> of -64.88 kcal/mol, CCOCTH<sub>2</sub> of 19.72 kcal/mol, CCT<sub>2</sub>H<sub>2</sub> of 112.43 kcal/mol, CDCB<sub>2</sub> of 60.86 kcal/mol, CDCBCD of 53.41 kcal/mol, CDCBCT of 94.96 kcal/mol, CDCD<sub>2</sub> of 48.68 kcal/mol, CDCDCT of 85.45 kcal/mol and CDCT<sub>2</sub> of 131.68 kcal/mol.

Groups for use in Benson type additivity estimation schemes are of value because they can allow accurate estimation of much larger molecules, where ab initio or density functional computational chemistry can not be used. Enthalpy, Entropy and  $C_p(T)$  properties are determined for two series of target groups in this study. The first series comprises unsaturated moieties bonded to methylene (-CH<sub>2</sub>-) C/CB<sub>2</sub>/H<sub>2</sub>, C/CB/CD/H<sub>2</sub>, C/CB/CO/H<sub>2</sub>, C/CB/CT/H<sub>2</sub>, C/CD<sub>2</sub>/H<sub>2</sub>, C/CD/CO/H<sub>2</sub>, C/CO<sub>2</sub>/H<sub>2</sub>, C/CO/CT/H<sub>2</sub>, C/CT<sub>2</sub>/H<sub>2</sub>. The second series of groups developed in this work are for unsaturated moieties bonded to the sp<sup>2</sup> hybridized carbon (ethylene, >C=CH<sub>2</sub>): CD/CB<sub>2</sub>, CD/CB/CD, CD/CB/CT, CD/CD<sub>2</sub>, CD/CD/CT, CD/CT<sub>2</sub> groups. Calculations result in Group Values for C/CB<sub>2</sub>/H<sub>2</sub> of -1.61 kcal/mol, C/CB/CD/H<sub>2</sub> of -2.16 kcal/mol, C/CB/CO/H<sub>2</sub> of -5.96 kcal/mol, C/CB/CT/H<sub>2</sub> of -1.81 kcal/mol, C/CD<sub>2</sub>/H<sub>2</sub> of -2.62 kcal/mol, C/CD/CO/H<sub>2</sub> of -6.13 kcal/mol, C/CO<sub>2</sub>/H<sub>2</sub> of -6.08 kcal/mol, C/CO/CT/H<sub>2</sub> of

-5.38 kcal/mol, C/CT<sub>2</sub>/H<sub>2</sub> of -3.43 kcal/mol, CD/CB<sub>2</sub> of 10 kcal/mol, CD/CB/CD of 11.81 kcal/mol, CD/CB/CT of 11.3 kcal/mol, CD/CD<sub>2</sub> of 12.19, CD/CD/CT of 11.05 kcal/mol, CD/CT<sub>2</sub> of 15.22 kcal/mol. Group values determined in this work show reasonable agreement with literature values; but only a limited number of literature values are available for comparison. Reasonable agreement between the calculated and previously reported values suggests that the use ofisodesmic reaction analysis results in effective cancellation of errors and thus accurate enthalpy values.

## 2.2 Background

The molecules studied in this work are specifically selected because of their relevance to formation and destruction processes in pyrolysis, vapor deposition, soot and carbon black formation and in combustion. Unsaturated hydrocarbons and oxygenated hydrocarbons are important intermediates in pyrolysis and combustion thermal processes including soot formation as well as in low-pressure vapor deposition processes. Thermochemical property data on these species are important to understanding their stability, reaction paths, and kinetics. Knowledge of the thermodynamic parameters for these species is central to understanding and predicting reaction pathways, rate constants and equilibrium constants. There is little or no experimental studies on the thermodynamic properties of these species, probably due (at least in part) to the difficulty in synthesis of pure compounds.

In this work, enthalpy,  $\Delta H_f^{\circ}_{298}$ , entropy,  $S^{\circ}_{298}$  and heat capacities  $C_p(T)$  are determined for the target species using density functional calculation methods. Enthalpies of formation are evaluated at B3LYP/6-31G(d) calculation level, using



working reactions for a high level of accuracy in the enthalpy values. The working reactions used are isodesmic, that is they have bond balance on both sides of the reaction for effective cancellation of errors.

Enthalpies of formation for the target species are estimated using total energies from the B3LYP calculations and isodesmic reactions. The B3LYP Density functional and ab initio calculations with ZPVE and thermal correction are performed for all four compounds in each reaction, and enthalpy of reaction  $\Delta H_{\text{rxn},298}^{\circ}$  is calculated. Since enthalpy of formation of three compounds, have been experimentally determined or theoretical calculated, the unknown enthalpy of formation of target compound is obtained.

As an example, the following formula illustrates the calculation of  $\Delta H_{\text{f},298}^{\circ}(\text{CCBCDH}_2)$  for a given level of calculation:

$$\Delta H_{\text{rxn},298}^{\circ} = E_{298}(\text{C}_7\text{H}_8) + E_{298}(\text{C}_4\text{H}_6) - E_{298}(\text{CCBCDH}_2) - E_{298}(\text{C}_2\text{H}_4)$$

$$\Delta H_{\text{f},298}^{\circ}(\text{CCBCDH}_2) = \Delta H_{\text{f},298}^{\circ}(\text{C}_7\text{H}_8) + \Delta H_{\text{f},298}^{\circ}(\text{C}_4\text{H}_6) - \Delta H_{\text{f},298}^{\circ}(\text{C}_2\text{H}_4) - \Delta H_{\text{rxn},298}^{\circ}$$

The enthalpies of formation ( $\Delta H_{\text{f},298}^{\circ}$ ) and their respective uncertainties for standard species used in the working reactions.

Contributions to Entropy and Heat Capacity from Internal Rotation also need to be evaluated. They are estimated using calculated barriers to internal rotation about the  $\text{CH}_2\text{—Cd}$ ,  $\text{CH}_2\text{—Ct}$ ,  $\text{CH}_2\text{—Cb}$  and  $\text{CH}_2\text{—C=O}$  single bonds, and foldness of the intramolecular rotation using the method of Pitzer and Gwinn.<sup>17</sup> Rotation barriers are determined with relaxed (fully optimized) and non-relaxed (scan mode in Gaussian where other rotors structure properties are held rigid) and the use of B3LYP density functional calculations.

## 2.3 Computational Methods

### 2.3.1 Selection of Method

All ab initio calculations are performed using the Gaussian 94 and Gaussian 98 program suites.<sup>18</sup> The structural parameters are fully optimized at the B3LYP/6-31g(d) level of theory. Harmonic vibration frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. The optimized geometrical parameters are used to obtain total electronic energies in the B3LYP/6-31G(d) single point calculations.<sup>19-21</sup>

B3LYP/6-31G(d) is chosen because it is commonly used and is reported to yield accurate geometries and reasonable energies.<sup>22,23</sup> Durant<sup>21,23</sup> has compared density functional calculations B3LYP and hybrid (BH and H) with MP2 and Hartree-Fock methods for geometry and vibration frequencies. He reports that these density functional methods provide excellent geometries and vibration frequencies, relative to MP2 at a reduced computational expense. Petersson et al.<sup>24</sup> currently recommends use of B3LYP for geometry and frequencies in several of his CBS calculation methods. Comparison of calculation results from B3LYP/6-31G(d) with use of working reactions for  $\Delta H_f^{\circ}{}_{298}$ , against data from higher calculation levels will provide some calibration of the B3LYP/6-31G(d) values for larger molecules where this may be one of the few available calculation methods (with similar working reactions). The geometry is obtained at the B3LYP/6-31G(d) level of theory, while the ZPE used is the scaled (by 0.9806) HF/6-31G value.

### 2.3.2 Enthalpies of Formation ( $\Delta H_f^\circ_{298}$ )

Enthalpies of formation ( $\Delta H_f^\circ_{298}$ ) for the species are estimated using total energies obtained by the B3LYP/6-31G(d) and isodesmic reactions. Total energies are corrected by zero-point vibration energies (ZPVE) which are scaled by 0.9806 as recommended by Scott et al.<sup>25</sup> Thermal correction, 0 K to 298.15 K, is calculated to estimate  $\Delta H_f^\circ_{298}$  at 298.15 K.<sup>26</sup>

The method of isodesmic reactions relies on the similarity of the bonding environments in the reactants and products that leads to partial cancellation of systematic errors in the density functional and ab initio molecular orbital calculations.<sup>26</sup> Reactions selected to determine  $\Delta H_f^\circ_{298}$  of each species are represented in Table 2.32. The basic requirement of an isodesmic reaction is that the number of each type of bond is conserved in the reaction; this leads to an accurate cancellation of error on both sides of a reaction and results in an accurate calculated enthalpy of reaction. This enthalpy of reaction is then used, in conjunction with the enthalpy of formation of the three standard molecules in the working reaction to find the enthalpy of formation on the target molecule. Density functional and ab initio calculations with ZPVE and thermal correction are performed for all four compounds in each reaction, and enthalpy of reaction  $\Delta H^\circ_{\text{rxn},298}$  is calculated. Since accurate enthalpies of formation of the three standard compounds, have been experimentally determined or theoretically calculated, along with the enthalpy of reaction, the unknown enthalpy of the target compound is obtained. The Density functional and ab initio calculations are performed on the most stable conformer of each compound, and the  $\Delta H_f^\circ_{298}$  of this conformer is calculated using isodesmic reactions.

Corrections have not been made to the  $\Delta H_f^\circ_{298}$  for each species to include other conformers beside the lowest energy conformer.

### **2.3.3 Entropy ( $S^\circ_{298}$ ) and Heat Capacities ( $C_p(T)$ 's, $300 \leq T/K \leq 1500$ ) and Hindered Rotation Contribution to Thermodynamic Parameters**

Entropies  $S^\circ_{298}$  and heat capacities ( $C_p(T)$ 's,  $300 \leq T/K \leq 1500$ ) are calculated using the rigid-rotor-harmonic-oscillator approximation based on frequencies and moments of inertia of the optimized B3LYP/6-31G(d) structures. Calculated Entropies are for the lowest Energy, most stable conformer and corrections have not been made for higher energy conformers. Contributions to entropy and heat capacity from internal rotation are estimated using the B3LYP determined barriers and foldness of the intramolecular rotation and the method of Pitzer and Gwinn<sup>17</sup>. Rotation barriers are determined with the B3LYP calculations. Potential energy as a function of internal rotation barrier is determined using relaxed and non relaxed calculations at using the B3LYP functional. Potential barriers for internal rotation are calculated at the B3LYP/6-31G(d) level, relaxed scan (optimized) for CCBCTH2 and CCD2H2; B3LYP/6-31G(d) with rigid scan for CDCBCT; B3LYP/6-31G(d,p) relaxed scan (optimized) for CCO2H2, CDCD2; B3LYP/6-31G(d,p) with rigid scan for CCBCOH2, CCOCTH2; B3LYP/6-31+G(d,p) relaxed scan (optimized) for CCDCOH2; B3LYP/3-21G relaxed scan (optimized) for CCB2H2, CCBCDH2, CDCB2, CDCBCD, CDCDCT.

## 2.4 Results and Discussion

### 2.4.1 Geometries and Vibrational Frequencies

The fully optimized geometries at the B3LYP/6-31g(d) density functional calculation level for the species are presented in Figures 2.1 to 2.15. Numerical values of the optimized structural parameters including carbon-hydrogen, carbon-oxygen, oxygen-oxygen, oxygen-hydrogen bond distances along with applicable bond angles and dihedral (twist) angles are listed in Tables 2.1 to 2.15.

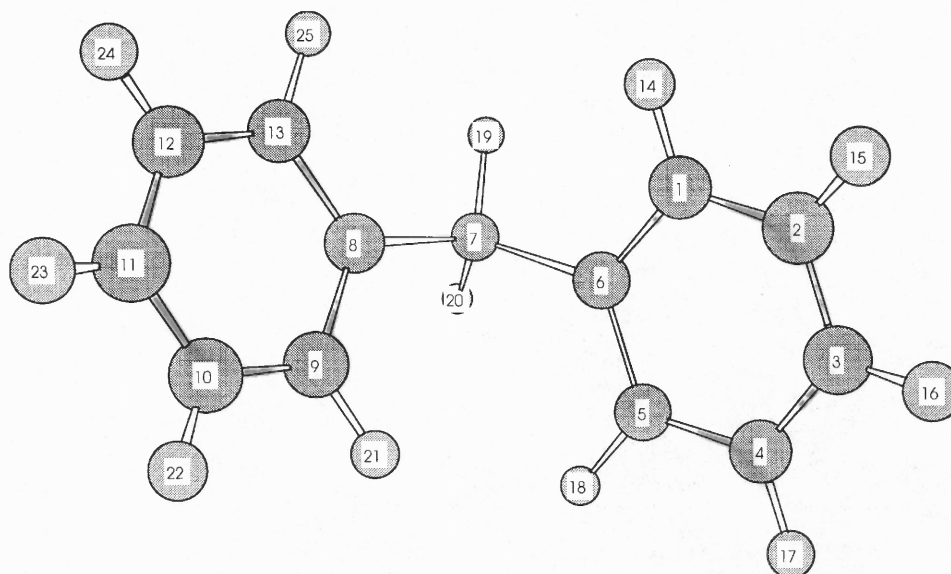
**Table 2.1 Structure Parameters<sup>a,b</sup> for CCB2H2**

| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.39                  |                           |                                    | 1                   |    |    |
| 3                     | C                  | 1.40                  | 120.24                    |                                    | 2                   | 1  |    |
| 4                     | C                  | 1.39                  | 119.48                    | -0.01                              | 3                   | 2  | 1  |
| 5                     | C                  | 1.40                  | 120.08                    | 0.05                               | 4                   | 3  | 2  |
| 6                     | C                  | 1.40                  | 120.83                    | -0.15                              | 1                   | 2  | 3  |
| 7                     | C                  | 1.52                  | 120.85                    | -178.58                            | 6                   | 1  | 2  |
| 8                     | C                  | 1.52                  | 114.71                    | -53.12                             | 7                   | 6  | 1  |
| 9                     | C                  | 1.40                  | 120.61                    | -61.27                             | 8                   | 7  | 6  |
| 10                    | C                  | 1.39                  | 120.86                    | -179.42                            | 9                   | 8  | 7  |
| 11                    | C                  | 1.40                  | 120.21                    | -0.13                              | 10                  | 9  | 8  |
| 12                    | C                  | 1.39                  | 119.51                    | 0.01                               | 11                  | 10 | 9  |
| 13                    | C                  | 1.40                  | 121.01                    | -179.58                            | 8                   | 7  | 9  |
| 14                    | H                  | 1.09                  | 119.77                    | 179.39                             | 1                   | 2  | 3  |
| 15                    | H                  | 1.09                  | 119.70                    | 179.96                             | 2                   | 1  | 6  |
| 16                    | H                  | 1.09                  | 120.24                    | -179.89                            | 3                   | 2  | 1  |
| 17                    | H                  | 1.09                  | 120.18                    | -179.82                            | 4                   | 3  | 2  |
| 18                    | H                  | 1.09                  | 119.63                    | 179.89                             | 5                   | 4  | 3  |
| 19                    | H                  | 1.10                  | 109.30                    | 69.18                              | 7                   | 6  | 1  |
| 20                    | H                  | 1.10                  | 108.55                    | -175.83                            | 7                   | 6  | 1  |
| 21                    | H                  | 1.09                  | 119.35                    | 0.97                               | 9                   | 8  | 7  |
| 22                    | H                  | 1.09                  | 119.74                    | 179.89                             | 10                  | 9  | 8  |
| 23                    | H                  | 1.09                  | 120.22                    | -179.96                            | 11                  | 10 | 9  |
| 24                    | H                  | 1.09                  | 120.18                    | -179.96                            | 12                  | 11 | 10 |
| 25                    | H                  | 1.09                  | 119.38                    | -0.25                              | 13                  | 8  | 7  |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Geometry Parameters optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.



**Figure 2.1** B3LYP/6-31G(d) optimized geometry of CCB<sub>2</sub>H<sub>2</sub>. See Table 2.1 for structure parameters.

**Table 2.2 Structure Parameters<sup>a,b</sup> for CCBCDH2**

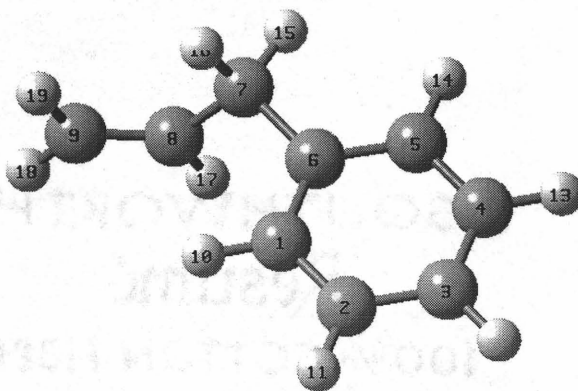
| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.39                  |                           |                                    | 1                   |    |    |
| 3                     | C                  | 1.40                  | 120.21                    |                                    | 2                   | 1  |    |
| 4                     | C                  | 1.39                  | 119.51                    | -0.02                              | 3                   | 2  | 1  |
| 5                     | C                  | 1.40                  | 120.08                    | 0.07                               | 4                   | 3  | 2  |
| 6                     | C                  | 1.40                  | 120.81                    | -0.20                              | 1                   | 2  | 3  |
| 7                     | C                  | 1.52                  | 120.58                    | -179.09                            | 6                   | 1  | 2  |
| 8                     | C                  | 1.51                  | 113.47                    | -54.09                             | 7                   | 6  | 1  |
| 9                     | C                  | 1.33                  | 124.96                    | 121.83                             | 8                   | 7  | 6  |
| 10                    | H                  | 1.09                  | 119.95                    | 179.41                             | 1                   | 2  | 3  |
| 11                    | H                  | 1.09                  | 119.75                    | 179.92                             | 2                   | 1  | 6  |
| 12                    | H                  | 1.09                  | 120.23                    | -179.90                            | 3                   | 2  | 1  |
| 13                    | H                  | 1.09                  | 120.15                    | -179.82                            | 4                   | 3  | 2  |
| 14                    | H                  | 1.09                  | 119.66                    | 179.96                             | 5                   | 4  | 3  |
| 15                    | H                  | 1.10                  | 108.56                    | -121.79                            | 7                   | 6  | 8  |
| 16                    | H                  | 1.10                  | 109.88                    | -115.92                            | 7                   | 6  | 15 |
| 17                    | H                  | 1.09                  | 115.61                    | -57.73                             | 8                   | 7  | 6  |
| 18                    | H                  | 1.09                  | 121.80                    | 179.78                             | 9                   | 8  | 7  |
| 19                    | H                  | 1.09                  | 121.67                    | 0.15                               | 9                   | 8  | 7  |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.





**Figure 2.2** B3LYP/6-31G(d) Optimized Geometry of CCBCDH2. See Table 2.2 for Structure Parameters.

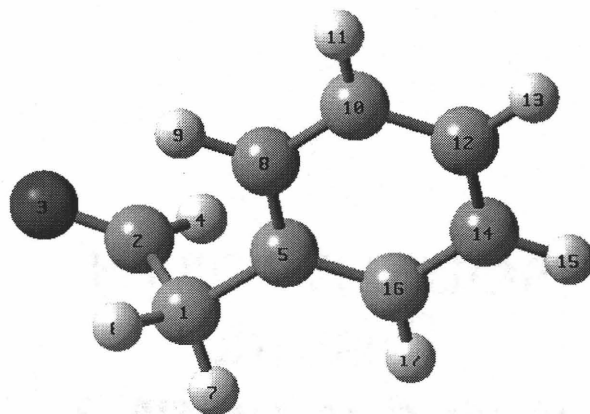
**Table 2.3 Structure Parameters<sup>a,b</sup> for CCBCOH2**

| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.52                  |                           |                                    | 1                   |    |    |
| 3                     | O                  | 1.21                  | 124.46                    |                                    | 2                   | 1  |    |
| 4                     | H                  | 1.11                  | 114.47                    | 178.90                             | 2                   | 1  | 3  |
| 5                     | C                  | 1.52                  | 110.74                    | -120.95                            | 1                   | 2  | 3  |
| 6                     | H                  | 1.09                  | 111.97                    | -120.52                            | 1                   | 5  | 2  |
| 7                     | H                  | 1.10                  | 109.83                    | 119.06                             | 1                   | 5  | 2  |
| 8                     | C                  | 1.40                  | 119.93                    | 74.43                              | 5                   | 1  | 2  |
| 9                     | H                  | 1.09                  | 119.42                    | 1.66                               | 8                   | 5  | 1  |
| 10                    | C                  | 1.39                  | 120.67                    | 179.88                             | 8                   | 5  | 9  |
| 11                    | H                  | 1.09                  | 119.75                    | 0.19                               | 10                  | 8  | 9  |
| 12                    | C                  | 1.40                  | 120.11                    | 180.00                             | 10                  | 11 | 8  |
| 13                    | H                  | 1.09                  | 120.17                    | 0.08                               | 12                  | 10 | 11 |
| 14                    | C                  | 1.40                  | 120.18                    | -179.88                            | 12                  | 13 | 10 |
| 15                    | H                  | 1.09                  | 120.15                    | 0.05                               | 14                  | 12 | 13 |
| 16                    | C                  | 1.40                  | 119.74                    | -179.80                            | 14                  | 15 | 12 |
| 17                    | H                  | 1.09                  | 119.72                    | 0.18                               | 16                  | 14 | 15 |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.



**Figure 2.3** B3LYP/6-31G(d) optimized geometry of CCBCOH<sub>2</sub>. See Table 2.3 for structure parameters.

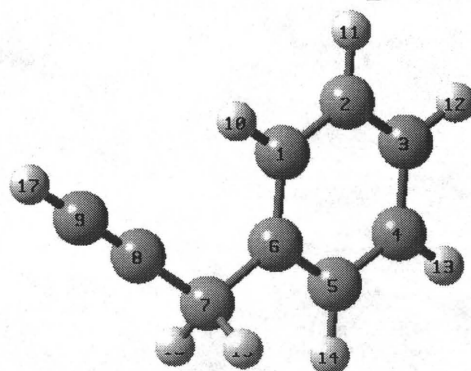
**Table 2.4 Structure Parameters<sup>a,b</sup> for CCBCTH2**

| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.40                  |                           |                                    | 1                   |    |    |
| 3                     | C                  | 1.39                  | 120.36                    |                                    | 2                   | 1  |    |
| 4                     | C                  | 1.40                  | 119.48                    | 0.05                               | 3                   | 2  | 1  |
| 5                     | C                  | 1.39                  | 120.08                    | -0.01                              | 4                   | 3  | 2  |
| 6                     | C                  | 1.40                  | 120.49                    | 0.00                               | 1                   | 2  | 3  |
| 7                     | C                  | 1.53                  | 122.54                    | 178.77                             | 6                   | 1  | 2  |
| 8                     | C                  | 1.46                  | 115.81                    | 11.33                              | 7                   | 6  | 1  |
| 9                     | C                  | 1.21                  | 179.16                    | -170.61                            | 8                   | 7  | 6  |
| 10                    | H                  | 1.09                  | 120.19                    | -179.69                            | 1                   | 2  | 3  |
| 11                    | H                  | 1.09                  | 119.55                    | 179.90                             | 2                   | 1  | 6  |
| 12                    | H                  | 1.09                  | 120.31                    | 179.90                             | 3                   | 2  | 1  |
| 13                    | H                  | 1.09                  | 120.16                    | 179.79                             | 4                   | 3  | 2  |
| 14                    | H                  | 1.09                  | 119.68                    | 179.85                             | 5                   | 4  | 3  |
| 15                    | H                  | 1.10                  | 108.83                    | -122.63                            | 7                   | 6  | 8  |
| 16                    | H                  | 1.10                  | 108.90                    | 123.04                             | 7                   | 6  | 8  |
| 17                    | H                  | 1.07                  | 179.75                    | -145.45                            | 9                   | 8  | 15 |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.



**Figure 2.4** B3LYP/6-31G(d) optimized geometry of CCBCTH2. See Table 2.4 for structure parameters.

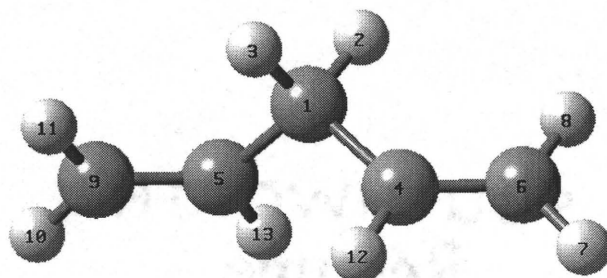
**Table 2.5 Structure Parameters<sup>a,b</sup> for CCD2H2**

| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | H                  | 1.10                  |                           |                                    | 1                   |    |    |
| 3                     | H                  | 1.10                  | 107.00                    |                                    | 1                   | 2  |    |
| 4                     | C                  | 1.51                  | 108.97                    | -118.65                            | 1                   | 2  | 3  |
| 5                     | C                  | 1.51                  | 112.18                    | 121.79                             | 1                   | 4  | 2  |
| 6                     | C                  | 1.33                  | 125.05                    | 118.22                             | 4                   | 1  | 5  |
| 7                     | H                  | 1.09                  | 121.81                    | -179.62                            | 6                   | 4  | 1  |
| 8                     | H                  | 1.09                  | 121.68                    | 0.67                               | 6                   | 4  | 1  |
| 9                     | C                  | 1.33                  | 125.06                    | 118.26                             | 5                   | 1  | 4  |
| 10                    | H                  | 1.09                  | 121.81                    | -179.64                            | 9                   | 5  | 1  |
| 11                    | H                  | 1.09                  | 121.69                    | -179.69                            | 9                   | 5  | 10 |
| 12                    | H                  | 1.09                  | 115.45                    | -60.79                             | 4                   | 1  | 5  |
| 13                    | H                  | 1.09                  | 119.49                    | 179.65                             | 5                   | 9  | 11 |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.



**Figure 2.5** B3LYP/6-31G(d) optimized geometry of CCD<sub>2</sub>H<sub>2</sub>. See Table 2.5 for structure parameters.

**Table 2.6 Structure Parameters <sup>a,b</sup> for CCDCOH2**

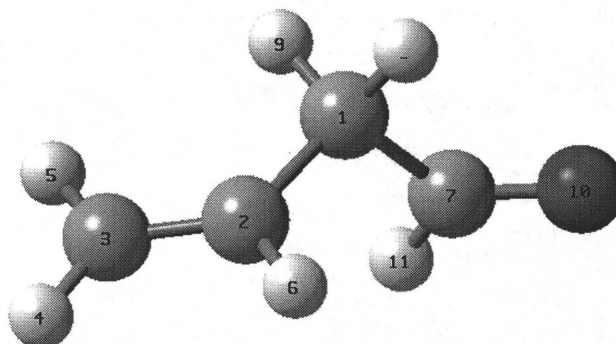
| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.51                  |                           |                                    | 1                   |    |    |
| 3                     | C                  | 1.33                  | 124.84                    |                                    | 2                   | 1  |    |
| 4                     | H                  | 1.09                  | 121.61                    | 178.72                             | 3                   | 2  | 1  |
| 5                     | H                  | 1.09                  | 121.85                    | -1.98                              | 3                   | 2  | 1  |
| 6                     | H                  | 1.09                  | 119.49                    | 0.65                               | 2                   | 3  | 4  |
| 7                     | C                  | 1.52                  | 110.88                    | 70.09                              | 1                   | 2  | 6  |
| 8                     | H                  | 1.10                  | 111.84                    | -120.42                            | 1                   | 2  | 7  |
| 9                     | H                  | 1.10                  | 109.64                    | -120.76                            | 1                   | 2  | 8  |
| 10                    | O                  | 1.21                  | 124.66                    | -119.68                            | 7                   | 1  | 2  |
| 11                    | H                  | 1.11                  | 114.19                    | 179.24                             | 7                   | 1  | 10 |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.





**Figure 2.6** B3LYP/6-31G(d) optimized geometry of CCDCOH<sub>2</sub>. See Table 2.6 for structure parameters.

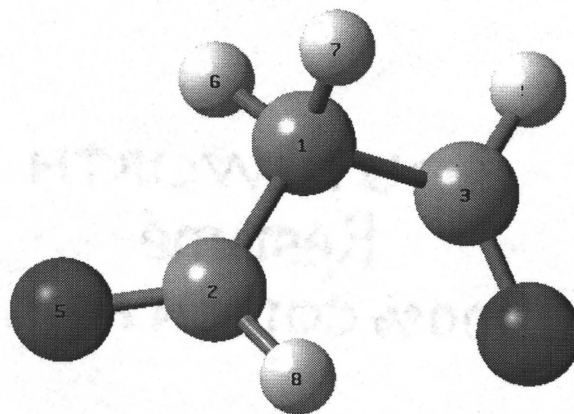
**Table 2.7 Structure Parameters<sup>a,b</sup> for CCO2H2**

| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.52                  | 1.00                      |                                    |                     |    |    |
| 3                     | C                  | 1.52                  | 114.01                    | 1.00                               | 2                   |    |    |
| 4                     | O                  | 1.21                  | 124.41                    | -4.71                              | 3                   | 1  | 2  |
| 5                     | O                  | 1.21                  | 123.11                    | -136.95                            | 2                   | 1  | 3  |
| 6                     | H                  | 1.10                  | 109.86                    | 124.53                             | 1                   | 2  | 3  |
| 7                     | H                  | 1.10                  | 108.82                    | -119.67                            | 1                   | 2  | 3  |
| 8                     | H                  | 1.11                  | 115.38                    | 42.08                              | 2                   | 1  | 4  |
| 9                     | H                  | 1.11                  | 114.65                    | 175.50                             | 3                   | 1  | 2  |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.



**Figure 2.7** B3LYP/6-31G(d) optimized geometry of CCO<sub>2</sub>H<sub>2</sub>. See Table 2.7 for structure parameters.

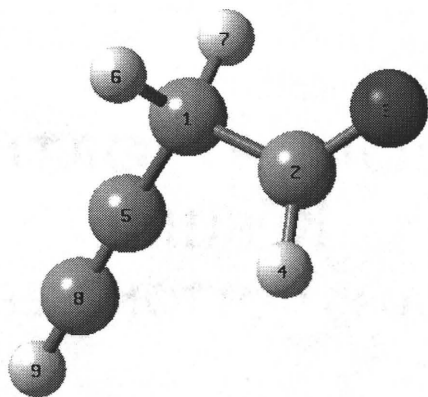
**Table 2.8 Structure Parameters <sup>a,b</sup> for CCOCTH2**

| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.53                  |                           |                                    | 1                   |    |    |
| 3                     | O                  | 1.21                  | 123.07                    |                                    | 2                   | 1  |    |
| 4                     | H                  | 1.11                  | 121.89                    | -178.63                            | 2                   | 3  | 1  |
| 5                     | C                  | 1.46                  | 112.88                    | -32.45                             | 1                   | 2  | 4  |
| 6                     | H                  | 1.10                  | 106.70                    | 121.01                             | 1                   | 2  | 5  |
| 7                     | H                  | 1.10                  | 108.07                    | -124.72                            | 1                   | 2  | 5  |
| 8                     | C                  | 1.21                  | 151.73                    | 176.11                             | 5                   | 6  | 1  |
| 9                     | H                  | 1.07                  | 161.74                    | -178.04                            | 8                   | 6  | 5  |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.



**Figure 2.8** B3LYP/6-31G(d) optimized geometry of CCOCTH2. See Table 2.8 for structure parameters.

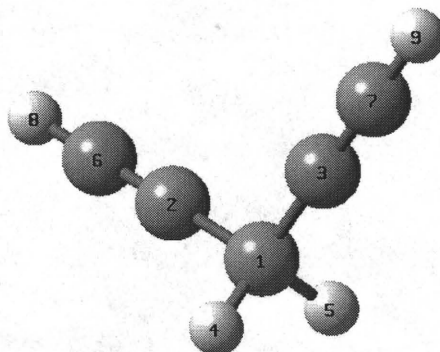
**Table 2.9 Structure Parameters <sup>a,b</sup> for CCT2H2**

| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.47                  | 1.00                      |                                    |                     |    |    |
| 3                     | C                  | 1.47                  | 113.65                    | 1.00                               | 2                   |    |    |
| 4                     | H                  | 1.10                  | 109.33                    | 122.46                             | 1                   | 2  | 3  |
| 5                     | H                  | 1.10                  | 109.33                    | -122.46                            | 1                   | 2  | 3  |
| 6                     | C                  | 1.21                  | 150.26                    | 179.32                             | 2                   | 4  | 1  |
| 7                     | C                  | 1.21                  | 150.24                    | 179.38                             | 3                   | 5  | 1  |
| 8                     | H                  | 1.07                  | 179.74                    | 123.03                             | 6                   | 2  | 4  |
| 9                     | H                  | 1.07                  | 179.75                    | 123.60                             | 7                   | 3  | 5  |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.



**Figure 2.9** B3LYP/6-31G(d) optimized geometry of CCT2H2. See Table 2.9 for structure parameters.

**Table 2.10 Structure Parameters<sup>a,b</sup> for CDCB2**

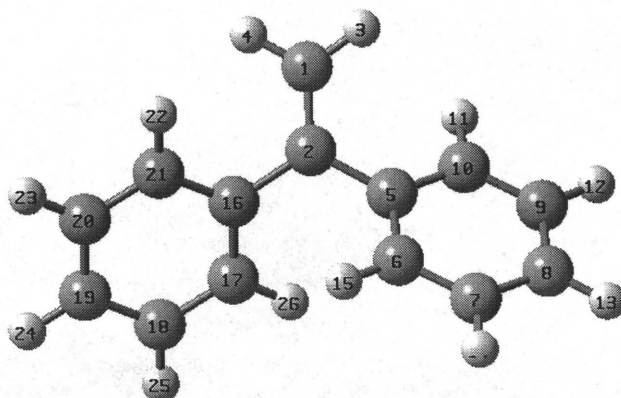
| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.35                  |                           |                                    | 1                   |    |    |
| 3                     | H                  | 1.09                  | 121.58                    |                                    | 1                   | 2  |    |
| 4                     | H                  | 1.09                  | 121.59                    | -180.00                            | 1                   | 2  | 3  |
| 5                     | C                  | 1.49                  | 120.63                    | -3.41                              | 2                   | 1  | 3  |
| 6                     | C                  | 1.41                  | 120.95                    | 139.80                             | 5                   | 2  | 1  |
| 7                     | C                  | 1.39                  | 120.88                    | -177.55                            | 6                   | 5  | 2  |
| 8                     | C                  | 1.40                  | 120.28                    | -0.57                              | 7                   | 6  | 5  |
| 9                     | C                  | 1.40                  | 119.49                    | -0.12                              | 8                   | 7  | 6  |
| 10                    | C                  | 1.41                  | 120.87                    | -178.58                            | 5                   | 2  | 6  |
| 11                    | H                  | 1.09                  | 119.12                    | -3.55                              | 10                  | 5  | 2  |
| 12                    | H                  | 1.09                  | 120.12                    | -179.08                            | 9                   | 8  | 7  |
| 13                    | H                  | 1.09                  | 120.25                    | -179.62                            | 8                   | 7  | 6  |
| 14                    | H                  | 1.09                  | 119.63                    | 179.34                             | 7                   | 6  | 5  |
| 15                    | H                  | 1.09                  | 119.36                    | 1.66                               | 6                   | 5  | 2  |
| 16                    | C                  | 1.49                  | 120.64                    | 176.59                             | 2                   | 1  | 3  |
| 17                    | C                  | 1.41                  | 120.95                    | 139.82                             | 16                  | 2  | 1  |
| 18                    | C                  | 1.39                  | 120.88                    | -177.54                            | 17                  | 16 | 2  |
| 19                    | C                  | 1.40                  | 120.28                    | -0.57                              | 18                  | 17 | 16 |
| 20                    | C                  | 1.40                  | 119.49                    | -0.11                              | 19                  | 18 | 17 |
| 21                    | C                  | 1.41                  | 120.87                    | -178.58                            | 16                  | 2  | 17 |
| 22                    | H                  | 1.09                  | 119.12                    | -3.56                              | 21                  | 16 | 2  |
| 23                    | H                  | 1.09                  | 120.12                    | -179.08                            | 20                  | 19 | 18 |
| 24                    | H                  | 1.09                  | 120.25                    | -179.62                            | 19                  | 18 | 17 |
| 25                    | H                  | 1.09                  | 119.63                    | 179.34                             | 18                  | 17 | 16 |
| 26                    | H                  | 1.09                  | 119.36                    | 1.66                               | 17                  | 16 | 2  |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.





**Figure 2.10** B3LYP/6-31G(d) optimized geometry of CDCB2. See Table 2.10 for structure parameters.

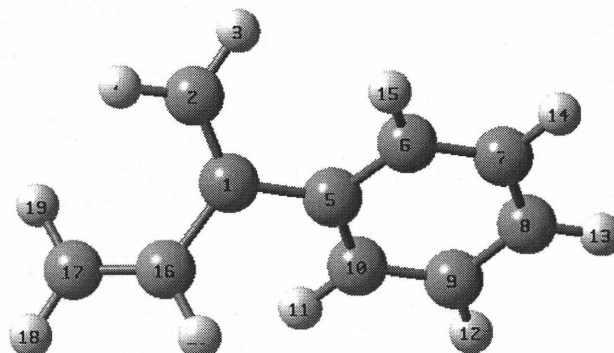
**Table 2.11 Structure Parameters <sup>a,b</sup> for CDCBCD**

| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.35                  |                           |                                    | 1                   |    |    |
| 3                     | H                  | 1.09                  | 121.86                    |                                    | 2                   | 1  |    |
| 4                     | H                  | 1.09                  | 121.21                    | 179.71                             | 2                   | 1  | 3  |
| 5                     | C                  | 1.49                  | 121.86                    | 4.44                               | 1                   | 2  | 3  |
| 6                     | C                  | 1.41                  | 121.46                    | 32.87                              | 5                   | 1  | 2  |
| 7                     | C                  | 1.39                  | 120.94                    | -179.02                            | 6                   | 5  | 1  |
| 8                     | C                  | 1.40                  | 120.26                    | -0.45                              | 7                   | 6  | 5  |
| 9                     | C                  | 1.40                  | 119.49                    | -0.14                              | 8                   | 7  | 6  |
| 10                    | C                  | 1.39                  | 120.20                    | 0.16                               | 9                   | 8  | 7  |
| 11                    | H                  | 1.09                  | 119.29                    | 0.31                               | 10                  | 5  | 1  |
| 12                    | H                  | 1.09                  | 120.12                    | 180.00                             | 9                   | 8  | 7  |
| 13                    | H                  | 1.09                  | 120.24                    | -179.68                            | 8                   | 7  | 6  |
| 14                    | H                  | 1.09                  | 119.66                    | -179.66                            | 7                   | 6  | 5  |
| 15                    | H                  | 1.09                  | 119.29                    | 2.49                               | 6                   | 5  | 1  |
| 16                    | C                  | 1.48                  | 121.08                    | -176.08                            | 1                   | 2  | 3  |
| 17                    | C                  | 1.34                  | 125.26                    | 38.74                              | 16                  | 1  | 2  |
| 18                    | H                  | 1.09                  | 121.40                    | -178.01                            | 17                  | 16 | 1  |
| 19                    | H                  | 1.09                  | 121.73                    | 2.50                               | 17                  | 16 | 1  |
| 20                    | H                  | 1.09                  | 115.82                    | -142.17                            | 16                  | 1  | 2  |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.



**Figure 2.11** B3LYP/6-31G(d) optimized geometry of CDCBCD. See Table 2.11 for structure parameters.

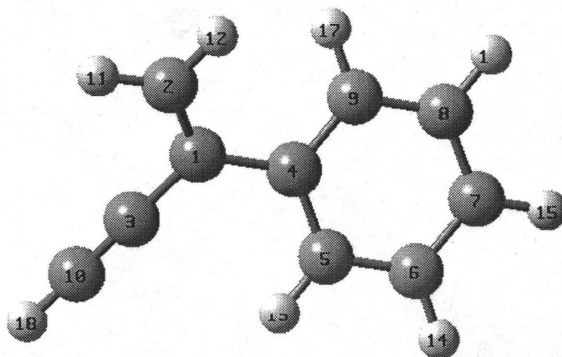
**Table 2.12 Structure Parameters <sup>a,b</sup> for CDCBCT**

| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.35                  |                           |                                    | 1                   |    |    |
| 3                     | C                  | 1.44                  | 119.19                    |                                    | 1                   | 2  |    |
| 4                     | C                  | 1.49                  | 123.25                    | -179.24                            | 1                   | 2  | 3  |
| 5                     | C                  | 1.40                  | 120.51                    | 154.07                             | 4                   | 1  | 2  |
| 6                     | C                  | 1.39                  | 120.80                    | -178.48                            | 5                   | 4  | 1  |
| 7                     | C                  | 1.40                  | 120.29                    | -0.56                              | 6                   | 5  | 4  |
| 8                     | C                  | 1.40                  | 119.46                    | -0.30                              | 7                   | 6  | 5  |
| 9                     | C                  | 1.41                  | 121.13                    | -179.79                            | 4                   | 1  | 5  |
| 10                    | C                  | 1.21                  | 179.28                    | 174.33                             | 3                   | 1  | 2  |
| 11                    | H                  | 1.08                  | 121.03                    | -1.67                              | 2                   | 1  | 3  |
| 12                    | H                  | 1.08                  | 121.64                    | 177.30                             | 2                   | 1  | 3  |
| 13                    | H                  | 1.09                  | 119.21                    | 1.13                               | 5                   | 4  | 1  |
| 14                    | H                  | 1.09                  | 119.58                    | 179.56                             | 6                   | 5  | 4  |
| 15                    | H                  | 1.09                  | 120.31                    | -179.69                            | 7                   | 6  | 5  |
| 16                    | H                  | 1.09                  | 120.11                    | -178.83                            | 8                   | 7  | 6  |
| 17                    | H                  | 1.09                  | 119.71                    | -3.10                              | 9                   | 4  | 1  |
| 18                    | H                  | 1.07                  | 179.14                    | 25.10                              | 10                  | 3  | 2  |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.



**Figure 2.12** B3LYP/6-31G(d) optimized geometry of CDCBCT. See Table 2.12 for structure parameters.

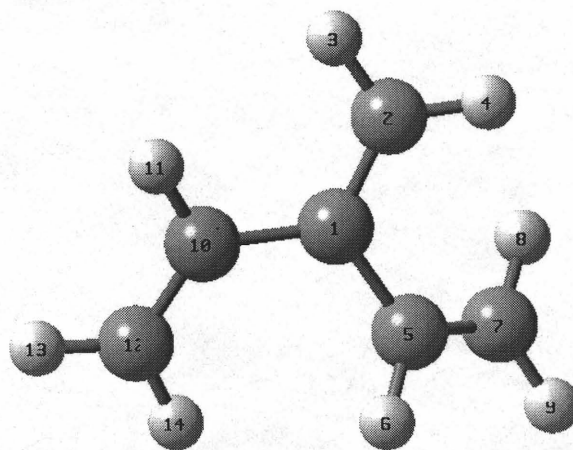
**Table 2.13 Structure Parameters <sup>a,b</sup> for CDCD2**

| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|------------------|----|----|
|                       |                    |                       |                           |                                    | NA               | NB | NC |
| 1                     | C                  |                       |                           |                                    |                  |    |    |
| 2                     | C                  | 1.35                  | 1.00                      |                                    |                  |    |    |
| 3                     | H                  | 1.09                  | 121.35                    | 2                                  | 1                |    |    |
| 4                     | H                  | 1.09                  | 121.67                    | 179.42461                          | 2                | 1  | 3  |
| 5                     | C                  | 1.48                  | 121.36                    | 178.96216                          | 1                | 2  | 3  |
| 6                     | H                  | 1.09                  | 115.95                    | 139.42916                          | 5                | 1  | 2  |
| 7                     | C                  | 1.34                  | 125.15                    | -40.8883                           | 5                | 1  | 2  |
| 8                     | H                  | 1.09                  | 121.80                    | -2.4857                            | 7                | 5  | 1  |
| 9                     | H                  | 1.09                  | 121.39                    | 178.12109                          | 7                | 5  | 1  |
| 10                    | C                  | 1.47                  | 119.87                    | -2.40                              | 1                | 2  | 3  |
| 11                    | H                  | 1.09                  | 115.05                    | -5.99                              | 10               | 1  | 2  |
| 12                    | C                  | 1.34                  | 126.15                    | 179.59                             | 10               | 1  | 11 |
| 13                    | H                  | 1.09                  | 121.12                    | 179.89                             | 12               | 10 | 1  |
| 14                    | H                  | 1.09                  | 122.41                    | -0.85                              | 12               | 10 | 1  |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.



**Figure 2.13** B3LYP/6-31G(d) optimized geometry of CDCD<sub>2</sub>. See Table 2.13 for structure parameters.

**Table 2.14 Structure Parameters<sup>a,b</sup> for CDCDCT**

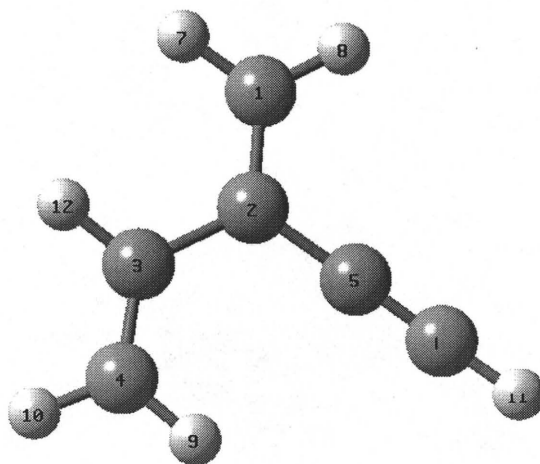
| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.35                  | 1.00                      |                                    |                     |    |    |
| 3                     | C                  | 1.47                  | 121.12                    | 2                                  | 1                   |    |    |
| 4                     | C                  | 1.34                  | 125.48                    | 179.99117                          | 3                   | 2  | 1  |
| 5                     | C                  | 1.43                  | 120.34                    | -179.98452                         | 2                   | 1  | 3  |
| 6                     | C                  | 1.21                  | 152.09                    | 179.98978                          | 5                   | 1  | 2  |
| 7                     | H                  | 1.09                  | 120.83                    | -179.98646                         | 1                   | 2  | 5  |
| 8                     | H                  | 1.08                  | 121.73                    | 179.98957                          | 1                   | 2  | 3  |
| 9                     | H                  | 1.09                  | 121.61                    | 0.00438                            | 4                   | 3  | 2  |
| 10                    | H                  | 1.09                  | 121.17                    | -179.99                            | 4                   | 3  | 2  |
| 11                    | H                  | 1.07                  | 160.39                    | -179.97                            | 6                   | 1  | 2  |
| 12                    | H                  | 1.09                  | 119.86                    | 179.99                             | 3                   | 4  | 2  |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.





**Figure 2.14** B3LYP/6-31G(d) optimized geometry of CDCDCT. See Table 2.14 for structure parameters.

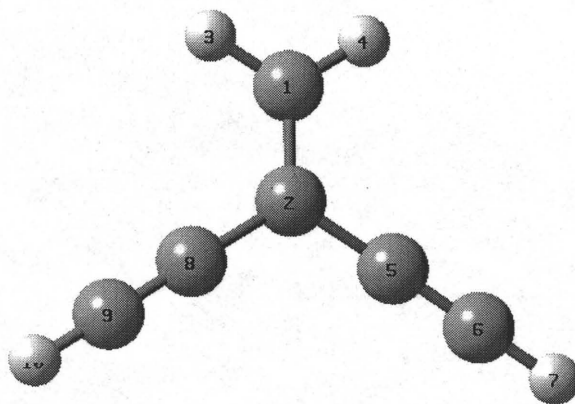
**Table 2.15 Structure Parameters<sup>a,b</sup> for CDCT2**

| Atom<br>Number<br>(I) | Chemical<br>Symbol | Bond Length<br>NA : I | Bond Angle<br>NB : NA : I | Dihedral Angle<br>NC : NB : NA : I | Connecting<br>Atoms |    |    |
|-----------------------|--------------------|-----------------------|---------------------------|------------------------------------|---------------------|----|----|
|                       |                    |                       |                           |                                    | NA                  | NB | NC |
| 1                     | C                  |                       |                           |                                    |                     |    |    |
| 2                     | C                  | 1.35                  | 1.00                      |                                    |                     |    |    |
| 3                     | H                  | 1.08                  | 120.82                    | 1                                  | 2                   |    |    |
| 4                     | H                  | 1.08                  | 120.82                    | 180                                | 1                   | 2  | 3  |
| 5                     | C                  | 1.44                  | 121.63                    | 180                                | 2                   | 1  | 3  |
| 6                     | C                  | 1.21                  | 152.95                    | 0                                  | 5                   | 1  | 4  |
| 7                     | H                  | 1.07                  | 161.58                    | 0                                  | 6                   | 1  | 4  |
| 8                     | C                  | 1.44                  | 121.63                    | 0                                  | 2                   | 1  | 3  |
| 9                     | C                  | 1.21                  | 152.95                    | 0                                  | 8                   | 1  | 3  |
| 10                    | H                  | 1.07                  | 161.58                    | 0.00                               | 9                   | 1  | 3  |

<sup>a</sup>Distances in Angstroms and Angles in Degrees.

<sup>b</sup>Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.

<sup>c</sup>Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.



**Figure 2.15** B3LYP/6-31G(d) optimized geometry of CDCT2. See Table 2.15 for structure parameters.

Harmonic vibrational frequencies are calculated for the species at the B3LYP/6-31G(d) level of theory on the basis of optimized geometries at the same level of theory. The unscaled vibrational frequencies and moments of inertia for the species are given in Tables 2.16 to 2.30 and 2.31 respectively. In Tables 2.16 to 2.30, the two lowest frequencies (corresponding to torsional motions) are omitted in calculation of entropies  $S^{\circ}_{298}$  and heat capacities  $C_p(T)$ , but their contributions have been replaced with values from analysis of the internal rotations (see Table 2.64).

**Table 2.16** Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CCB2H2

|         |         |         |
|---------|---------|---------|
| 24.14   | 26.21   | 66.05   |
| 195.13  | 226.91  | 290.39  |
| 344.53  | 416.98  | 417.74  |
| 462.71  | 483.01  | 565.19  |
| 623.73  | 635.21  | 637.64  |
| 712.22  | 716.53  | 752.49  |
| 754.81  | 833.20  | 837.34  |
| 861.00  | 861.67  | 908.39  |
| 931.06  | 954.55  | 966.44  |
| 967.13  | 994.35  | 994.42  |
| 1018.50 | 1018.79 | 1058.60 |
| 1059.80 | 1107.23 | 1117.17 |
| 1192.05 | 1192.39 | 1212.42 |
| 1214.15 | 1214.98 | 1221.53 |
| 1231.84 | 1321.09 | 1362.34 |
| 1364.94 | 1373.13 | 1382.76 |
| 1499.47 | 1500.16 | 1513.33 |
| 1546.00 | 1547.40 | 1642.21 |
| 1646.24 | 1662.32 | 1667.37 |
| 3033.40 | 3066.99 | 3172.51 |
| 3173.06 | 3178.41 | 3179.81 |
| 3188.27 | 3188.94 | 3196.35 |
| 3196.88 | 3207.74 | 3208.28 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.17 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CCBCDH2**

|         |         |         |
|---------|---------|---------|
| 26.35   | 85.23   | 147.21  |
| 274.93  | 330.53  | 399.91  |
| 417.74  | 498.08  | 538.51  |
| 635.68  | 668.54  | 715.78  |
| 758.05  | 834.65  | 862.13  |
| 913.76  | 934.10  | 940.29  |
| 951.70  | 967.45  | 994.56  |
| 1018.47 | 1037.26 | 1059.21 |
| 1109.30 | 1136.97 | 1192.06 |
| 1214.07 | 1221.26 | 1248.01 |
| 1322.68 | 1339.14 | 1363.46 |
| 1375.61 | 1472.27 | 1498.87 |
| 1507.52 | 1546.22 | 1644.21 |
| 1664.49 | 1728.50 | 3026.45 |
| 3061.24 | 3148.98 | 3158.15 |
| 3172.82 | 3179.64 | 3189.36 |
| 3197.26 | 3208.43 | 3235.23 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.18 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CCBCOH2**

|         |         |         |
|---------|---------|---------|
| 29.31   | 52.79   | 142.85  |
| 292.34  | 322.71  | 416.76  |
| 449.11  | 519.61  | 577.49  |
| 635.52  | 715.48  | 765.82  |
| 780.37  | 858.43  | 862.43  |
| 923.17  | 968.66  | 998.34  |
| 1013.20 | 1020.87 | 1058.00 |
| 1063.57 | 1117.89 | 1193.62 |
| 1205.79 | 1215.67 | 1225.23 |
| 1308.50 | 1358.55 | 1370.54 |
| 1433.48 | 1492.17 | 1502.14 |
| 1545.54 | 1644.12 | 1663.20 |
| 1831.82 | 2910.79 | 3046.27 |
| 3115.73 | 3177.24 | 3181.60 |
| 3191.27 | 3200.39 | 3211.34 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.19 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CCBCTH2**

|         |         |         |
|---------|---------|---------|
| 15.35   | 130.73  | 196.06  |
| 312.16  | 332.37  | 416.28  |
| 424.17  | 472.22  | 594.78  |
| 610.01  | 632.58  | 635.03  |
| 709.80  | 744.83  | 806.24  |
| 862.80  | 905.72  | 967.65  |
| 974.54  | 978.53  | 998.87  |
| 1019.41 | 1059.96 | 1113.47 |
| 1192.61 | 1209.11 | 1215.94 |
| 1251.09 | 1313.92 | 1366.45 |
| 1379.26 | 1493.27 | 1501.83 |
| 1546.85 | 1646.58 | 1665.89 |
| 2242.86 | 3018.85 | 3048.09 |
| 3170.00 | 3183.14 | 3193.68 |
| 3205.80 | 3213.46 | 3495.13 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^0_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.20 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CCD2H2**

|         |         |         |
|---------|---------|---------|
| 90.66   | 104.62  | 299.65  |
| 372.81  | 454.35  | 614.77  |
| 679.80  | 906.15  | 918.64  |
| 941.45  | 942.54  | 972.51  |
| 1037.13 | 1039.32 | 1094.49 |
| 1179.66 | 1275.86 | 1319.53 |
| 1332.80 | 1346.12 | 1470.63 |
| 1472.67 | 1502.55 | 1722.09 |
| 1736.19 | 3022.52 | 3061.07 |
| 3148.48 | 3149.01 | 3158.03 |
| 3158.63 | 3234.86 | 3234.98 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^0_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.21 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CCDCOH2**

|         |         |         |
|---------|---------|---------|
| 62.13   | 86.84   | 312.57  |
| 394.02  | 502.64  | 649.44  |
| 814.73  | 946.04  | 952.01  |
| 973.20  | 1037.65 | 1066.15 |
| 1150.02 | 1255.98 | 1301.06 |
| 1339.29 | 1430.64 | 1469.31 |
| 1489.36 | 1724.52 | 1836.13 |
| 2909.63 | 3039.40 | 3107.15 |
| 3157.14 | 3164.50 | 3240.90 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.22 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CCO2H2**

|         |         |         |
|---------|---------|---------|
| 26.24   | 95.55   | 232.14  |
| 462.30  | 640.45  | 699.28  |
| 860.84  | 922.33  | 1067.75 |
| 1098.45 | 1226.14 | 1324.61 |
| 1431.87 | 1439.06 | 1454.85 |
| 1828.50 | 1841.35 | 2921.36 |
| 2974.88 | 3014.35 | 3094.05 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.23 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CCOCTH2**

|         |         |         |
|---------|---------|---------|
| 53.93   | 174.13  | 330.55  |
| 462.86  | 507.82  | 609.47  |
| 635.63  | 732.09  | 984.80  |
| 1036.73 | 1051.32 | 1230.64 |
| 1307.95 | 1427.67 | 1468.56 |
| 1841.14 | 2245.76 | 2942.24 |
| 3016.11 | 3094.32 | 3494.33 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .



**Table 2.24 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CCT2H2**

|         |         |         |
|---------|---------|---------|
| 138.17  | 313.88  | 329.84  |
| 340.86  | 558.42  | 604.55  |
| 605.65  | 628.32  | 631.12  |
| 908.51  | 953.55  | 1003.76 |
| 1254.00 | 1359.96 | 1486.12 |
| 2247.74 | 2253.56 | 3019.08 |
| 3044.57 | 3494.88 | 3495.45 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.25 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CDCB2**

|         |         |         |
|---------|---------|---------|
| 45.63   | 63.41   | 81.59   |
| 142.93  | 220.06  | 236.89  |
| 296.38  | 345.12  | 419.61  |
| 423.52  | 449.23  | 461.94  |
| 579.65  | 603.39  | 629.44  |
| 634.87  | 655.77  | 705.71  |
| 714.53  | 726.69  | 738.99  |
| 791.94  | 801.93  | 850.54  |
| 862.98  | 865.19  | 919.23  |
| 936.87  | 937.88  | 972.48  |
| 974.00  | 996.75  | 997.22  |
| 1017.37 | 1017.42 | 1056.25 |
| 1058.18 | 1097.63 | 1114.24 |
| 1120.26 | 1179.57 | 1192.91 |
| 1193.14 | 1215.60 | 1217.12 |
| 1319.56 | 1339.61 | 1357.18 |
| 1367.00 | 1367.93 | 1456.32 |
| 1490.76 | 1493.72 | 1542.02 |
| 1545.30 | 1631.84 | 1633.21 |
| 1659.51 | 1661.52 | 1681.65 |
| 3174.01 | 3180.86 | 3181.44 |
| 3188.96 | 3189.11 | 3200.04 |
| 3200.22 | 3206.80 | 3207.31 |
| 3212.29 | 3212.63 | 3254.77 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.26 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CDCBCD**

|         |         |         |
|---------|---------|---------|
| 62.74   | 106.08  | 132.51  |
| 227.97  | 295.03  | 350.75  |
| 383.03  | 420.22  | 470.95  |
| 527.04  | 628.41  | 638.42  |
| 693.56  | 717.92  | 760.05  |
| 776.21  | 796.81  | 863.63  |
| 911.99  | 926.07  | 936.58  |
| 944.97  | 972.37  | 997.19  |
| 1017.46 | 1037.00 | 1057.13 |
| 1100.12 | 1111.40 | 1129.84 |
| 1193.16 | 1217.01 | 1298.85 |
| 1333.74 | 1349.83 | 1368.22 |
| 1455.17 | 1474.17 | 1494.72 |
| 1544.71 | 1633.44 | 1661.90 |
| 1678.73 | 1711.09 | 3151.69 |
| 3167.52 | 3175.41 | 3180.39 |
| 3187.79 | 3198.26 | 3204.42 |
| 3211.34 | 3247.01 | 3256.75 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.27 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CDCBCT**

|         |         |         |
|---------|---------|---------|
| 45.41   | 122.84  | 161.50  |
| 257.87  | 301.59  | 401.85  |
| 417.42  | 422.32  | 483.73  |
| 574.99  | 612.59  | 630.75  |
| 634.04  | 651.56  | 706.19  |
| 733.78  | 743.20  | 793.59  |
| 860.03  | 918.96  | 921.55  |
| 935.91  | 970.91  | 997.15  |
| 1018.11 | 1057.77 | 1112.97 |
| 1134.71 | 1193.90 | 1219.09 |
| 1308.43 | 1349.45 | 1370.18 |
| 1450.96 | 1495.01 | 1544.94 |
| 1634.06 | 1661.24 | 1669.95 |
| 2220.71 | 3182.84 | 3186.62 |
| 3191.83 | 3202.94 | 3210.10 |
| 3216.05 | 3272.81 | 3494.03 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.28 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CDCD2**

|         |         |         |
|---------|---------|---------|
| 107.94  | 153.72  | 248.81  |
| 311.65  | 379.38  | 501.84  |
| 528.58  | 636.26  | 767.16  |
| 785.42  | 798.50  | 922.72  |
| 932.45  | 945.36  | 954.86  |
| 1034.44 | 1042.42 | 1069.06 |
| 1099.39 | 1303.98 | 1341.85 |
| 1349.38 | 1440.40 | 1476.93 |
| 1488.10 | 1666.64 | 1708.66 |
| 1719.57 | 3155.14 | 3156.34 |
| 3166.82 | 3170.04 | 3174.85 |
| 3245.33 | 3251.47 | 3254.84 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.29 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CDCDCT**

|         |         |         |
|---------|---------|---------|
| 151.47  | 161.56  | 276.12  |
| 307.47  | 468.20  | 506.51  |
| 584.43  | 613.04  | 631.38  |
| 724.39  | 759.63  | 777.27  |
| 918.76  | 945.62  | 954.20  |
| 1027.97 | 1068.43 | 1330.65 |
| 1337.45 | 1435.81 | 1476.03 |
| 1655.68 | 1712.63 | 2226.05 |
| 3165.26 | 3177.98 | 3179.00 |
| 3259.40 | 3269.04 | 3494.90 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .

**Table 2.30 Vibration Frequencies <sup>a,b</sup> (cm<sup>-1</sup>)  
for CDCT2**

|         |         |         |
|---------|---------|---------|
| 137.35  | 235.02  | 249.02  |
| 359.63  | 488.32  | 584.79  |
| 584.94  | 590.82  | 630.43  |
| 632.71  | 685.93  | 737.33  |
| 762.09  | 927.50  | 961.66  |
| 1288.09 | 1439.56 | 1651.56 |
| 2226.68 | 2233.17 | 3188.28 |
| 3283.52 | 3494.41 | 3495.04 |

<sup>a</sup>Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.

<sup>b</sup>Torsion frequencies are not included in the calculation of Entropies  $S^{\circ}_{298}$  and Heat Capacities  $C_p(T)$ .

#### 2.4.2 Enthalpies of Formation ( $\Delta H_f^{\circ}_{298}$ )

Enthalpies of formation ( $\Delta H_f^{\circ}_{298}$ ) are estimated using total energies and calculated  $\Delta H^{\circ}_{\text{rxn},298}$  for the listed reactions (Table 2.32). Calculated  $\Delta H^{\circ}_{\text{rxn},298}$  for each reaction and evaluated literature thermodynamic properties for these reference reactants and products are utilized to estimate  $\Delta H_f^{\circ}_{298}$  of the target species. Enthalpies of reaction ( $\Delta H^{\circ}_{\text{rxn},298}$ ) are estimated using total energies obtained by the density functional calculations. Zero-point energies (ZPVE's) and thermal correction to 298.15 K are taken into account. The total energies at 298 K from B3LYP/6-31G(d) calculation level, ZPVE's, and thermal corrections to 298.15 K are listed in Table 2.31.

**Table 2.31 Total Energies at 298 K**

| Formula | Species | Molecular Weight | ZPVE <sup>b</sup> | Therm. Corr. <sup>c</sup> | Electronic Energy <sup>d</sup> | B3LYP /6-31G(d) <sup>a</sup> |
|---------|---------|------------------|-------------------|---------------------------|--------------------------------|------------------------------|
| C13H12  | CCB2H2  | 168              | 0.210357          | 0.221618                  | -502.615372                    | -502.187604                  |
| C9H10   | CCBCDH2 | 118              | 0.162145          | 0.17121                   | -348.956969                    | -348.626857                  |
| C8H8O   | CCBCO   | 120              | 0.138079          | 0.146927                  | -384.879569                    | -384.597325                  |
| C9H8    | CCBCT   | 116              | 0.137694          | 0.145687                  | -347.700884                    | -347.420257                  |
| C7H12   | CCD2H2  | 68               | 0.113897          | 0.120847                  | -195.297772                    | -195.065306                  |
| C4H6O   | CCDCO   | 70               | 0.089788          | 0.096552                  | -231.219843                    | -231.035299                  |
| C3H4O2  | CCO2H2  | 72               | 0.065284          | 0.071919                  | -267.139597                    | -267.0037                    |
| C5H4    | CCT2H2  | 68               | 0.06532           | 0.071867                  | -192.782876                    | -192.646995                  |
| C4H4O   | CCTCO   | 64               | 0.065265          | 0.071863                  | -229.963583                    | -229.82776                   |
| C14H12  | CDCB2   | 180              | 0.215327          | 0.227283                  | -540.702694                    | -540.264391                  |
| C10H10  | CDCBCD  | 130              | 0.167325          | 0.177011                  | -387.045971                    | -386.704982                  |
| C10H8   | CDCBCT  | 128              | 0.142837          | 0.152408                  | -385.79032                     | -385.497932                  |
| C6H8    | CDCD2   | 80               | 0.119126          | 0.126657                  | -233.387827                    | -233.144427                  |
| C6H6    | CDCDCT  | 78               | 0.094763          | 0.102116                  | -232.135083                    | -231.940099                  |
| C6H4    | CDCT2   | 76               | 0.070322          | 0.077552                  | -230.873763                    | -230.727295                  |

<sup>a</sup> Total Energy. Calculation based on the geometries optimized at B3LYP/6-31G(d) level of theory, ZPVE's and thermal corrections to 298 K are included. Units in Hartree.

<sup>b</sup> ZPVE: scaled zero-point energies in hartrees. Two hindered rotational frequencies are included in ZPVE which are scaled by 0.9806 (Scott<sup>25</sup> and Radom).

<sup>c</sup> Therm.Corr.: Thermal corrections in hartrees.

<sup>d</sup> B3LYP/6-31G(d) Electronic Energy (without considering ZPVE or Thermal Correction) Unit is Hartrees.

As an example, one reaction used to calculate  $\Delta H_f^\circ_{298}$  for CCB2H2 is:



$$\Delta H^\circ_{\text{rxn},298} = \Delta H_f^\circ_{298}(\text{C7H8}) + \Delta H_f^\circ_{298}(\text{C4H6}) - \Delta H_f^\circ_{298}(\text{C2H4}) - \Delta H_f^\circ_{298}(\text{CCBCDH2})$$

The reaction enthalpies and  $\Delta H_f^\circ_{298}$ 's of the species obtained from use of the reaction schemes are tabulated in Tables 2.32. Enthalpies of formation and uncertainties of reference species (data from literature) which are used to determine  $\Delta H_f^\circ_{298}$  values of species studied in this work are listed in Table 2.33.

Isodesmic reaction used for Enthalpy calculation of each species is shown in Table 2.32.

$\Delta H_{f,298}^{\circ}$  of CCD2H2 is calculated as:

$$\Delta H_{\text{rxn},298}^{\circ} = E_{298}(\text{C3H6}) + E_{298}(\text{C4H6}) - E_{298}(\text{CCD2H2}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_{f,298}^{\circ}(\text{CCD2H2}) = \Delta H_{f,298}^{\circ}(\text{C3H6}) + \Delta H_{f,298}^{\circ}(\text{C4H6}) - \Delta H_{f,298}^{\circ}(\text{C2H4}) - \Delta H_{\text{rxn},298}^{\circ}$$

where  $\Delta H_{f,298}^{\circ}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCD2H2).

$\Delta H_{f,298}^{\circ}(\text{CCD2H2})$  is calculated in this work to be 27.08 kcal/mol which is in reasonable agreement with the literature<sup>41</sup> reported value of 25.41 kcal/mol.

$\Delta H_{f,298}^{\circ}$  of CCB2H2 is calculated as:

$$\Delta H_{\text{rxn},298}^{\circ} = E_{298}(\text{C7H8}) + E_{298}(\text{C8H8}) - E_{298}(\text{CCB2H2}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_{f,298}^{\circ}(\text{CCB2H2}) = \Delta H_{f,298}^{\circ}(\text{C7H8}) + \Delta H_{f,298}^{\circ}(\text{C8H8}) - \Delta H_{f,298}^{\circ}(\text{C2H4}) - \Delta H_{\text{rxn},298}^{\circ}$$

where  $\Delta H_{f,298}^{\circ}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCB2H2).

$\Delta H_{f,298}^{\circ}(\text{CCB2H2})$  is calculated in this work to be 42.41 kcal/mol which is in reasonable agreement with the literature<sup>44</sup> reported value of 39.39 kcal/mol.

$\Delta H_{f,298}^{\circ}$  of CCDCT is calculated as:

$$\Delta H_{\text{rxn},298}^{\circ} = E_{298}(\text{C3H4}) + E_{298}(\text{C4H6}) - E_{298}(\text{CCDCT}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_{f,298}^{\circ}(\text{CCDCT}) = \Delta H_{f,298}^{\circ}(\text{C3H4}) + \Delta H_{f,298}^{\circ}(\text{C4H6}) - \Delta H_{f,298}^{\circ}(\text{C2H4}) - \Delta H_{\text{rxn},298}^{\circ}$$

where  $\Delta H_{f,298}^{\circ}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCDCT).

$\Delta H_f^\circ_{298}(\text{CCDCT})$  is calculated in this work to be 67.62 kcal/mol. No  $\Delta H_f^\circ_{298}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

$\Delta H_f^\circ_{298}$  of CCBCDH2 is calculated as:

$$\Delta H^\circ_{\text{rxn},298} = E_{298}(\text{C7H8}) + E_{298}(\text{C4H6}) - E_{298}(\text{CCBCDH2}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ_{298}(\text{CCBCDH2}) = \Delta H_f^\circ_{298}(\text{C7H8}) + \Delta H_f^\circ_{298}(\text{C4H6}) - \Delta H_f^\circ_{298}(\text{C2H4}) - \Delta H^\circ_{\text{rxn},298}$$

where  $\Delta H_f^\circ_{298}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCBCDH2).

$\Delta H_f^\circ_{298}(\text{CCBCDH2})$  is calculated in this work to be 34.71 kcal/mol. No  $\Delta H_f^\circ_{298}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

$\Delta H_f^\circ_{298}$  of CCT2H2 is calculated as:

$$\Delta H^\circ_{\text{rxn},298} = E_{298}(\text{C4H4}) + E_{298}(\text{C3H4}) - E_{298}(\text{CCT2H2}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ_{298}(\text{CCT2H2}) = \Delta H_f^\circ_{298}(\text{C4H4}) + \Delta H_f^\circ_{298}(\text{C3H4}) - \Delta H_f^\circ_{298}(\text{C2H4}) - \Delta H^\circ_{\text{rxn},298}$$

where  $\Delta H_f^\circ_{298}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCT2H2).

$\Delta H_f^\circ_{298}(\text{CCT2H2})$  is calculated in this work to be 112.43 kcal/mol. No  $\Delta H_f^\circ_{298}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

$\Delta H_f^\circ_{298}$  of CCBCT is calculated as:

$$\Delta H^\circ_{\text{rxn},298} = E_{298}(\text{C3H4}) + E_{298}(\text{C8H8}) - E_{298}(\text{CCBCT}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^{\circ}{}_{298}(\text{CCBCT}) = \Delta H_f^{\circ}{}_{298}(\text{C}_3\text{H}_4) + \Delta H_f^{\circ}{}_{298}(\text{C}_8\text{H}_8) - \Delta H_f^{\circ}{}_{298}(\text{C}_2\text{H}_4) - \Delta H^{\circ}{}_{\text{rxn},298}$$

where  $\Delta H_f^{\circ}{}_{298}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCBCT).

$\Delta H_f^{\circ}{}_{298}(\text{CCBCT})$  is calculated in this work to be 74.06 kcal/mol. No  $\Delta H_f^{\circ}{}_{298}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

$\Delta H_f^{\circ}{}_{298}$  of CCO<sub>2</sub>H<sub>2</sub> is calculated as:

$$\Delta H^{\circ}{}_{\text{rxn},298} = E_{298}(\text{C}_2\text{H}_4\text{O}) + E_{298}(\text{C}_3\text{H}_4\text{O}) - E_{298}(\text{CCO}_2\text{H}_2) - E_{298}(\text{C}_2\text{H}_4)$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^{\circ}{}_{298}(\text{CCO}_2\text{H}_2) = \Delta H_f^{\circ}{}_{298}(\text{C}_2\text{H}_4\text{O}) + \Delta H_f^{\circ}{}_{298}(\text{C}_3\text{H}_4\text{O}) - \Delta H_f^{\circ}{}_{298}(\text{C}_2\text{H}_4) - \Delta H^{\circ}{}_{\text{rxn},298}$$

where  $\Delta H_f^{\circ}{}_{298}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCO<sub>2</sub>H<sub>2</sub>).

$\Delta H_f^{\circ}{}_{298}(\text{CCO}_2\text{H}_2)$  is calculated in this work to be -64.88 kcal/mol. No  $\Delta H_f^{\circ}{}_{298}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

$\Delta H_f^{\circ}{}_{298}$  of CDCD<sub>2</sub> is calculated as:

$$\Delta H^{\circ}{}_{\text{rxn},298} = E_{298}(\text{C}_4\text{H}_6) + E_{298}(\text{C}_4\text{H}_6) - E_{298}(\text{CDCD}_2) - E_{298}(\text{C}_2\text{H}_4)$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^{\circ}{}_{298}(\text{CDCD}_2) = \Delta H_f^{\circ}{}_{298}(\text{C}_4\text{H}_6) + \Delta H_f^{\circ}{}_{298}(\text{C}_4\text{H}_6) - \Delta H_f^{\circ}{}_{298}(\text{C}_2\text{H}_4) - \Delta H^{\circ}{}_{\text{rxn},298}$$

where  $\Delta H_f^{\circ}{}_{298}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CDCD<sub>2</sub>).

$\Delta H_f^{\circ}{}_{298}(\text{CDCD}_2)$  is calculated in this work to be 44.54 kcal/mol. No  $\Delta H_f^{\circ}{}_{298}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>



$\Delta H_f^\circ_{298}$  of CDCDCT is calculated as:

$$\Delta H^\circ_{\text{rxn},298} = E_{298}(\text{C4H4}) + E_{298}(\text{C4H6}) - E_{298}(\text{CDCDCT}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ_{298}(\text{CDCDCT}) = \Delta H_f^\circ_{298}(\text{C4H4}) + \Delta H_f^\circ_{298}(\text{C4H6}) - \Delta H_f^\circ_{298}(\text{C2H4}) - \Delta H^\circ_{\text{rxn},298}$$

where  $\Delta H_f^\circ_{298}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CDCDCT).

$\Delta H_f^\circ_{298}(\text{CDCDCT})$  is calculated in this work to be 85.45 kcal/mol. No  $\Delta H_f^\circ_{298}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

$\Delta H_f^\circ_{298}$  of CDCBCT is calculated as:

$$\Delta H^\circ_{\text{rxn},298} = E_{298}(\text{C8H8}) + E_{298}(\text{C4H4}) - E_{298}(\text{CDCBCT}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ_{298}(\text{CDCBCT}) = \Delta H_f^\circ_{298}(\text{C8H8}) + \Delta H_f^\circ_{298}(\text{C4H4}) - \Delta H_f^\circ_{298}(\text{C2H4}) - \Delta H^\circ_{\text{rxn},298}$$

where  $\Delta H_f^\circ_{298}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CDCBCT).

$\Delta H_f^\circ_{298}(\text{CDCBCT})$  is calculated in this work to be 94.96 kcal/mol. No  $\Delta H_f^\circ_{298}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

$\Delta H_f^\circ_{298}$  of CCDCO is calculated as:

$$\Delta H^\circ_{\text{rxn},298} = E_{298}(\text{C3H6}) + E_{298}(\text{C3H4O}) - E_{298}(\text{CCDCO}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ_{298}(\text{CCDCO}) = \Delta H_f^\circ_{298}(\text{C3H6}) + \Delta H_f^\circ_{298}(\text{C3H4O}) - \Delta H_f^\circ_{298}(\text{C2H4}) - \Delta H^\circ_{\text{rxn},298}$$

where  $\Delta H_f^\circ_{298}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCDCO).

$\Delta H_f^\circ_{298}(\text{CCDCO})$  is calculated in this work to be -20.68 kcal/mol. No  $\Delta H_f^\circ_{298}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

$\Delta H_f^\circ_{298}$  of CCTCO is calculated as:

$$\Delta H^\circ_{\text{rxn},298} = E_{298}(\text{C3H4}) + E_{298}(\text{C3H4O}) - E_{298}(\text{CCTCO}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ_{298}(\text{CCTCO}) = \Delta H_f^\circ_{298}(\text{C3H4}) + \Delta H_f^\circ_{298}(\text{C3H4O}) - \Delta H_f^\circ_{298}(\text{C2H4}) - \Delta H^\circ_{\text{rxn},298}$$

where  $\Delta H_f^\circ_{298}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCTCO).

$\Delta H_f^\circ_{298}(\text{CCTCO})$  is calculated in this work to be 19.72 kcal/mol. No  $\Delta H_f^\circ_{298}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

$\Delta H_f^\circ_{298}$  of CCBCO is calculated as:

$$\Delta H^\circ_{\text{rxn},298} = E_{298}(\text{C7H8}) + E_{298}(\text{C3H4O}) - E_{298}(\text{CCBCO}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ_{298}(\text{CCBCO}) = \Delta H_f^\circ_{298}(\text{C7H8}) + \Delta H_f^\circ_{298}(\text{C3H4O}) - \Delta H_f^\circ_{298}(\text{C2H4}) - \Delta H^\circ_{\text{rxn},298}$$

where  $\Delta H_f^\circ_{298}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCBCO).

$\Delta H_f^\circ_{298}(\text{CCBCO})$  is calculated in this work to be -13.35 kcal/mol. No  $\Delta H_f^\circ_{298}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

$\Delta H_f^\circ_{298}$  of CDCBCD is calculated as:

$$\Delta H^\circ_{\text{rxn},298} = E_{298}(\text{C4H4}) + E_{298}(\text{C4H4}) - E_{298}(\text{CDCBCD}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_{f,298}^{\circ}(\text{CDCBCD}) = \Delta H_{f,298}^{\circ}(\text{C4H4}) + \Delta H_{f,298}^{\circ}(\text{C4H4}) - \Delta H_{f,298}^{\circ}(\text{C2H4}) - \Delta H_{\text{rxn},298}^{\circ}$$

where  $\Delta H_{f,298}^{\circ}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CDCBCD).

$\Delta H_{f,298}^{\circ}(\text{CDCBCD})$  is calculated in this work to be 52.34 kcal/mol. No  $\Delta H_{f,298}^{\circ}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

$\Delta H_{f,298}^{\circ}$  of CDCT2 is calculated as:

$$\Delta H_{\text{rxn},298}^{\circ} = E_{298}(\text{C4H4}) + E_{298}(\text{C4H4}) - E_{298}(\text{CDCT2}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_{f,298}^{\circ}(\text{CDCT2}) = \Delta H_{f,298}^{\circ}(\text{C4H4}) + \Delta H_{f,298}^{\circ}(\text{C4H4}) - \Delta H_{f,298}^{\circ}(\text{C2H4}) - \Delta H_{\text{rxn},298}^{\circ}$$

where  $\Delta H_{f,298}^{\circ}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CDCT2).

$\Delta H_{f,298}^{\circ}(\text{CDCT2})$  is calculated in this work to be 131.68 kcal/mol. No  $\Delta H_{f,298}^{\circ}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

$\Delta H_{f,298}^{\circ}$  of CDCB2 is calculated as:

$$\Delta H_{\text{rxn},298}^{\circ} = E_{298}(\text{C8H8}) + E_{298}(\text{C8H8}) - E_{298}(\text{CDCB2}) - E_{298}(\text{C2H4})$$

where  $E_{298}$  is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_{f,298}^{\circ}(\text{CDCB2}) = \Delta H_{f,298}^{\circ}(\text{C8H8}) + \Delta H_{f,298}^{\circ}(\text{C8H8}) - \Delta H_{f,298}^{\circ}(\text{C2H4}) - \Delta H_{\text{rxn},298}^{\circ}$$

where  $\Delta H_{f,298}^{\circ}$  is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CDCB2).

$\Delta H_{f,298}^{\circ}(\text{CDCB2})$  is calculated in this work to be 60.86 kcal/mol. No  $\Delta H_{f,298}^{\circ}$  value for this species were found in the literature.<sup>11,12,13,14,15</sup>

**Table 2.32 Calculated Enthalpies at 298K**

|                | Reaction |                    | $\Delta H_{\text{rxn}}^{\circ} 298^{\text{a}}$ | $\Delta H_{\text{f}}^{\circ} 298^{\text{a}}$ |
|----------------|----------|--------------------|--|--|
| C5H8(CCD2H2)   | + C2H4   | ---> C3H6 + C4H6   | -8.74  | 27.08  |
| C13H12(CCB2H2) | + C2H4   | ---> C7H8 + C8H8   | -7.87  | 42.39  |
| C5H6(CCDCT)    | + C2H4   | ---> C3H4 + C4H6   | -9.84  | 67.62  |
| C9H10(CCBCDH2) | + C2H4   | ---> C7H8 + C4H6   | -9.29  | 34.71  |
| C5H4(CCT2H2)   | + C2H4   | ---> C4H4 + C3H4   | -10.15   | 112.43                                       |
| C9H8(CCBCT)    | + C2H4   | ---> C8H8 + C3H4   | -7.18  | 74.06  |
| C3H4O2(CCO2H2) | + C2H4   | ---> C2H4O + C3H4O | -8.54  | -64.88                                       |
| C6H8(CDCD2)    | + C2H4   | ---> C4H6 + C4H6   | -5.07  | 44.54  |
| C6H6(CDCDCT)   | + C2H4   | ---> C4H6 + C4H4   | -1.48  | 85.45  |
| C10H8(CDCBCT)  | + C2H4   | ---> C8H8 + C4H4   | -1.88  | 94.96  |
| C4H6O(CCDCO)   | + C2H4   | ---> C3H6 + C3H4O  | -7.06  | -20.68                                       |
| C4H4O(CCTCO)   | + C2H4   | ---> C3H4 + C3H4O  | -8.03  | 19.72  |
| C8H8O(CCBCO)   | + C2H4   | ---> C7H8 + C3H4O  | -7.32  | -13.35                                       |
| C10H10(CDCBCD) | + C2H4   | ---> C4H6 + C8H8   | -3.77  | 52.34  |
| C6H4(CDCT2)    | + C2H4   | ---> C4H4 + C4H4   | -3.20  | 131.68                                       |
| C14H12(CDCB2)  | + C2H4   | ---> C8H8 + C8H8   | -3.18  | 60.86  |

<sup>a</sup> Reaction enthalpies obtained at B3LYP/6-31G(d). Reaction enthalpies include thermal correction and zero-point energy. Units in kcal/mol. Reactions are isodesmic. No reaction series conserves groups. Uncertainties of reference compound enthalpy not included. Species Enthalpy Values are for the lowest energy conformer and corrections have not been made for higher energy conformers.

**Table 2.33 Total Energies at 298 K and  $\Delta H_{\text{f}}^{\circ} 298$  for Reference Species in the Reaction Schemes**

| Name           | Formula | B3LYP<br>/6-31G(d) <sup>a</sup> | ZPVE <sup>b</sup> | Therm.<br>Corr. <sup>c</sup> | $\Delta H_{\text{f}}^{\circ} 298^{\text{d}}$ |
|----------------|---------|---------------------------------|-------------------|------------------------------|--|
| Ethylene       | C2H4    | -78.482054                      | 0.05122           | 0.055207                     | 12.54 <sup>e</sup>                           |
| Propylene      | C3H6    | -117.744                        | 0.080067          | 0.085085                     | 4.87 <sup>f</sup>                            |
| Acetaldehyde   | C2H4O   | -153.71475                      | 0.055824          | 0.060661                     | -40.8 <sup>g</sup> ± 0.35                    |
| Acrolein       | C3H4O   | -191.7846                       | 0.061652          | 0.066951                     | -20.08 <sup>h</sup>                          |
| Vinylacetylene | C4H4    | -154.60723                      | 0.061176          | 0.066619                     | 70.51 <sup>i</sup>                           |
| Propyne        | C3H4    | -116.538                        | 0.055721          | 0.060661                     | 44.31 <sup>j</sup> ± 0.21                    |
| Styrene        | C8H8    | -309.37576                      | 0.133732          | 0.141446                     | 35.11 <sup>k</sup> ± 0.24                    |
| Toluene        | C7H8    | -271.30644                      | 0.128231          | 0.134519                     | 11.95 <sup>l</sup> ± 0.15                    |
| 1,3-Butadiene  | C4H6    | -155.81728                      | 0.085492          | 0.091081                     | 26.00 <sup>m</sup> ± 0.19                    |

<sup>a</sup> Total Energy. Calculation based on the geometries optimized at B3LYP/6-31G(d) level of theory, ZPVE's and thermal corrections to 298 K are included. Units in Hartree.

<sup>b</sup> ZPVE: scaled zero-point

energies in hartrees. Two hindered rotational frequencies are included in ZPVE which are scaled by 0.9806 (Scott and Radom).

<sup>c</sup> Therm. Corr.: Thermal corrections in hartrees.

<sup>d</sup> Units in kcal/mol.

The uncertainties are given in the reference.

<sup>e</sup>Reference 34 <sup>f</sup>Reference 35 <sup>g</sup>Reference 36 <sup>h</sup>Reference 11

<sup>i</sup>Reference 37 <sup>j</sup>Reference 38 <sup>k</sup>Reference 39 <sup>l</sup>Reference 39

<sup>m</sup>Reference 40

The accuracy of the enthalpies of formation obtained theoretically is controlled by several factors: the level of sophistication (method + basis set) applied to calculate the electronic energy, the reliability of the enthalpies of formation of the reference compounds, the uncertainty in the thermal corrections, and the choice of the working chemical reaction used in the cancellation of calculation errors. The ZPVE and thermal correction in data of Table 2.31 have small contributions to the error on relative base. Scott<sup>25</sup> and Radom report errors after scaling (0.9806) for B3LYP/6-31G(d,p) of 0.1 kcal/mol for ZPVE in their study on 39 molecules incorporating 1066 known vibrations. They also report errors of 0.01 kcal/mol for thermal correction from 0 to 298 K in density function theory.<sup>25</sup> These reported error values are likely smaller than in this study; but in this work it has been assumed that the errors are non-random and that they are cancelled in the isodesmic reactions to a significant extent.

### 2.4.3 Rotational Barriers

Potential barriers for internal rotations of C-C bonds in the species are calculated at the B3LYP/3-21G, B3LYP/6-31G(d), B3LYP/6-31G(d,p) and in some cases at the B3LYP/6-31+g(d,p) levels of theory (please refer to the Figures 2.16 to 2.37 for details). Potential energy as function of dihedral angle is determined by scanning the torsion angles from 0° to 360° at 15° intervals and allowing the remaining molecular structural

parameters to be optimized – relaxed scan. Some molecules have the internal rotation potentials calculated using a rigid scan method as noted in the Figures 2.17 to 2.37, on a case-by-case basis.

Rotation data for the C–C bonds in the species are shown in Table 2.34, which indicates the rotational barriers and the foldness obtained from the rotations. The geometries at the points of these minima are optimized at the B3LYP/6-31G(d) level. The barriers for internal rotations are calculated from the differences between the total energy of each structure and that of the global equilibrium. The total energies and calculated rotation barriers about C–C bond for each rotational structure of the species listed in Tables 2.35 to 2.47. Potential Energy vs. Torsion angle diagrams for internal rotations about C–C bond of the species are shown in Figures 2.16 to 2.37. Points are values calculated using relaxed and non-relaxed density functional B3LYP calculations.

**Table 2.34 Moments of Inertia of Rotors, Rotational Barrier and Foldness**

| Species         | MI-1 <sup>a</sup> | MI-2 <sup>b</sup> | V <sup>c</sup> | n <sup>d</sup> |
|-----------------|-------------------|-------------------|----------------|----------------|
| <b>CCB2H2</b>   |                   |                   |                |                |
| C6H5-CH2C6H5    | 89                | 161.15            | 0.62           | 4              |
| C6H5-CH2C6H5    | 89                | 161.15            | 1.84           | 2              |
| <b>CCBCDH2</b>  |                   |                   |                |                |
| C6H5-CH2C2H3    | 89                | 58.6              | 2.27           | 2              |
| C2H3-CH2C6H5    | 19.73             | 161.15            | 3.83           | 3              |
| <b>CCBCOH2</b>  |                   |                   |                |                |
| C6H5-CH2CHO     | 89                | 62.78             | 6.7            | 2              |
| CHO-CH2C6H5     | 18.74             | 161.15            | 2.23           | 2              |
| <b>CCBCTH2</b>  |                   |                   |                |                |
| C6H5-CH2C2H     | 89                | 54.41             | 0.39           | 2              |
| <b>CCD2H2</b>   |                   |                   |                |                |
| CH2(C2H3)-C2H3  | 58.6              | 19.73             | 2.47           | 2              |
| CH2(C2H3)-C2H3  | 58.6              | 19.73             | 1.79           | 2              |
| <b>CCDCOH2</b>  |                   |                   |                |                |
| CHO-CH2C2H3     | 18.74             | 58.6              | 2.32           | 3              |
| C2H3-CH2CHO     | 19.73             | 62.78             | 2.63           | 3              |
| <b>CCO2H2</b>   |                   |                   |                |                |
| CHO-CH2CHO      | 18.74             | 62.78             | 0.66           | 4              |
| CHO-CH2CHO      | 18.74             | 62.78             | 0.54           | 4              |
| <b>CCOCTH2</b>  |                   |                   |                |                |
| CHO-CH2C2H      | 18.74             | 54.41             | 2.65           | 2              |
| <b>CDCB2</b>    |                   |                   |                |                |
| C6H5-C(CH2)C6H  | 89                | 154.04            | 2.57           | 4              |
| C6H5-C(CH2)C6H  | 89                | 154.04            | 9.37           | 2              |
| <b>CDCBCD</b>   |                   |                   |                |                |
| C6H5-C(CH2)C2H3 | 89                | 66.26             | 2.69           | 4              |
| <b>CDCBCT</b>   |                   |                   |                |                |
| C6H5-C(CH2)C2H  | 89                | 62.75             | 2.97           | 2              |
| <b>CDCD2</b>    |                   |                   |                |                |
| C2H3-C(CH2)C2H  | 19.73             | 66.26             | 4.99           | 2              |
| C2H3-C(CH2)C2H  | 19.73             | 66.26             | 5.71           | 4              |
| <b>CDCDCT</b>   |                   |                   |                |                |
| C2H3-C(CH2)C2H  | 19.73             | 62.75             | 5.76           | 2              |

<sup>a</sup> Moment of Inertia of the group on left of rotor (as represented here), Units in amu-Bohr<sup>2</sup>

<sup>b</sup> Moment of Inertia of the group on right of rotor (as represented here), Units in amu-Bohr<sup>2</sup>

<sup>c</sup> Rotation Barrier, Units in kcal

<sup>d</sup> Foldness from Rotation Plot shown in Figures 2.16 to 2.37

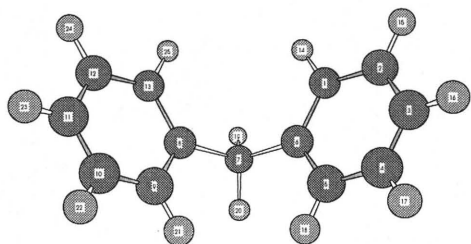
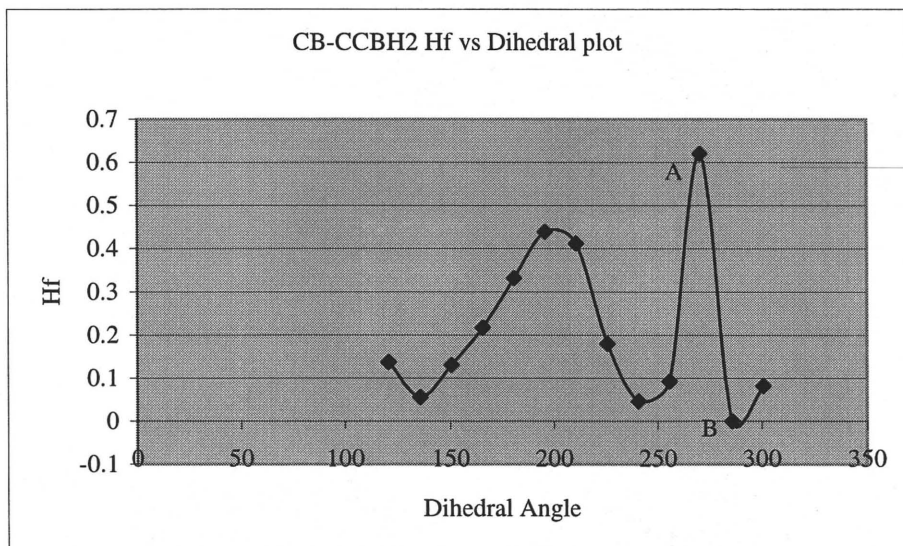
**Table 2.35 Total Energy and Internal Rotation Barriers for CCB2H2**

| CB-CCBH2         |                              |                                    | CB-CCBH2         |                              |                                    |
|------------------|------------------------------|------------------------------------|------------------|------------------------------|------------------------------------|
| Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> | Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> |
| 120.71           | -499.859379                  | 0.14                               | 89.70            | -499.858547                  | 0.55                               |
| 135.71           | -499.859509                  | 0.06                               | 134.70           | -499.859419                  | 0.00                               |
| 150.71           | -499.859391                  | 0.13                               | 179.70           | -499.858806                  | 0.38                               |
| 165.71           | -499.859253                  | 0.22                               | 224.70           | -499.856487                  | 1.84                               |
| 180.71           | -499.859069                  | 0.33                               | 269.70           | -499.858597                  | 0.52                               |
| 195.71           | -499.858898                  | 0.44                               |                  |                              |                                    |
| 210.71           | -499.858941                  | 0.41                               |                  |                              |                                    |
| 225.71           | -499.859312                  | 0.18                               |                  |                              |                                    |
| 240.71           | -499.859524                  | 0.05                               |                  |                              |                                    |
| 255.71           | -499.85945                   | 0.09                               |                  |                              |                                    |
| 270.71           | -499.85861                   | 0.62                               |                  |                              |                                    |
| 285.71           | -499.859598                  | 0.00                               |                  |                              |                                    |
| 300.71           | -499.859467                  | 0.08                               |                  |                              |                                    |

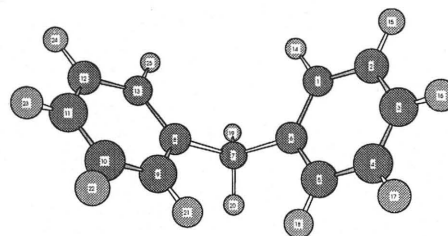
<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



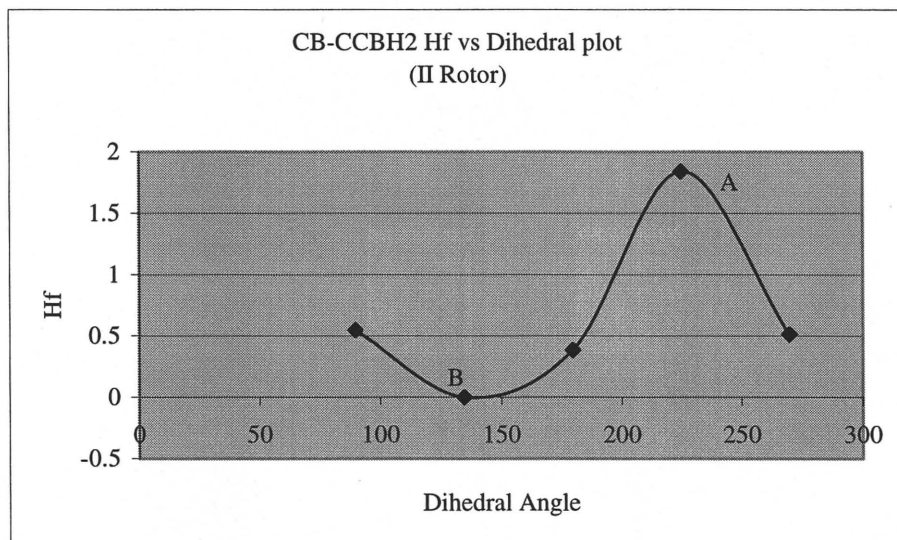


Structure at point A

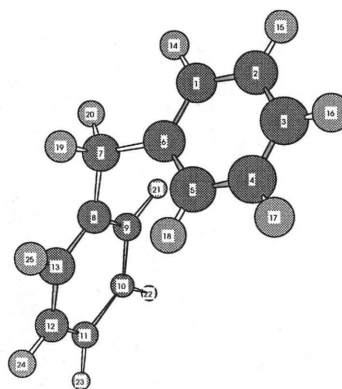


Structure at point B

**Figure 2.16** Potential Barriers for Internal Rotation about CB-CCBH2 bond (Dihedral 9-8-7-6) of CCB2H2. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.35 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*



Structure at point A



Structure at point B

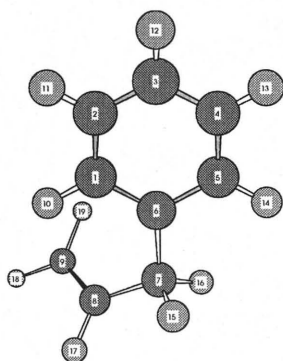
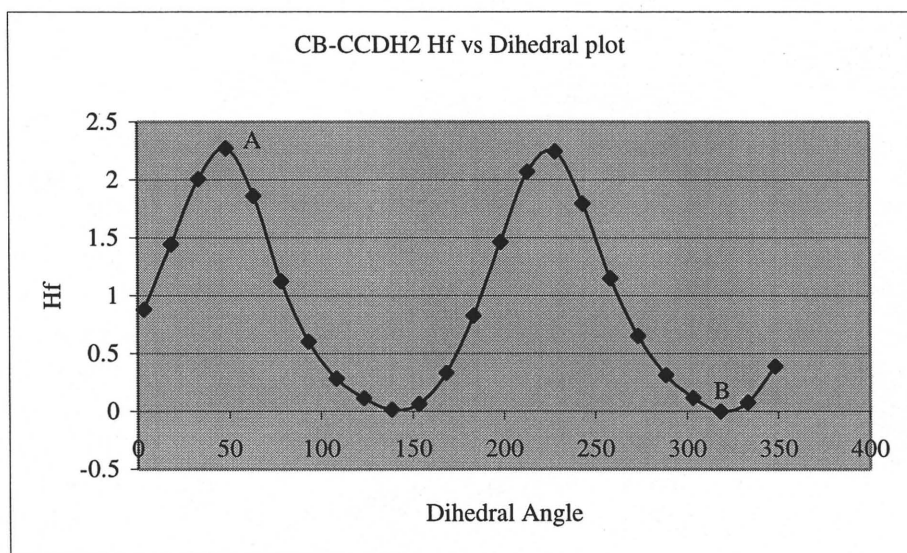
**Figure 2.17** Potential Barriers for Internal Rotation about CB-CCBH2 bond (Dihedral 8-7-6-1) of CCB2H2. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.35 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

**Table 2.36 Total Energy and Internal Rotation Barriers for CCBCDH2**

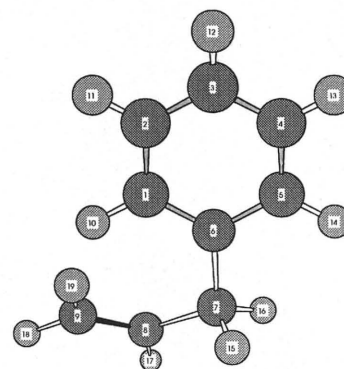
| CB-CCDH2         |                              |                                    | CD-CCBH2         |                              |                                    |
|------------------|------------------------------|------------------------------------|------------------|------------------------------|------------------------------------|
| Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> | Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> |
| 3.35             | -347.046208                  | 0.88                               | 7.67             | -347.045797                  | 1.05                               |
| 18.35            | -347.04531                   | 1.44                               | 22.67            | -347.044465                  | 1.88                               |
| 33.35            | -347.044415                  | 2.01                               | 37.67            | -347.043223                  | 2.66                               |
| 48.35            | -347.043992                  | 2.27                               | 52.67            | -347.04286                   | 2.89                               |
| 63.35            | -347.044647                  | 1.86                               | 67.67            | -347.043896                  | 2.24                               |
| 78.35            | -347.045817                  | 1.13                               | 82.67            | -347.045796                  | 1.05                               |
| 93.35            | -347.046651                  | 0.60                               | 97.67            | -347.047326                  | 0.09                               |
| 108.35           | -347.047157                  | 0.28                               | 112.67           | -347.047398                  | 0.04                               |
| 123.35           | -347.047431                  | 0.11                               | 127.67           | -347.046586                  | 0.55                               |
| 138.35           | -347.047587                  | 0.01                               | 142.67           | -347.045253                  | 1.39                               |
| 153.35           | -347.047507                  | 0.07                               | 157.67           | -347.044057                  | 2.14                               |
| 168.35           | -347.047081                  | 0.33                               | 172.67           | -347.043968                  | 2.19                               |
| 183.35           | -347.046292                  | 0.83                               | 187.67           | -347.045226                  | 1.40                               |
| 198.35           | -347.045278                  | 1.46                               | 202.67           | -347.046657                  | 0.51                               |
| 213.35           | -347.044315                  | 2.07                               | 217.67           | -347.047462                  | 0.00                               |
| 228.35           | -347.044034                  | 2.24                               | 232.67           | -347.04736                   | 0.06                               |
| 243.35           | -347.04475                   | 1.80                               | 247.67           | -347.046171                  | 0.81                               |
| 258.35           | -347.045779                  | 1.15                               | 262.67           | -347.043838                  | 2.27                               |
| 273.35           | -347.046572                  | 0.65                               | 277.67           | -347.041351                  | 3.83                               |
| 288.35           | -347.047109                  | 0.31                               | 292.67           | -347.042587                  | 3.06                               |
| 303.35           | -347.047426                  | 0.12                               | 307.67           | -347.044537                  | 1.84                               |
| 318.35           | -347.047611                  | 0.00                               | 322.67           | -347.045893                  | 0.98                               |
| 333.35           | -347.047485                  | 0.08                               | 337.67           | -347.046647                  | 0.51                               |
| 348.35           | -347.046992                  | 0.39                               | 352.67           | -347.046609                  | 0.54                               |

<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.

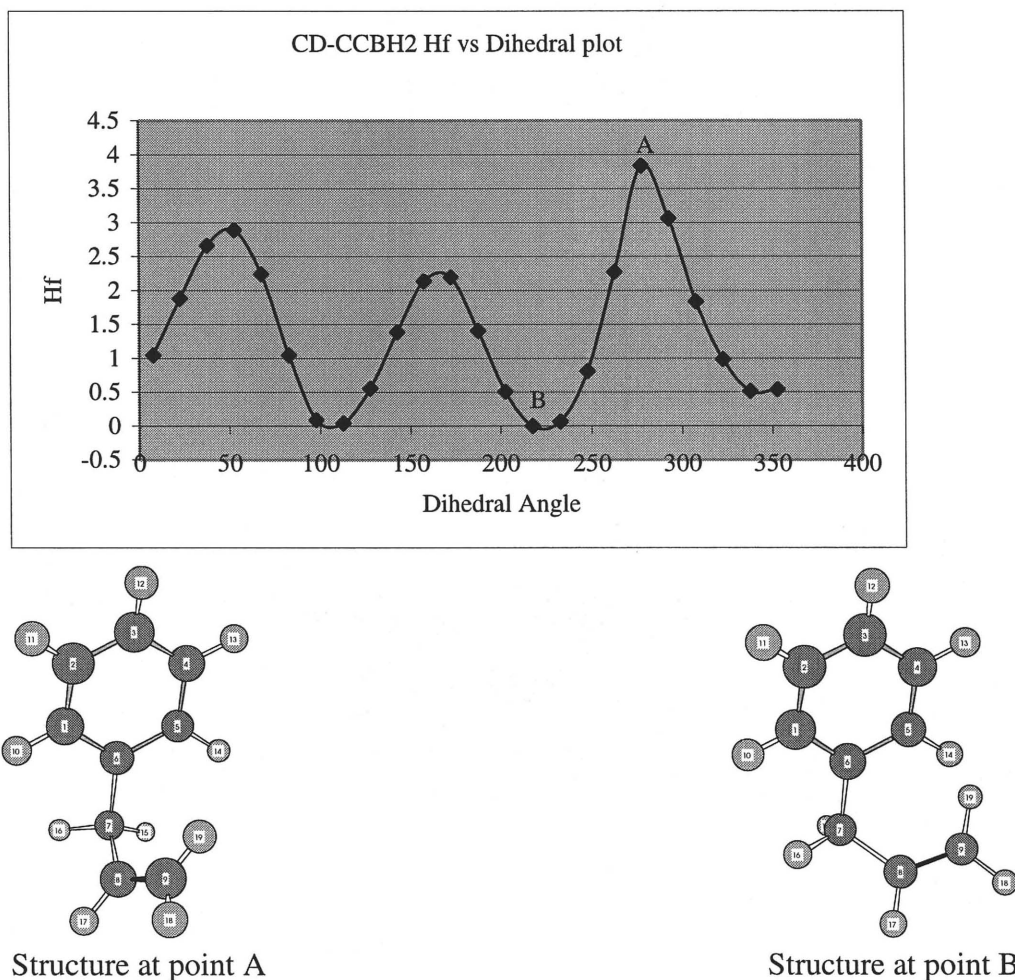


Structure at point A



Structure at point B

**Figure 2.19** Potential Barriers for Internal Rotation about CB-CCDH2 bond (Dihedral 9-8-7-6) of CCBCDH2. Points are Calculated Values at B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.36 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*



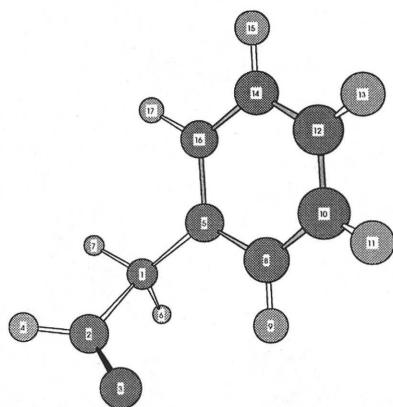
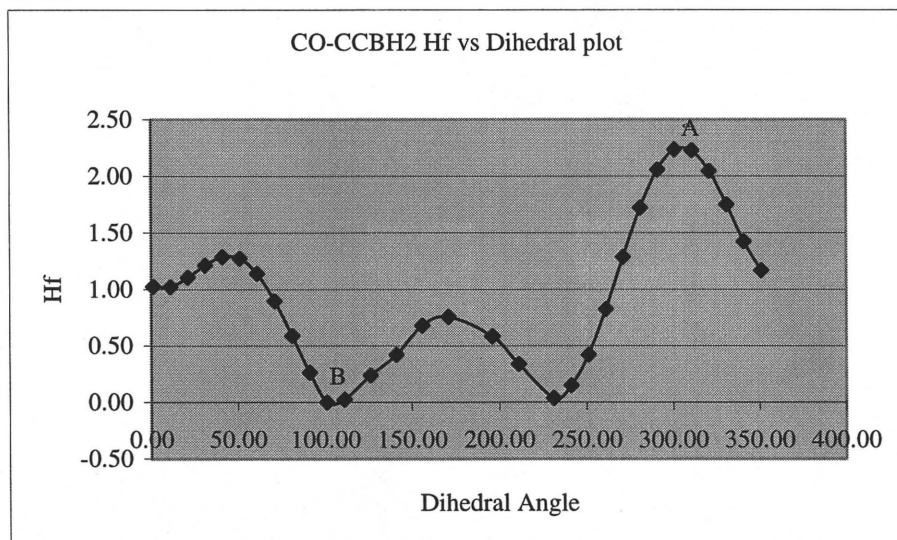
**Figure 2.18** Potential Barriers for Internal Rotation about CD-CCBH2 bond (Dihedral 8-7-6-1) of CCBCDH2. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.36 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral  $a-b-c-d$  infers rotation of angle of Atom  $a$  with respect to Atom  $d$  about Rotation Axis  $c-b$

**Table 2.37 Total Energy and Internal Rotation Barriers for CCBCOH2**

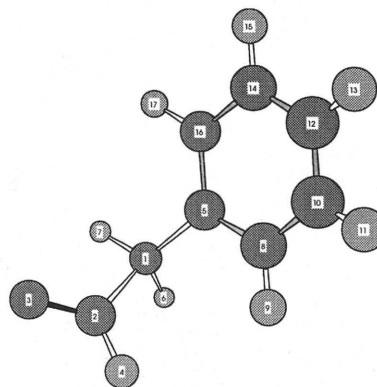
| CO-CCBH2         |                              |                                    | CB-CCOH2         |                              |                                    |
|------------------|------------------------------|------------------------------------|------------------|------------------------------|------------------------------------|
| Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> | Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> |
| 1.14             | -384.887657                  | 1.03                               | 101.58           | -384.889172                  | 0.10                               |
| 11.14            | -384.887665                  | 1.02                               | 111.58           | -384.888833                  | 0.31                               |
| 21.14            | -384.887534                  | 1.10                               | 121.58           | -384.887992                  | 0.84                               |
| 31.14            | -384.887361                  | 1.21                               | 131.58           | -384.886313                  | 1.89                               |
| 41.14            | -384.887241                  | 1.29                               | 141.58           | -384.883715                  | 3.52                               |
| 51.14            | -384.887265                  | 1.27                               | 151.58           | -384.880772                  | 5.37                               |
| 61.14            | -384.887476                  | 1.14                               | 161.58           | -384.87872                   | 6.66                               |
| 71.14            | -384.887862                  | 0.90                               | 171.58           | -384.878661                  | 6.70                               |
| 81.14            | -384.888353                  | 0.59                               | 181.58           | -384.880455                  | 5.57                               |
| 91.14            | -384.888868                  | 0.27                               | 191.58           | -384.883041                  | 3.95                               |
| 101.14           | -384.889291                  | 0.00                               | 201.58           | -384.885403                  | 2.46                               |
| 221.14           | -384.889172                  | 0.07                               | 211.58           | -384.887105                  | 1.40                               |
| 231.14           | -384.889233                  | 0.04                               | 221.58           | -384.88816                   | 0.73                               |
| 241.14           | -384.889051                  | 0.15                               | 231.58           | -384.88877                   | 0.35                               |
| 251.14           | -384.888619                  | 0.42                               | 241.58           | -384.889095                  | 0.15                               |
| 261.14           | -384.887977                  | 0.82                               | 251.58           | -384.889263                  | 0.04                               |
| 271.14           | -384.887244                  | 1.28                               | 261.58           | -384.889331                  | 0.00                               |
| 281.14           | -384.886551                  | 1.72                               | 271.58           | -384.889317                  | 0.01                               |
| 291.14           | -384.886014                  | 2.06                               | 281.58           | -384.88917                   | 0.10                               |
| 301.14           | -384.88573                   | 2.23                               | 291.58           | -384.888829                  | 0.31                               |
| 311.14           | -384.885744                  | 2.23                               | 301.58           | -384.887986                  | 0.84                               |
| 321.14           | -384.886031                  | 2.05                               | 311.58           | -384.886308                  | 1.90                               |
| 331.14           | -384.886502                  | 1.75                               | 321.58           | -384.883718                  | 3.52                               |
| 341.14           | -384.887023                  | 1.42                               | 331.58           | -384.880796                  | 5.36                               |
| 351.14           | -384.887433                  | 1.17                               | 341.58           | -384.878776                  | 6.62                               |

<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.

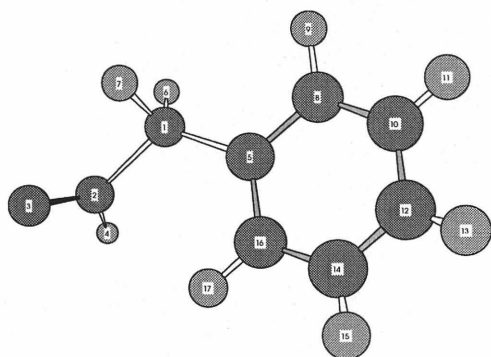
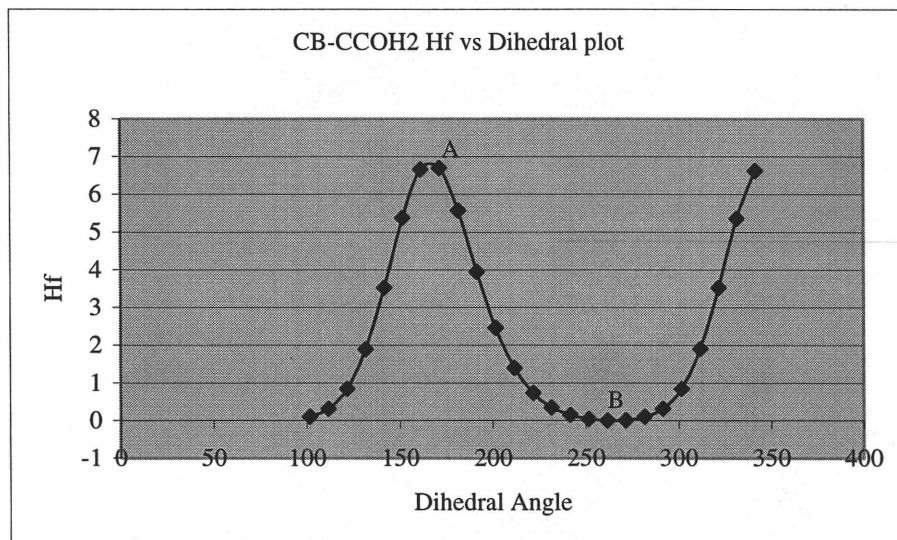


Structure at point A

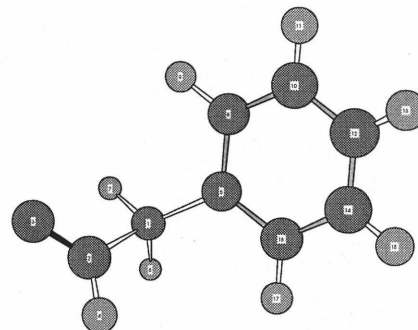


Structure at point B

**Figure 2.20** Potential Barriers for Internal Rotation about CO-CCBH2 bond (Dihedral 5-1-2-3) of CCBCOH2. Points are Calculated Values at relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.37 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*. Energy Values between 101 degrees and 231 degrees have been estimated from the energy values for CO-CCDH2 plot. (Figure 2.25)



Structure at point A



Structure at point B

**Figure 2.21** Potential Barriers for Internal Rotation about CB-CCOH<sub>2</sub> bond (Dihedral 8-5-1-2) of CCBCOH<sub>2</sub>. Points are Calculated Values at relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.37 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

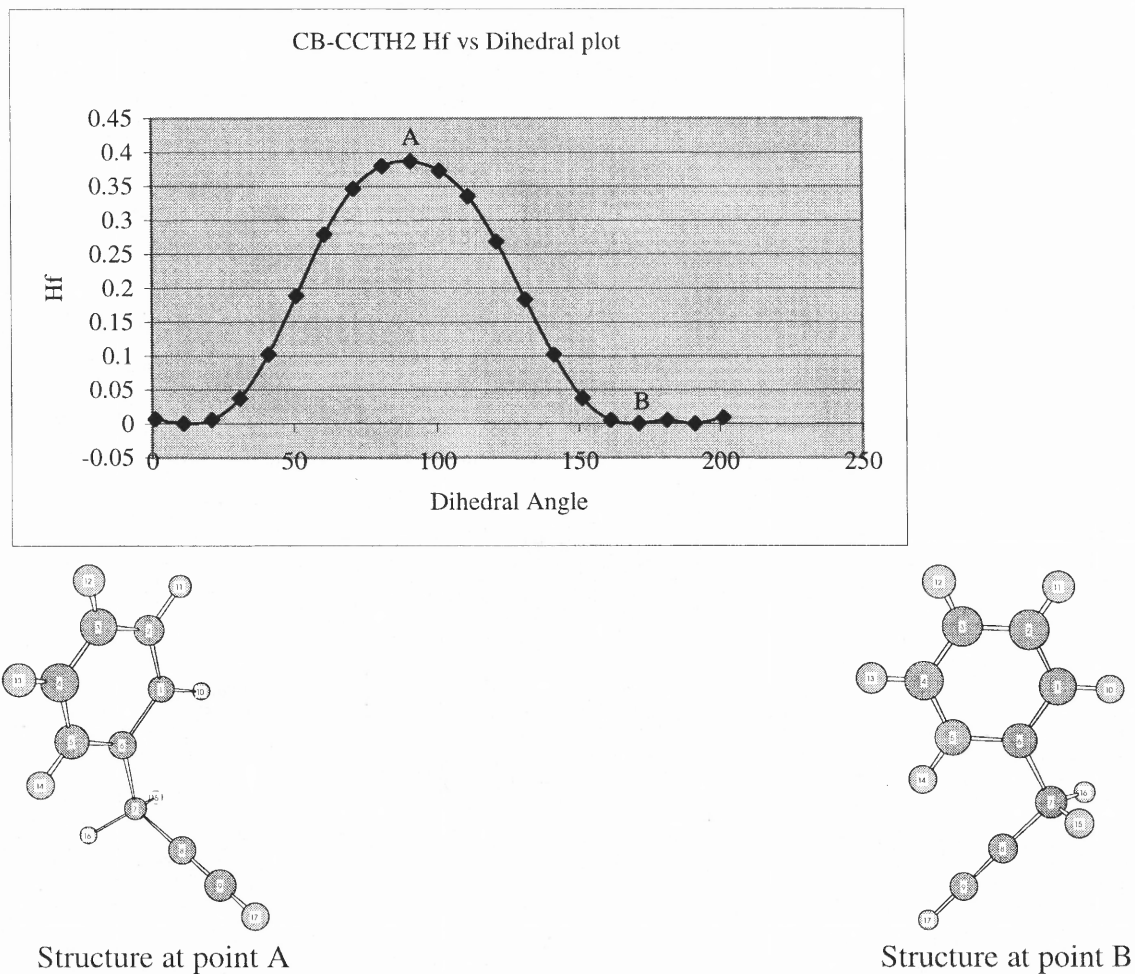


**Table 2.38 Total Energy and Internal Rotation Barriers for CCBCTH2**

| CB-CCTH2 |                     |                      |
|----------|---------------------|----------------------|
| Torsion  | Total               | Rotational           |
| Angle    | Energy <sup>a</sup> | barrier <sup>b</sup> |
| 1.06     | -347.700881         | 0.01                 |
| 11.06    | -347.700891         | 0.00                 |
| 21.06    | -347.700883         | 0.01                 |
| 31.06    | -347.700832         | 0.04                 |
| 41.06    | -347.700729         | 0.10                 |
| 51.06    | -347.700592         | 0.19                 |
| 61.06    | -347.700447         | 0.28                 |
| 71.06    | -347.70034          | 0.35                 |
| 81.06    | -347.700287         | 0.38                 |
| 91.06    | -347.700276         | 0.39                 |
| 101.06   | -347.700298         | 0.37                 |
| 111.06   | -347.700358         | 0.34                 |
| 121.06   | -347.700464         | 0.27                 |
| 131.06   | -347.7006           | 0.18                 |
| 141.06   | -347.70073          | 0.10                 |
| 151.06   | -347.700832         | 0.04                 |
| 161.06   | -347.700884         | 0.01                 |
| 171.06   | -347.700891         | 0.00                 |
| 181.06   | -347.700884         | 0.01                 |
| 191.06   | -347.700892         | 0.00                 |
| 201.06   | -347.700877         | 0.01                 |

<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



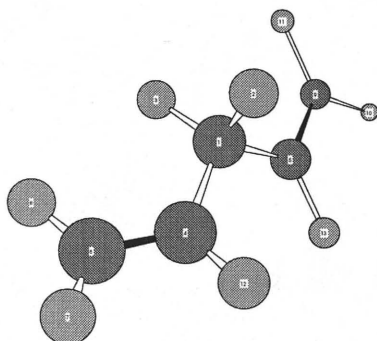
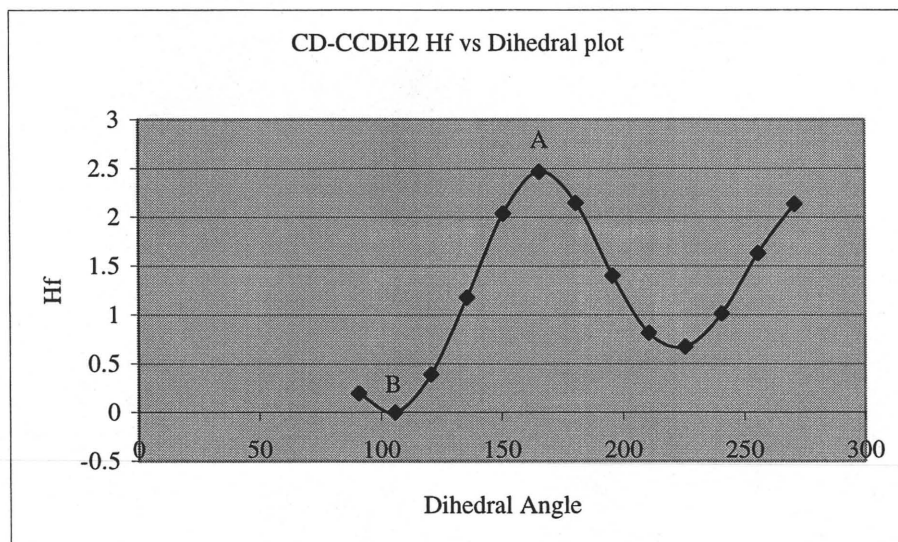
**Figure 2.22** Potential Barriers for Internal Rotation about CB-CCTH2 bond (Dihedral 8-7-6-1) of CCBCTH2. Points are Calculated Values at non-relaxed B3LYP/6-31G(d) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.38 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral  $a-b-c-d$  infers rotation of angle of Atom  $a$  with respect to Atom  $d$  about Rotation Axis  $c-b$

**Table 2.39 Total Energy and Internal Rotation Barriers for CCD2H2**

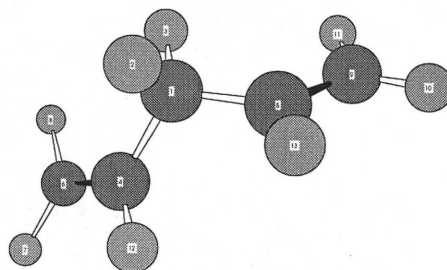
| CD-CCDH2      |                           |                                 | CD-CCDH2      |                           |                                 |
|---------------|---------------------------|---------------------------------|---------------|---------------------------|---------------------------------|
| Torsion Angle | Total Energy <sup>a</sup> | Rotational barrier <sup>b</sup> | Torsion Angle | Total Energy <sup>a</sup> | Rotational barrier <sup>b</sup> |
| 90.74         | -195.297358               | 0.20                            | 60.74         | -195.294227               | 1.49                            |
| 105.74        | -195.29767                | 0.00                            | 75.74         | -195.294277               | 1.46                            |
| 120.74        | -195.297048               | 0.39                            | 90.74         | -195.296141               | 0.29                            |
| 135.74        | -195.295794               | 1.18                            | 105.74        | -195.296602               | 0.00                            |
| 150.74        | -195.294425               | 2.04                            | 120.74        | -195.295313               | 0.81                            |
| 165.74        | -195.29374                | 2.47                            | 135.74        | -195.295313               | 0.81                            |
| 180.74        | -195.294248               | 2.15                            | 150.74        | -195.294205               | 1.50                            |
| 195.74        | -195.295439               | 1.40                            | 165.74        | -195.293749               | 1.79                            |
| 210.74        | -195.296373               | 0.81                            | 180.74        | -195.294483               | 1.33                            |
| 225.74        | -195.2966                 | 0.67                            | 195.74        | -195.294557               | 1.28                            |
| 240.74        | -195.296056               | 1.01                            |               |                           |                                 |
| 255.74        | -195.295067               | 1.63                            |               |                           |                                 |
| 270.74        | -195.294267               | 2.14                            |               |                           |                                 |
| 285.74        | -195.294233               | 2.16                            |               |                           |                                 |
| 300.74        | -195.295118               | 1.60                            |               |                           |                                 |
| 315.74        | -195.296241               | 0.90                            |               |                           |                                 |
| 330.74        | -195.296764               | 0.57                            |               |                           |                                 |
| 345.74        | -195.296354               | 0.83                            |               |                           |                                 |
| 360.74        | -195.295234               | 1.53                            |               |                           |                                 |

<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.

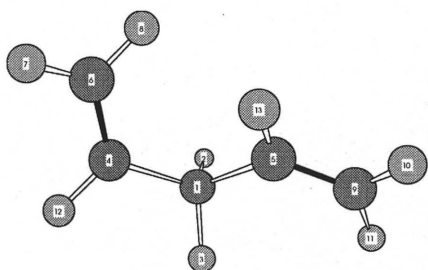
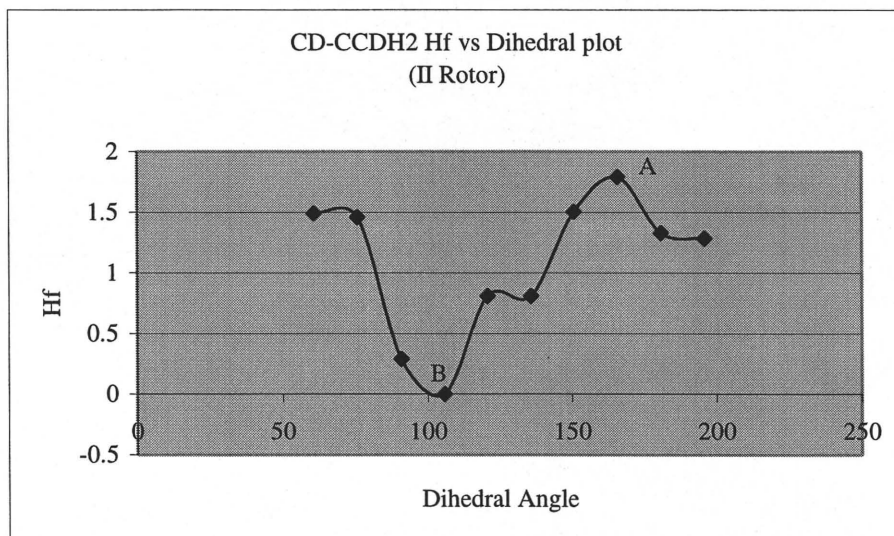


Structure at point A

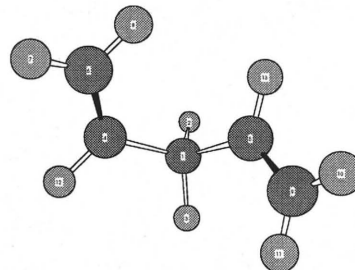


Structure at point B

**Figure 2.23** Potential Barriers for Internal Rotation about CD-CCDH2 bond (Dihedral 9-5-1-4) of CCD2H2. Points are Calculated Values at non-relaxed B3LYP/6-31G(d) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.39 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*



Structure at point A



Structure at point B

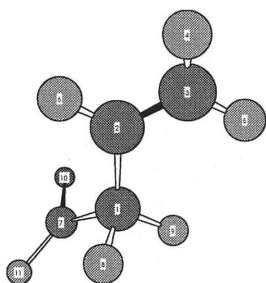
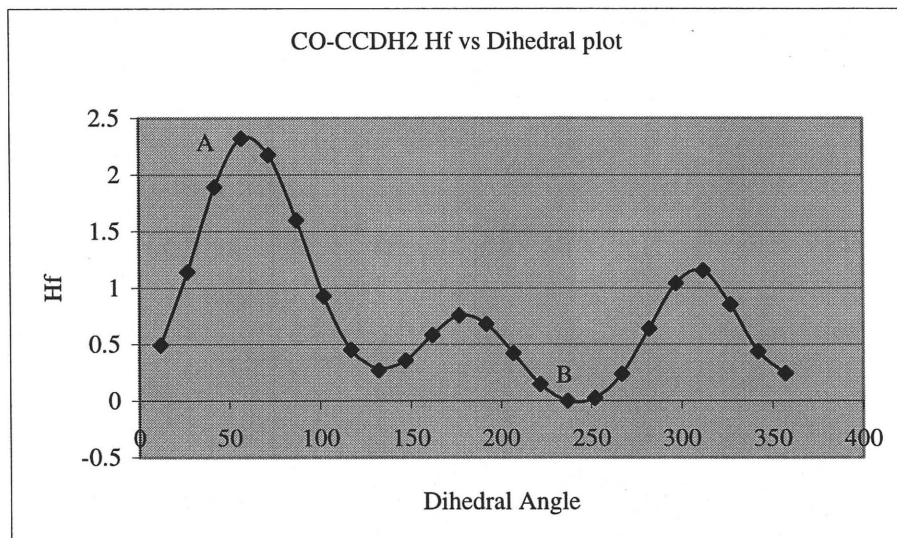
**Figure 2.24** Potential Barriers for Internal Rotation about CD-CCDH2 bond (Dihedral 9-5-1-4) of CCD2H2. Points are Calculated Values at non-relaxed B3LYP/6-31G(d) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.39 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

**Table 2.40 Total Energy and Internal Rotation Barriers for CCDCOH2**

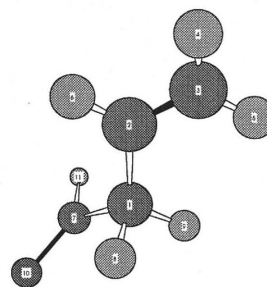
| CO-CCDH2         |                              |                                    | CD-CCOH2         |                              |                                    |
|------------------|------------------------------|------------------------------------|------------------|------------------------------|------------------------------------|
| Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> | Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> |
| 11.95            | -231.241165                  | 0.50                               | 0.90             | -231.238214                  | 2.35                               |
| 26.95            | -231.240139                  | 1.14                               | 15.90            | -231.238936                  | 1.89                               |
| 41.95            | -231.23894                   | 1.89                               | 30.90            | -231.240122                  | 1.15                               |
| 56.95            | -231.238255                  | 2.32                               | 45.90            | -231.241136                  | 0.51                               |
| 71.95            | -231.23849                   | 2.18                               | 60.90            | -231.241524                  | 0.27                               |
| 86.95            | -231.23941                   | 1.60                               | 60.90            | -231.241524                  | 0.27                               |
| 101.95           | -231.240479                  | 0.93                               | 75.90            | -231.241235                  | 0.45                               |
| 116.95           | -231.241236                  | 0.45                               | 90.90            | -231.240494                  | 0.92                               |
| 131.95           | -231.241524                  | 0.27                               | 105.90           | -231.239775                  | 1.37                               |
| 131.95           | -231.241525                  | 0.27                               | 120.90           | -231.23951                   | 1.53                               |
| 146.95           | -231.241388                  | 0.36                               | 135.90           | -231.239735                  | 1.39                               |
| 161.95           | -231.241026                  | 0.58                               | 150.90           | -231.240028                  | 1.21                               |
| 176.95           | -231.240749                  | 0.76                               | 165.90           | -231.239868                  | 1.31                               |
| 191.95           | -231.240872                  | 0.68                               | 180.90           | -231.23913                   | 1.77                               |
| 206.95           | -231.241287                  | 0.42                               | 195.90           | -231.238192                  | 2.36                               |
| 221.95           | -231.241719                  | 0.15                               | 210.90           | -231.237769                  | 2.63                               |
| 236.95           | -231.241956                  | 0.00                               | 225.90           | -231.238258                  | 2.32                               |
| 251.95           | -231.241916                  | 0.02                               | 240.90           | -231.239315                  | 1.66                               |
| 266.95           | -231.241573                  | 0.24                               | 255.90           | -231.24046                   | 0.94                               |
| 281.95           | -231.240936                  | 0.64                               | 270.90           | -231.24143                   | 0.33                               |
| 296.95           | -231.240297                  | 1.04                               | 285.90           | -231.241955                  | 0.00                               |
| 311.95           | -231.240122                  | 1.15                               | 300.90           | -231.24178                   | 0.11                               |
| 326.95           | -231.240594                  | 0.85                               | 315.90           | -231.240882                  | 0.67                               |
| 341.95           | -231.241257                  | 0.44                               | 330.90           | -231.239585                  | 1.49                               |
| 356.95           | -231.241568                  | 0.24                               | 345.90           | -231.238483                  | 2.18                               |

<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.

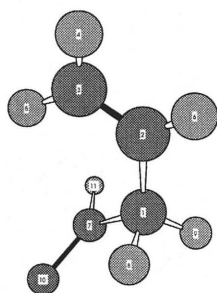
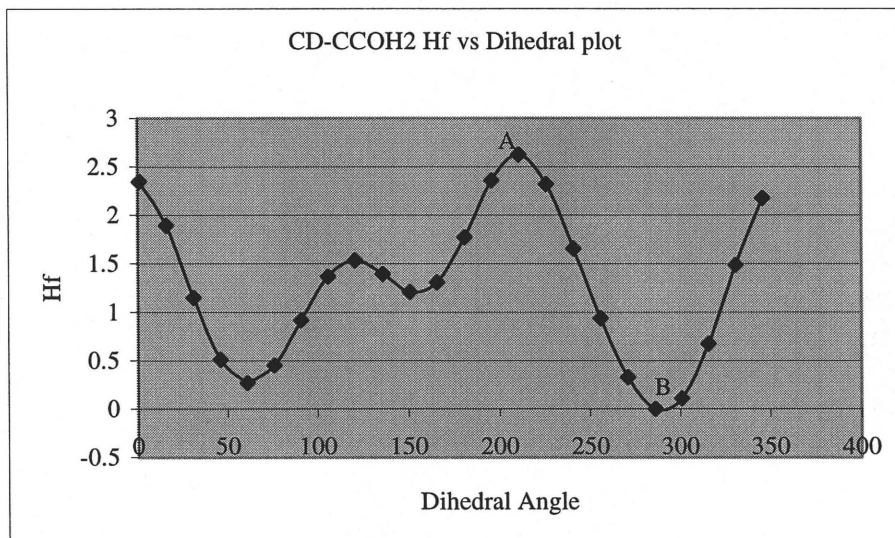


Structure at point A

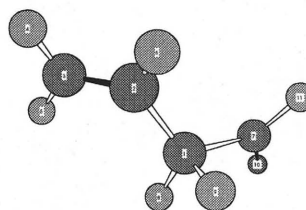


Structure at point B

**Figure 2.25** Potential Barriers for Internal Rotation about CO-CCDH2 bond (Dihedral 10-7-1-2) of CCDCOH2. Points are Calculated Values at non-relaxed B3LYP/6-31+G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.40 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*



Structure at point A



Structure at point B

**Figure 2.26** Potential Barriers for Internal Rotation about CD-CCOH<sub>2</sub> bond (Dihedral 7-1-2-6) of CCDCOH<sub>2</sub>. Points are Calculated Values at non-relaxed B3LYP/6-31+G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.40 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*



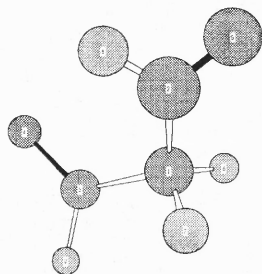
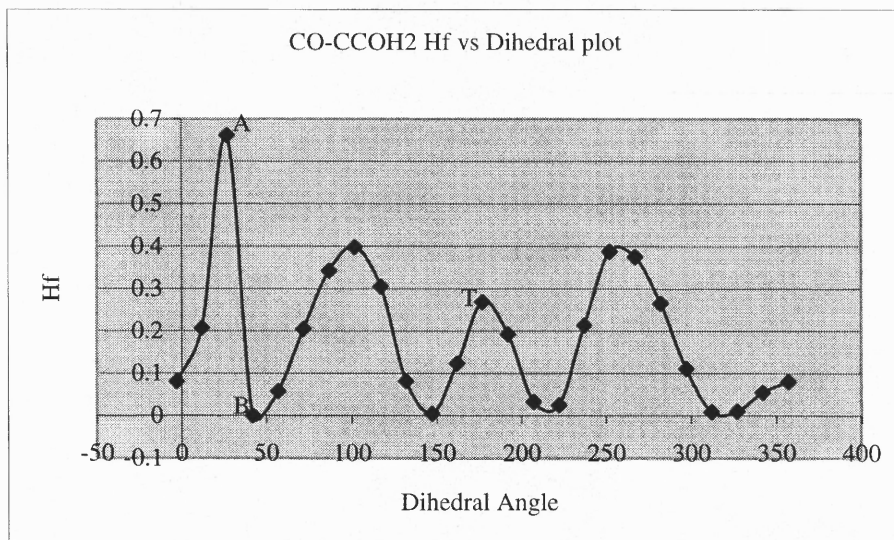
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**Table 2.41 Total Energy and Internal Rotation Barriers for CCO2H2**

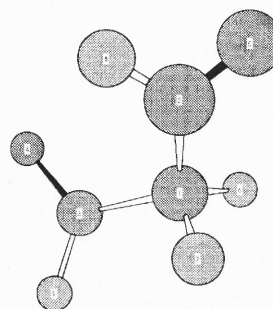
| CO-CCOH2         |                              |                                    | CO-CCOH2         |                              |                                    |
|------------------|------------------------------|------------------------------------|------------------|------------------------------|------------------------------------|
| Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> | Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> |
| 12.02            | -267.145021                  | 0.21                               | 9.05             | -267.1451                    | 0.16                               |
| 27.02            | -267.144297                  | 0.66                               | 24.05            | -267.144489                  | 0.54                               |
| 42.02            | -267.145351                  | 0.00                               | 39.05            | -267.145349                  | 0.00                               |
| 57.02            | -267.145259                  | 0.06                               | 54.05            | -267.145285                  | 0.04                               |
| 72.02            | -267.145024                  | 0.21                               | 69.05            | -267.145075                  | 0.17                               |
| 87.02            | -267.144805                  | 0.34                               | 84.05            | -267.144847                  | 0.31                               |
| 102.02           | -267.144717                  | 0.40                               | 99.05            | -267.144724                  | 0.39                               |
| 117.02           | -267.144865                  | 0.31                               | 114.05           | -267.14481                   | 0.34                               |
| 132.02           | -267.145221                  | 0.08                               | 129.05           | -267.14516                   | 0.12                               |
| 147.02           | -267.145344                  | 0.00                               | 144.05           | -267.145347                  | 0.00                               |
| 162.02           | -267.145155                  | 0.12                               | 144.05           | -267.145348                  | 0.00                               |
| 177.02           | -267.144923                  | 0.27                               | 159.05           | -267.145215                  | 0.08                               |
| 192.02           | -267.145044                  | 0.19                               | 174.05           | -267.144953                  | 0.25                               |
| 207.02           | -267.145299                  | 0.03                               | 189.05           | -267.144995                  | 0.22                               |
| 222.02           | -267.145311                  | 0.02                               | 204.05           | -267.145266                  | 0.05                               |
| 237.02           | -267.14501                   | 0.21                               | 219.05           | -267.145335                  | 0.01                               |
| 252.02           | -267.144734                  | 0.39                               | 234.05           | -267.145088                  | 0.16                               |
| 267.02           | -267.144754                  | 0.37                               | 249.05           | -267.144762                  | 0.37                               |
| 282.02           | -267.144927                  | 0.27                               | 264.05           | -267.144733                  | 0.39                               |
| 297.02           | -267.145175                  | 0.11                               | 279.05           | -267.144889                  | 0.29                               |
| 312.02           | -267.145337                  | 0.01                               | 294.05           | -267.145126                  | 0.14                               |
| 327.02           | -267.145334                  | 0.01                               | 309.05           | -267.145312                  | 0.02                               |
| 342.02           | -267.145263                  | 0.06                               | 324.05           | -267.145344                  | 0.00                               |
| 357.02           | -267.145222                  | 0.08                               | 339.05           | -267.145279                  | 0.04                               |
| 357.02           | -267.145222                  | 0.08                               | 354.05           | -267.145236                  | 0.07                               |

<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.

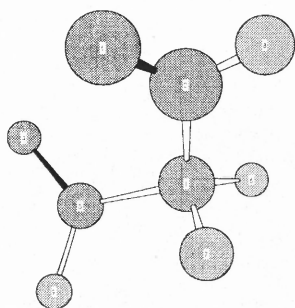
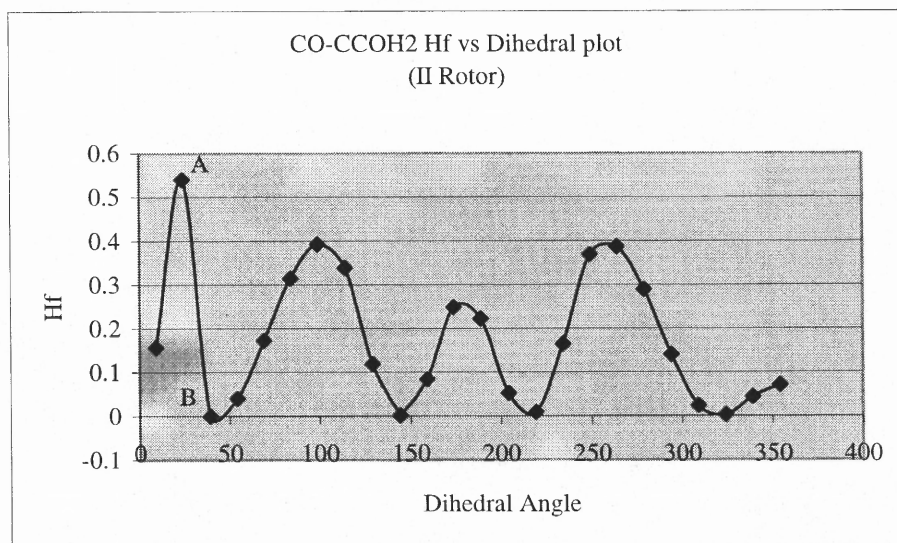


Structure at point A

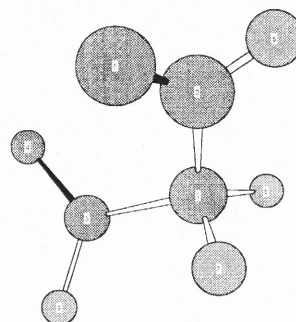


Structure at point B

**Figure 2.27** Potential Barriers for Internal Rotation about CO-CCOH<sub>2</sub> bond (Dihedral 4-3-1-2) of CCO<sub>2</sub>H<sub>2</sub>. Points are Calculated Values at non-relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.41 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*



Structure at point A



Structure at point B

**Figure 2.28** Potential Barriers for Internal Rotation about CO-CCOH<sub>2</sub> bond (Dihedral 5-2-1-3) of CCO<sub>2</sub>H<sub>2</sub>. Points are Calculated Values at non-relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.41 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

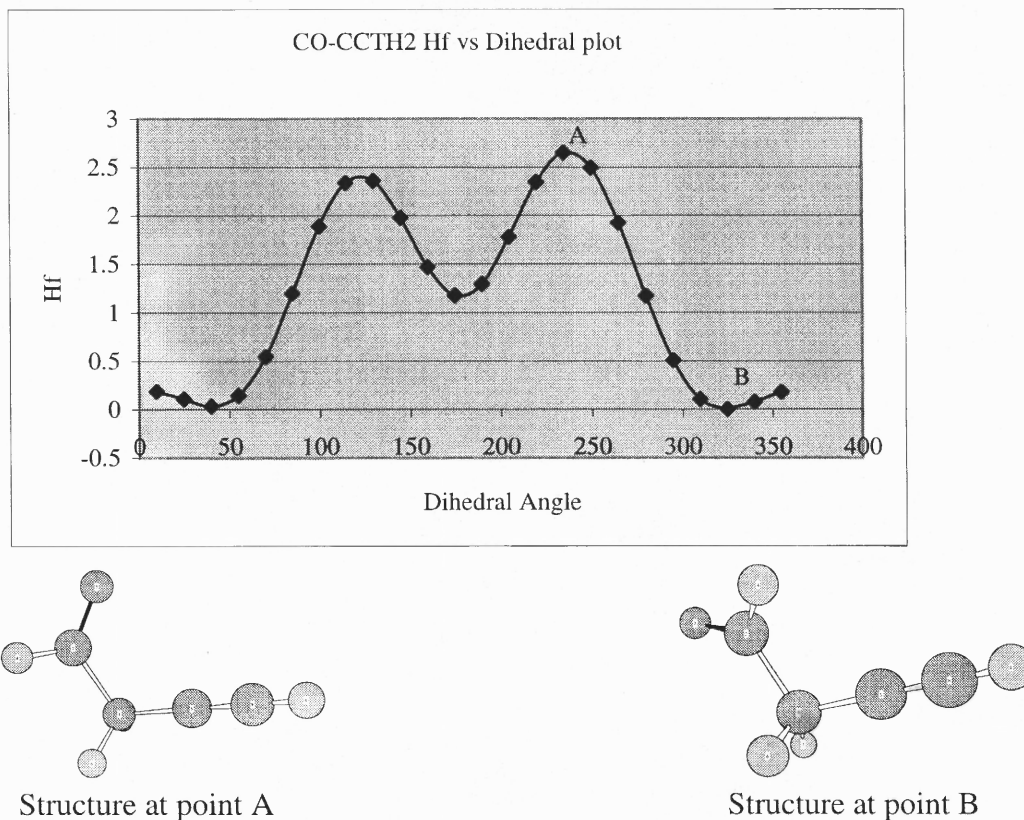
**Table 2.42 Total Energy and Internal Rotation Barriers for CCOCTH2**

CO-CCTH2

| Torsion | Total               | Rotational           |
|---------|---------------------|----------------------|
| Angle   | Energy <sup>a</sup> | barrier <sup>b</sup> |
| 9.68    | -229.967124         | 0.19                 |
| 24.68   | -229.967255         | 0.11                 |
| 39.68   | -229.96737          | 0.03                 |
| 54.68   | -229.967196         | 0.14                 |
| 69.68   | -229.966555         | 0.54                 |
| 84.68   | -229.965515         | 1.20                 |
| 99.68   | -229.964414         | 1.89                 |
| 114.68  | -229.963702         | 2.34                 |
| 129.68  | -229.963667         | 2.36                 |
| 144.68  | -229.96427          | 1.98                 |
| 159.68  | -229.965078         | 1.47                 |
| 174.68  | -229.965552         | 1.17                 |
| 189.68  | -229.965362         | 1.29                 |
| 204.68  | -229.964589         | 1.78                 |
| 219.68  | -229.96369          | 2.34                 |
| 234.68  | -229.963206         | 2.65                 |
| 249.68  | -229.963453         | 2.49                 |
| 264.68  | -229.964355         | 1.93                 |
| 279.68  | -229.965556         | 1.17                 |
| 294.68  | -229.96662          | 0.50                 |
| 309.68  | -229.967256         | 0.10                 |
| 324.68  | -229.967424         | 0.00                 |
| 324.68  | -229.967424         | 0.00                 |
| 339.68  | -229.967302         | 0.08                 |
| 354.68  | -229.967144         | 0.18                 |

<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



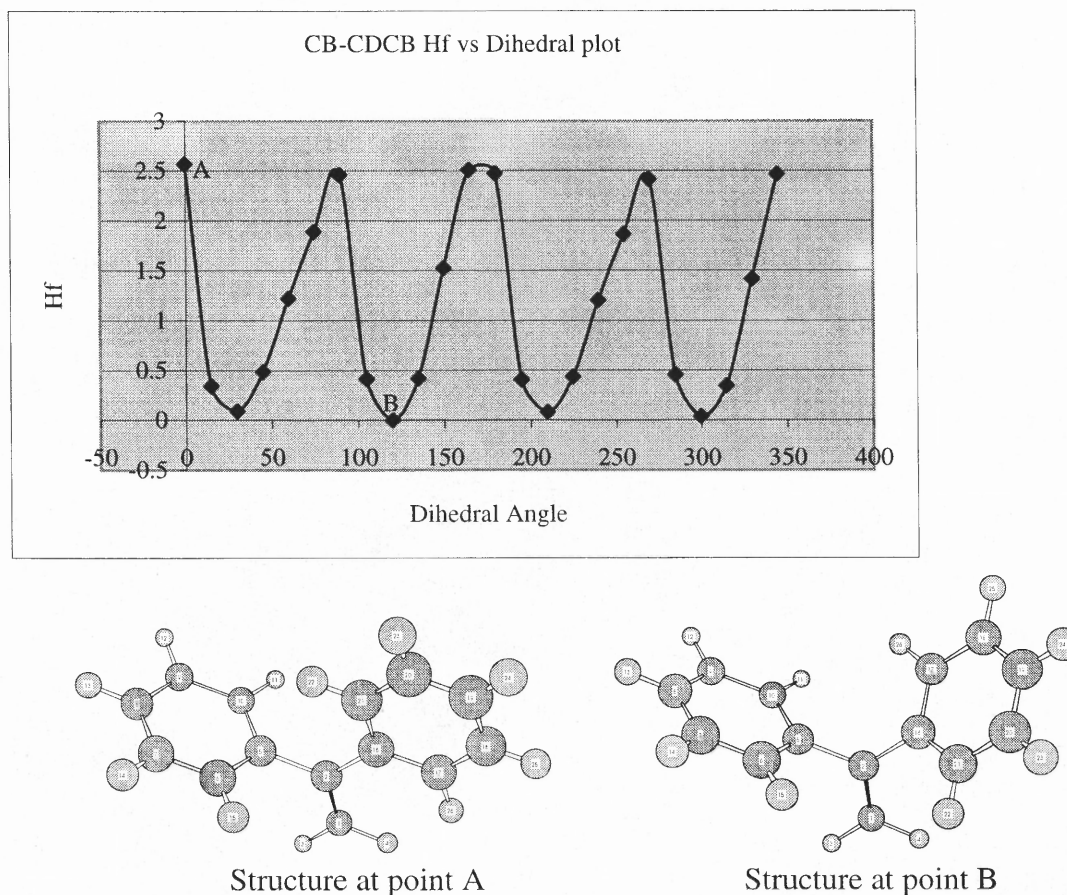
**Figure 2.29** Potential Barriers for Internal Rotation about CO-CCTH2 bond (Dihedral 5-1-2-4) of CCOCTH2. Points are Calculated Values at relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.42 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral  $a-b-c-d$  infers rotation of angle of Atom  $a$  with respect to Atom  $d$  about Rotation Axis  $c-b$

**Table 2.43 Total Energy and Internal Rotation Barriers for CDCB2**

| CB-CDCB       |                           |                                 | CB-CDCB       |                           |                                 |
|---------------|---------------------------|---------------------------------|---------------|---------------------------|---------------------------------|
| Torsion Angle | Total Energy <sup>a</sup> | Rotational barrier <sup>b</sup> | Torsion Angle | Total Energy <sup>a</sup> | Rotational barrier <sup>b</sup> |
| -0.41         | -537.730048               | 2.57                            | 0.00          | -540.824434               | 3.79                            |
| 14.59         | -537.733599               | 0.34                            | 10.00         | -540.822213               | 5.23                            |
| 29.59         | -537.733997               | 0.09                            | 20.00         | -540.819631               | 6.80                            |
| 44.59         | -537.733365               | 0.49                            | 30.00         | -540.817139               | 8.36                            |
| 59.59         | -537.732203               | 1.22                            | 40.00         | -540.815826               | 9.19                            |
| 74.59         | -537.73113                | 1.89                            | 50.00         | -540.816989               | 8.46                            |
| 89.59         | -537.730226               | 2.46                            | 60.00         | -540.819896               | 6.63                            |
| 104.59        | -537.733485               | 0.41                            | 70.00         | -540.822671               | 4.89                            |
| 119.59        | -537.734141               | 0.00                            | 80.00         | -540.824422               | 3.79                            |
| 134.59        | -537.733481               | 0.41                            | 90.00         | -540.825511               | 3.11                            |
| 149.59        | -537.731711               | 1.52                            | 100.00        | -540.826539               | 2.47                            |
| 164.59        | -537.730148               | 2.51                            | 110.00        | -540.827691               | 1.74                            |
| 179.59        | -537.730197               | 2.47                            | 120.00        | -540.828931               | 0.96                            |
| 194.59        | -537.733492               | 0.41                            | 130.00        | -540.829974               | 0.31                            |
| 209.59        | -537.734015               | 0.08                            | 140.00        | -540.830467               | 0.00                            |
| 224.59        | -537.733448               | 0.43                            | 150.00        | -540.830145               | 0.20                            |
| 239.59        | -537.732228               | 1.20                            | 160.00        | -540.828818               | 1.03                            |
| 254.59        | -537.731169               | 1.86                            | 170.00        | -540.826734               | 2.34                            |
| 269.59        | -537.730296               | 2.41                            | 180.00        | -540.82441                | 3.80                            |
| 284.59        | -537.733417               | 0.45                            | 190.00        | -540.822012               | 5.31                            |
| 299.59        | -537.734078               | 0.04                            | 200.00        | -540.819412               | 6.94                            |
| 314.59        | -537.73359                | 0.35                            | 210.00        | -540.816849               | 8.55                            |
| 329.59        | -537.73188                | 1.42                            | 220.00        | -540.815541               | 9.37                            |
| 344.59        | -537.730213               | 2.46                            | 230.00        | -540.816787               | 8.58                            |

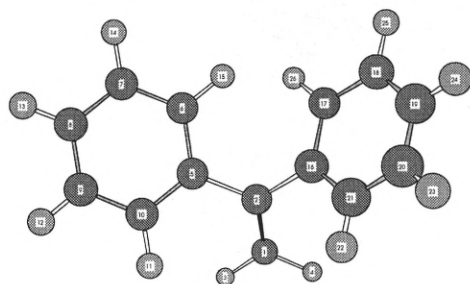
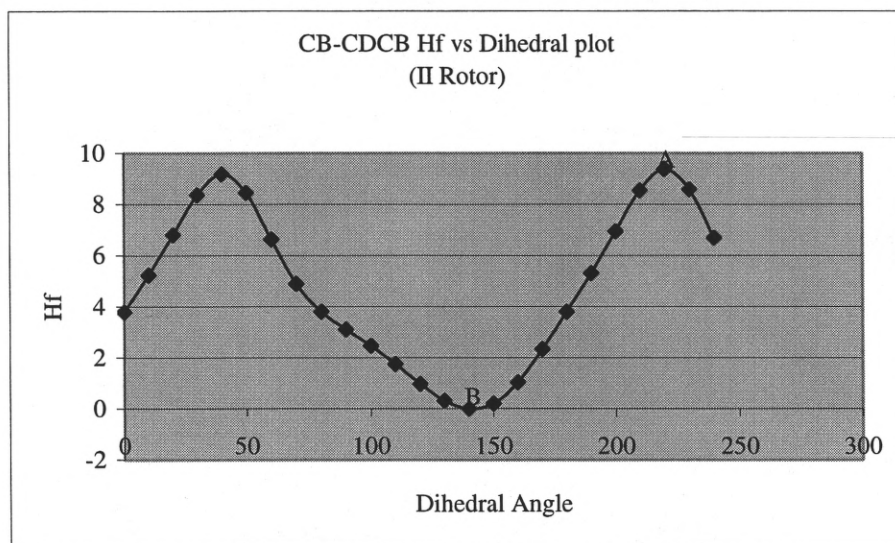
<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.

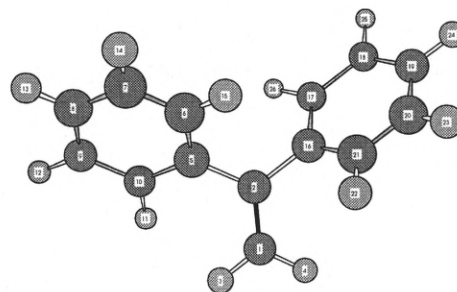


**Figure 2.30** Potential Barriers for Internal Rotation about CB-CDCB bond (Dihedral 17-16-1-2) of CDCB2. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.43 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral  $a-b-c-d$  infers rotation of angle of Atom  $a$  with respect to Atom  $d$  about Rotation Axis  $c-b$





Structure at point A



Structure at point B

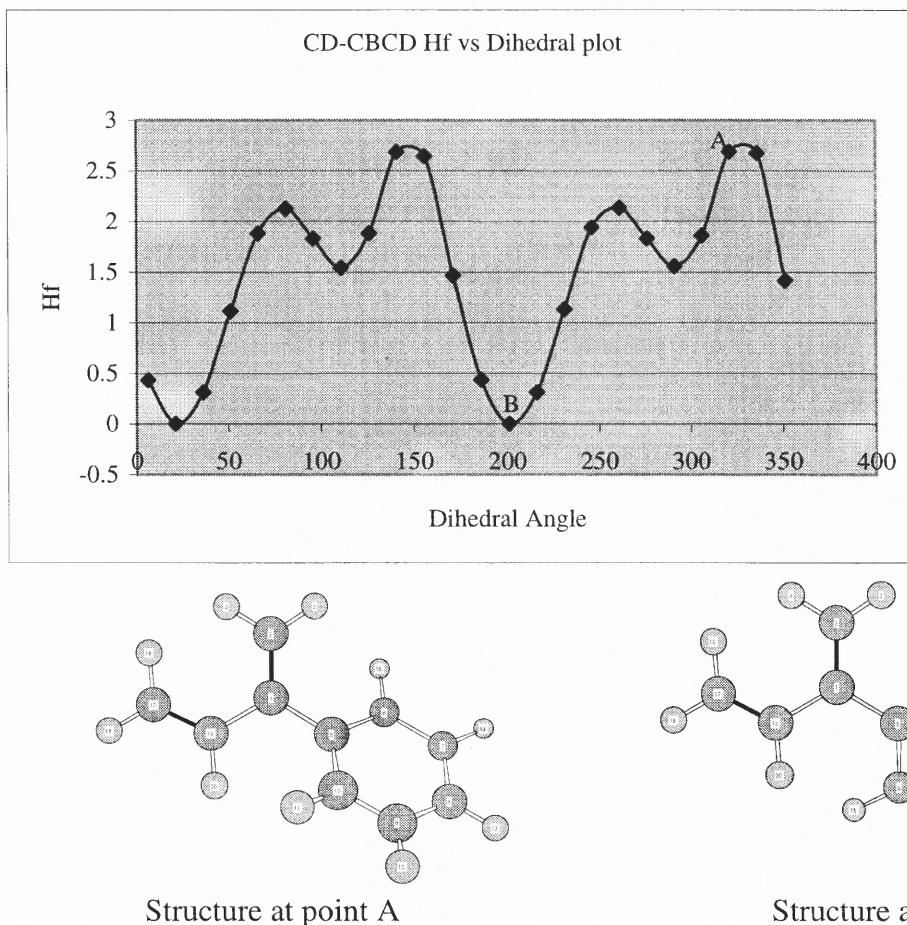
**Figure 2.31** Potential Barriers for Internal Rotation about CB-CDCB bond (Dihedral 6-5-2-1) of CDCB2. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.43 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

**Table 2.44 Total Energy and Internal Rotation Barriers for CDCBCD**

| CB-CDCD |                     |                      |
|---------|---------------------|----------------------|
| Torsion | Total               | Rotational           |
| Angle   | Energy <sup>a</sup> | barrier <sup>b</sup> |
| 6.03    | -384.920858         | 0.43                 |
| 21.03   | -384.921547         | 0.00                 |
| 36.03   | -384.921051         | 0.31                 |
| 51.03   | -384.919771         | 1.11                 |
| 66.03   | -384.918551         | 1.88                 |
| 81.03   | -384.918163         | 2.12                 |
| 96.03   | -384.918634         | 1.83                 |
| 111.03  | -384.919094         | 1.54                 |
| 126.03  | -384.918548         | 1.88                 |
| 141.03  | -384.917269         | 2.68                 |
| 156.03  | -384.917339         | 2.64                 |
| 171.03  | -384.919211         | 1.47                 |
| 186.03  | -384.920854         | 0.44                 |
| 201.03  | -384.921548         | 0.00                 |
| 216.03  | -384.921051         | 0.31                 |
| 231.03  | -384.919739         | 1.14                 |
| 246.03  | -384.918456         | 1.94                 |
| 261.03  | -384.918146         | 2.13                 |
| 276.03  | -384.918634         | 1.83                 |
| 291.03  | -384.919066         | 1.56                 |
| 306.03  | -384.918582         | 1.86                 |
| 321.03  | -384.917266         | 2.69                 |
| 336.03  | -384.91729          | 2.67                 |
| 351.03  | -384.919288         | 1.42                 |

<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



**Figure 2.32** Potential Barriers for Internal Rotation about CD-CBCD bond (Dihedral 6-5-1-2) of CDCBCD. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.44 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral  $a-b-c-d$  infers rotation of angle of Atom  $a$  with respect to Atom  $d$  about Rotation Axis  $c-b$

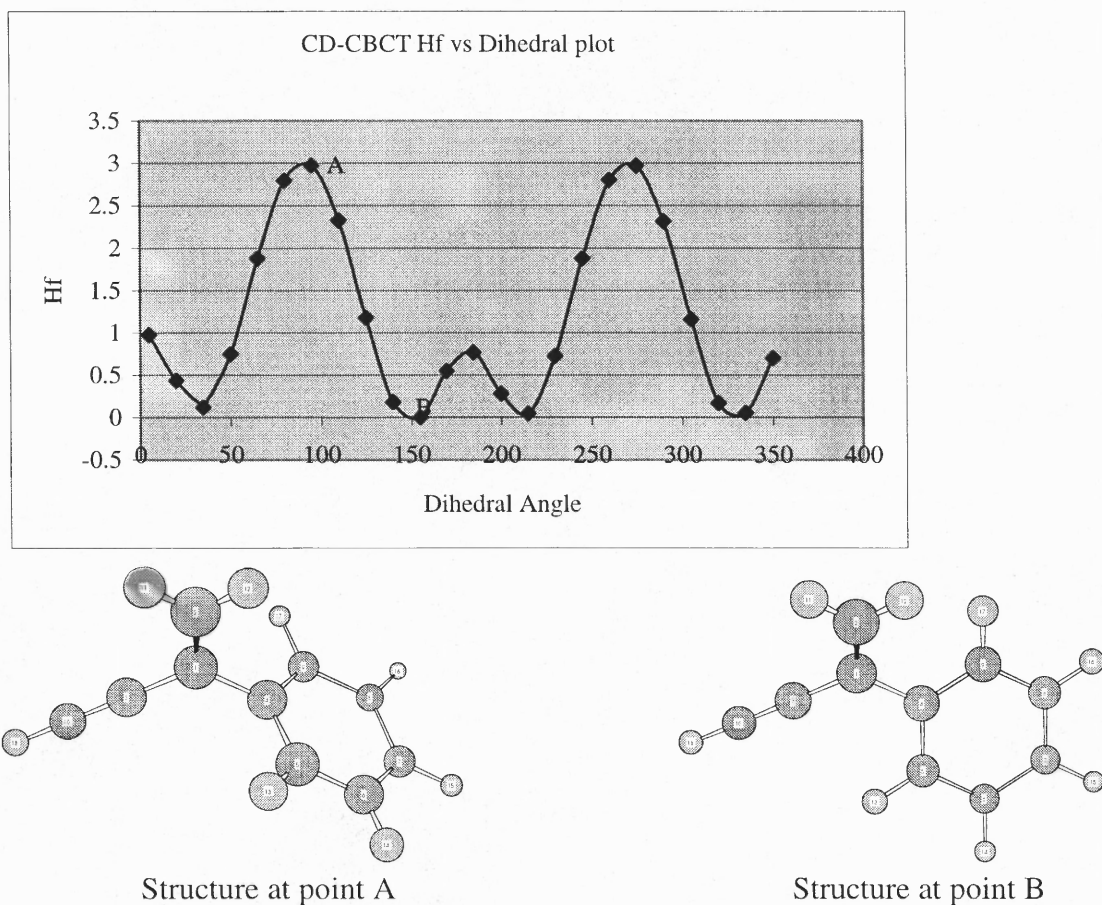
**Table 2.45 Total Energy and Internal  
Rotation Barriers for CDCBCT**

CB-CDCT

| Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> |
|------------------|------------------------------|------------------------------------|
| 4.76             | -385.786472                  | 0.98                               |
| 19.76            | -385.787327                  | 0.44                               |
| 34.76            | -385.787835                  | 0.12                               |
| 34.76            | -385.787835                  | 0.12                               |
| 49.76            | -385.786835                  | 0.75                               |
| 64.76            | -385.785034                  | 1.88                               |
| 79.76            | -385.783574                  | 2.79                               |
| 94.76            | -385.783291                  | 2.97                               |
| 109.76           | -385.784318                  | 2.33                               |
| 124.76           | -385.786149                  | 1.18                               |
| 139.76           | -385.787737                  | 0.18                               |
| 154.76           | -385.788026                  | 0.00                               |
| 169.76           | -385.787157                  | 0.55                               |
| 184.76           | -385.786805                  | 0.77                               |
| 199.76           | -385.787579                  | 0.28                               |
| 214.76           | -385.787954                  | 0.04                               |
| 229.76           | -385.786873                  | 0.72                               |
| 244.76           | -385.785036                  | 1.88                               |
| 259.76           | -385.783566                  | 2.80                               |
| 274.76           | -385.783292                  | 2.97                               |
| 289.76           | -385.784337                  | 2.31                               |
| 304.76           | -385.786185                  | 1.16                               |
| 319.76           | -385.787752                  | 0.17                               |
| 334.76           | -385.787942                  | 0.05                               |
| 349.76           | -385.786912                  | 0.70                               |

<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



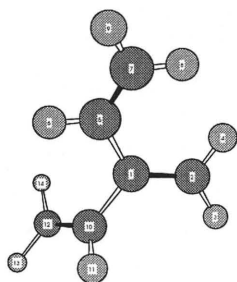
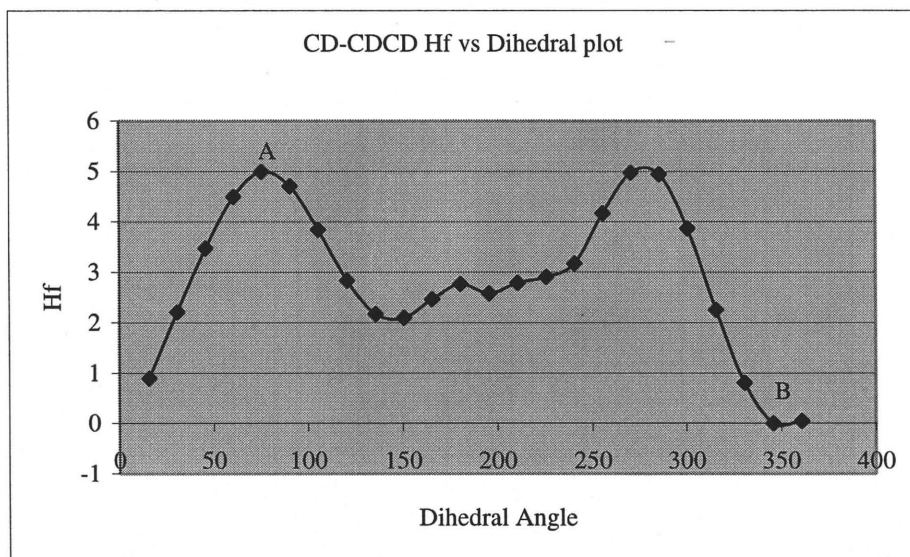
**Figure 2.33** Potential Barriers for Internal Rotation about CD-CBCT bond (Dihedral 5-4-1-2) of CDCBCT. Points are Calculated Values at relaxed B3LYP/6-31G(d) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.45 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral  $a-b-c-d$  infers rotation of angle of Atom  $a$  with respect to Atom  $d$  about Rotation Axis  $c-b$

**Table 2.46 Total Energy and Internal Rotation Barriers for CDCD2**

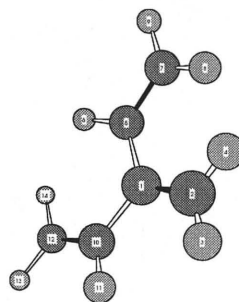
| CD-CDCD          |                              |                                    | CD-CDCD          |                              |                                    |
|------------------|------------------------------|------------------------------------|------------------|------------------------------|------------------------------------|
| Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> | Torsion<br>Angle | Total<br>Energy <sup>a</sup> | Rotational<br>barrier <sup>b</sup> |
| 15.67            | -232.109868                  | 0.90                               | 4.43             | -233.394349                  | 3.71                               |
| 30.67            | -232.107777                  | 2.21                               | 19.43            | -233.391163                  | 5.71                               |
| 45.67            | -232.105761                  | 3.48                               | 34.43            | -233.397073                  | 2.00                               |
| 60.67            | -232.104138                  | 4.49                               | 49.43            | -233.396114                  | 2.61                               |
| 75.67            | -232.103345                  | 4.99                               | 64.43            | -233.395861                  | 2.76                               |
| 90.67            | -232.103803                  | 4.70                               | 79.43            | -233.396761                  | 2.20                               |
| 105.67           | -232.10517                   | 3.85                               | 94.43            | -233.398408                  | 1.17                               |
| 120.67           | -232.106784                  | 2.83                               | 109.43           | -233.3998                    | 0.29                               |
| 135.67           | -232.107838                  | 2.17                               | 124.43           | -233.400267                  | 0.00                               |
| 150.67           | -232.107962                  | 2.09                               | 139.43           | -233.399672                  | 0.37                               |
| 165.67           | -232.107368                  | 2.47                               | 154.43           | -233.398512                  | 1.10                               |
| 180.67           | -232.106896                  | 2.76                               | 169.43           | -233.398009                  | 1.42                               |
| 195.67           | -232.107184                  | 2.58                               | 184.43           | -233.399215                  | 0.66                               |
| 210.67           | -232.10685                   | 2.79                               | 199.43           | -233.400185                  | 0.05                               |
| 225.67           | -232.106667                  | 2.91                               | 214.43           | -233.400059                  | 0.13                               |
| 240.67           | -232.106246                  | 3.17                               | 229.43           | -233.398983                  | 0.81                               |
| 255.67           | -232.104661                  | 4.17                               | 244.43           | -233.397428                  | 1.78                               |
| 270.67           | -232.103379                  | 4.97                               | 259.43           | -233.396178                  | 2.57                               |
| 285.67           | -232.103421                  | 4.94                               | 274.43           | -233.396001                  | 2.68                               |
| 300.67           | -232.105133                  | 3.87                               | 289.43           | -233.396783                  | 2.19                               |
| 315.67           | -232.107708                  | 2.25                               | 304.43           | -233.397594                  | 1.68                               |
| 330.67           | -232.110011                  | 0.81                               | 319.43           | -233.398088                  | 1.37                               |
| 345.67           | -232.111299                  | 0.00                               | 334.43           | -233.398088                  | 1.37                               |
| 360.67           | -232.11122                   | 0.05                               | 349.43           | -233.396716                  | 2.23                               |

<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.

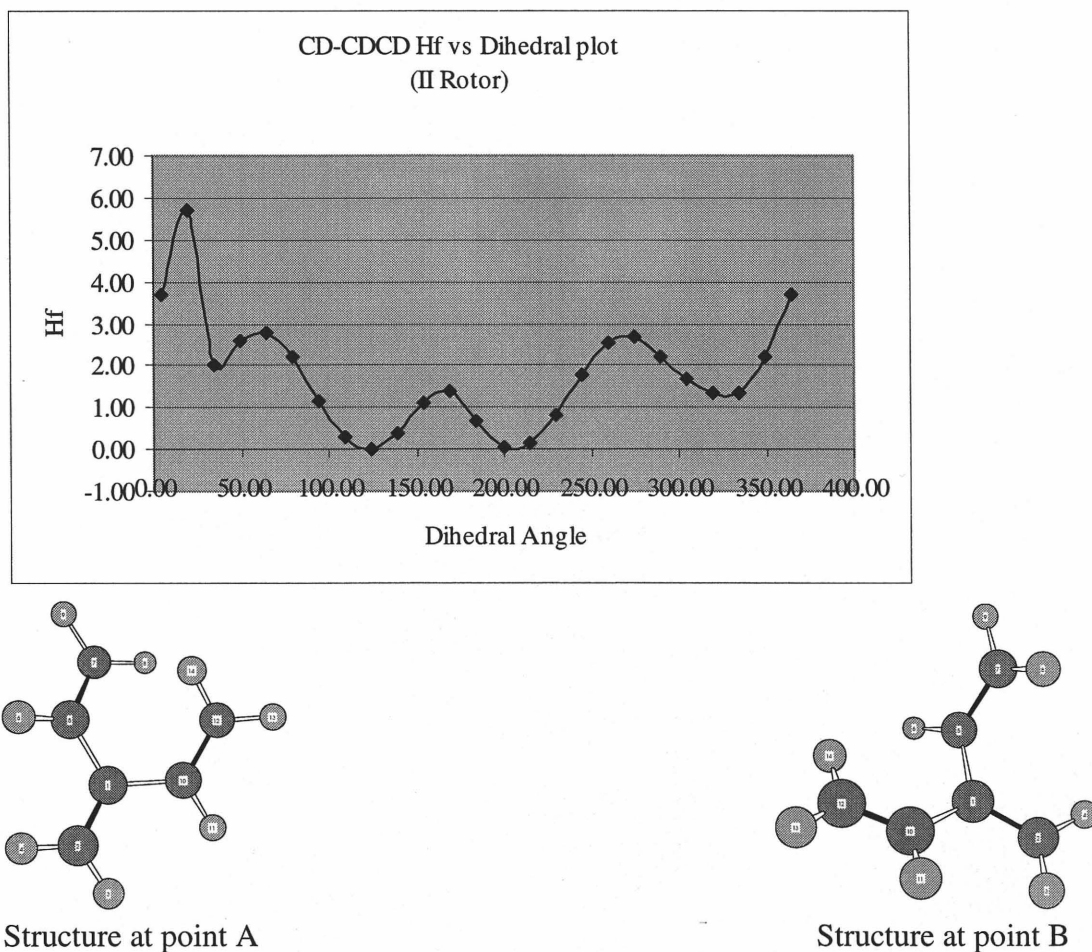


Structure at point A



Structure at point B

**Figure 2.34** Potential Barriers for Internal Rotation about CD-CDCD bond (Dihedral 11-10-1-2) of CDCD2. Points are Calculated Values at non-relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.46 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*



**Figure 2.35** Potential Barriers for Internal Rotation about CD-CDCD bond (Dihedral 6-5-1-2) of CDCD2. Points are Calculated Values at non-relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.46 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

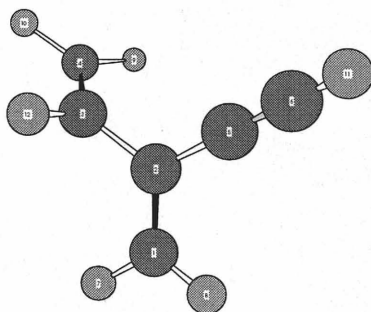
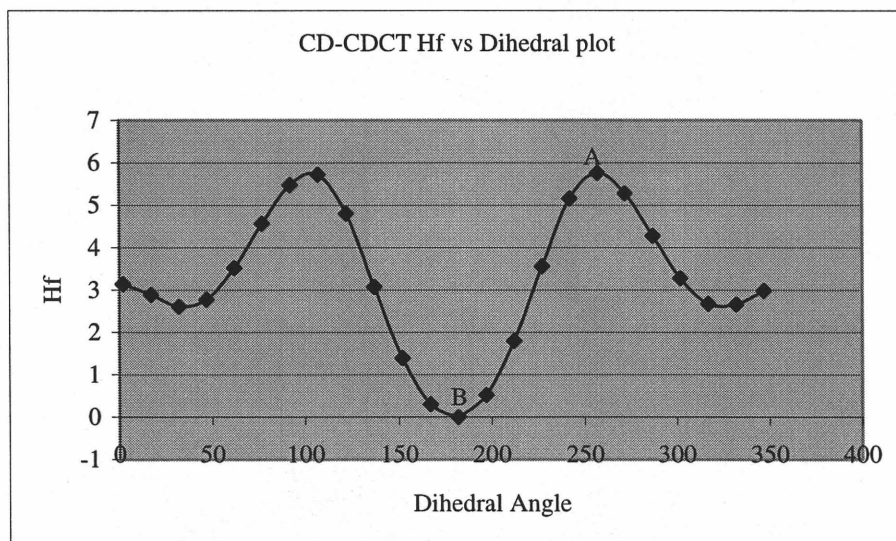


**Table 2.47 Total Energy and Internal Rotation Barriers for CDCDCT**

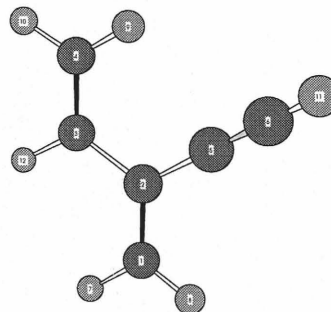
| CD-CDCT |                     |                      |
|---------|---------------------|----------------------|
| Torsion | Total               | Rotational           |
| Angle   | Energy <sup>a</sup> | barrier <sup>b</sup> |
| 1.99    | -230.859567         | 3.14                 |
| 16.99   | -230.859961         | 2.89                 |
| 31.99   | -230.860404         | 2.61                 |
| 46.99   | -230.86014          | 2.78                 |
| 61.99   | -230.858956         | 3.52                 |
| 76.99   | -230.857293         | 4.56                 |
| 91.99   | -230.855838         | 5.48                 |
| 106.99  | -230.855451         | 5.72                 |
| 121.99  | -230.856919         | 4.80                 |
| 136.99  | -230.859677         | 3.07                 |
| 151.99  | -230.862338         | 1.40                 |
| 166.99  | -230.864083         | 0.30                 |
| 181.99  | -230.864567         | 0.00                 |
| 181.99  | -230.864567         | 0.00                 |
| 196.99  | -230.863735         | 0.52                 |
| 211.99  | -230.861703         | 1.80                 |
| 226.99  | -230.858902         | 3.56                 |
| 241.99  | -230.856344         | 5.16                 |
| 256.99  | -230.855394         | 5.76                 |
| 271.99  | -230.856158         | 5.28                 |
| 286.99  | -230.857746         | 4.28                 |
| 301.99  | -230.859343         | 3.28                 |
| 316.99  | -230.860305         | 2.67                 |
| 331.99  | -230.860329         | 2.66                 |
| 346.99  | -230.859815         | 2.98                 |

<sup>a</sup> Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

<sup>b</sup> Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



Structure at point A



Structure at point B

**Figure 2.36** Potential Barriers for Internal Rotation about CD-CDCT bond (Dihedral 4-3-2-1) of CDCDCT. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.47 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

#### 2.4.4 Entropy ( $S^{\circ}_{298}$ ) and Heat Capacity ( $C_p(T)$ 's ( $300 \leq T/K \leq 1500$ ))

$S^{\circ}_{298}$  and  $C_p(T)$ 's calculation results using B3LYP/6-31G(d) determined geometries and frequencies are summarized in Table 2.65. TVR, represents the sum of the contributions from translations, external rotations and vibrations for  $S^{\circ}_{298}$  and  $C_p(T)$ 's. The torsion frequencies calculated for the internal rotors are not included in TVR. Instead, a more exact contribution from hindered rotations is calculated using the method of Pitzer and Gwinn.<sup>17</sup> I.R., represents the contributions from the internal rotation about C-C bond for  $S^{\circ}_{298}$  and  $C_p(T)$ 's. Translation, Vibration and External Rotation contributions to Entropy and Heat Capacity are calculated over the temperature range 298 K to 5000 K and represented in Tables 2.48 to 2.62. Table 2.47 shows the number of Internal Rotors, Symmetry and Moments of Inertia. Internal Rotation Contributions to Entropy and Heat Capacity are represented in Table 2.64.

**Table 2.48 Number of Internal Rotors, Symmetry and Moments of Inertia<sup>a,b</sup> used in the estimation of contributions to Entropy<sup>c</sup> and Heat Capacity<sup>c</sup>**

| Species | Formula | Molecular |     |                |                |                |          |
|---------|---------|-----------|-----|----------------|----------------|----------------|----------|
|         |         | Rotors    | Wt. | I <sub>a</sub> | I <sub>b</sub> | I <sub>c</sub> | Symmetry |
| CCB2H2  | C13H12  | 2         | 168 | 874.54         | 4363.73        | 4396.75        | 8        |
| CCBCDH2 | C9H10   | 2         | 118 | 427.78         | 1859.67        | 2187.07        | 2        |
| CCBCOH2 | C8H8O   | 2         | 120 | 442.18         | 1844.95        | 2123.22        | 2        |
| CCBCTH2 | C9H8    | 1         | 116 | 415.76         | 1743.27        | 2141.93        | 2        |
| CCD2H2  | C5H8    | 2         | 68  | 90.39          | 773.85         | 779.82         | 2        |
| CCDCOH2 | C4H6O   | 2         | 70  | 90.34          | 743.24         | 751.16         | 1        |
| CCO2H2  | C3H4O2  | 2         | 72  | 121.93         | 596.56         | 684.03         | 2        |
| CCOCTH2 | C4H4O   | 1         | 68  | 70.95          | 717.00         | 761.49         | 1        |
| CCT2H2  | C5H4    | 0         | 64  | 94.54          | 637.33         | 720.83         | 2        |
| CDCB2   | C14H12  | 2         | 180 | 1124.62        | 4371.24        | 4986.43        | 8        |
| CDCBCD  | C10H10  | 1         | 130 | 575.63         | 2094.66        | 2583.37        | 2        |
| CDCBCT  | C10H8   | 1         | 128 | 637.59         | 1886.77        | 2460.12        | 2        |
| CDCD2   | C6H8    | 2         | 80  | 322.54         | 634.56         | 927.28         | 2        |
| CDCDCT  | C6H6    | 1         | 78  | 380.54         | 513.76         | 894.30         | 1        |
| CDCT2   | C6H4    | 0         | 76  | 290.82         | 634.53         | 925.36         | 2        |

<sup>a</sup> Optimized at the B3LYP/6-31G(d) level of theory.

<sup>b</sup> Units in amu-Bohr<sup>2</sup>.

<sup>c</sup> Multiplicity of all species is 1, Spin of all species is 0, Number of Optical Isomers for all species is 1

**Table 2.49 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CCB<sub>2</sub>H<sub>2</sub> at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 39.04                       | 89.14          | 5.94                      |
| 300            | 39.36                       | 89.40          | 6.02                      |
| 400            | 54.45                       | 102.84         | 10.72                     |
| 500            | 67.42                       | 116.45         | 16.82                     |
| 600            | 77.96                       | 129.72         | 24.10                     |
| 700            | 86.49                       | 142.42         | 32.33                     |
| 800            | 93.49                       | 154.46         | 41.34                     |
| 900            | 99.32                       | 165.83         | 50.97                     |
| 1000           | 104.23                      | 176.57         | 61.15                     |
| 1100           | 108.41                      | 186.72         | 71.78                     |
| 1200           | 111.98                      | 196.32         | 82.79                     |
| 1300           | 115.05                      | 205.42         | 94.13                     |
| 1400           | 117.70                      | 214.06         | 105.76                    |
| 1500           | 120.00                      | 222.27         | 117.64                    |
| 1600           | 122.00                      | 230.09         | 129.73                    |
| 1700           | 123.75                      | 237.56         | 142.00                    |
| 1800           | 125.28                      | 244.68         | 154.44                    |
| 1900           | 126.63                      | 251.50         | 167.03                    |
| 2000           | 127.83                      | 258.04         | 179.74                    |
| 2500           | 132.10                      | 287.11         | 244.75                    |
| 3000           | 134.64                      | 311.47         | 311.42                    |
| 3500           | 136.26                      | 332.38         | 379.10                    |
| 4000           | 137.34                      | 350.68         | 447.45                    |
| 4500           | 138.10                      | 366.92         | 516.25                    |
| 5000           | 138.65                      | 381.53         | 585.37                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.50 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CCBCDH2 at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 28.85                       | 79.37          | 4.65                      |
| 300            | 29.07                       | 79.56          | 4.71                      |
| 400            | 39.78                       | 89.42          | 8.15                      |
| 500            | 49.11                       | 99.35          | 12.61                     |
| 600            | 56.79                       | 109.02         | 17.91                     |
| 700            | 63.09                       | 118.27         | 23.91                     |
| 800            | 68.31                       | 127.06         | 30.48                     |
| 900            | 72.71                       | 135.38         | 37.53                     |
| 1000           | 76.44                       | 143.25         | 44.98                     |
| 1100           | 79.65                       | 150.70         | 52.79                     |
| 1200           | 82.40                       | 157.76         | 60.88                     |
| 1300           | 84.78                       | 164.46         | 69.24                     |
| 1400           | 86.85                       | 170.83         | 77.81                     |
| 1500           | 88.64                       | 176.89         | 86.58                     |
| 1600           | 90.21                       | 182.67         | 95.52                     |
| 1700           | 91.58                       | 188.19         | 104.60                    |
| 1800           | 92.79                       | 193.46         | 113.81                    |
| 1900           | 93.85                       | 198.52         | 123.13                    |
| 2000           | 94.79                       | 203.36         | 132.56                    |
| 2500           | 98.18                       | 224.94         | 180.83                    |
| 3000           | 100.19                      | 243.06         | 230.41                    |
| 3500           | 101.47                      | 258.63         | 280.79                    |
| 4000           | 102.33                      | 272.26         | 331.71                    |
| 4500           | 102.94                      | 284.36         | 382.98                    |
| 5000           | 103.38                      | 295.25         | 434.51                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.51 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CCBCOH2 at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 26.98                       | 80.00          | 4.47                      |
| 300            | 27.17                       | 80.18          | 4.53                      |
| 400            | 36.66                       | 89.32          | 7.72                      |
| 500            | 44.92                       | 98.43          | 11.81                     |
| 600            | 51.72                       | 107.25         | 16.65                     |
| 700            | 57.29                       | 115.67         | 22.11                     |
| 800            | 61.89                       | 123.64         | 28.06                     |
| 900            | 65.74                       | 131.16         | 34.45                     |
| 1000           | 68.99                       | 138.27         | 41.18                     |
| 1100           | 71.76                       | 144.99         | 48.21                     |
| 1200           | 74.13                       | 151.35         | 55.50                     |
| 1300           | 76.17                       | 157.37         | 63.01                     |
| 1400           | 77.93                       | 163.09         | 70.71                     |
| 1500           | 79.46                       | 168.53         | 78.58                     |
| 1600           | 80.78                       | 173.71         | 86.58                     |
| 1700           | 81.94                       | 178.64         | 94.71                     |
| 1800           | 82.96                       | 183.36         | 102.95                    |
| 1900           | 83.85                       | 187.88         | 111.28                    |
| 2000           | 84.64                       | 192.21         | 119.70                    |
| 2500           | 87.47                       | 211.45         | 162.75                    |
| 3000           | 89.15                       | 227.58         | 206.89                    |
| 3500           | 90.21                       | 241.43         | 251.71                    |
| 4000           | 90.93                       | 253.54         | 296.96                    |
| 4500           | 91.43                       | 264.30         | 342.51                    |
| 5000           | 91.79                       | 273.96         | 388.27                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.52 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CCBC<sub>2</sub>H<sub>2</sub> at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 30.34                       | 81.47          | 5.01                      |
| 300            | 30.55                       | 81.67          | 5.07                      |
| 400            | 40.09                       | 91.81          | 8.61                      |
| 500            | 48.12                       | 101.66         | 13.03                     |
| 600            | 54.63                       | 111.04         | 18.17                     |
| 700            | 59.94                       | 119.88         | 23.90                     |
| 800            | 64.32                       | 128.19         | 30.12                     |
| 900            | 68.01                       | 136.00         | 36.73                     |
| 1000           | 71.14                       | 143.34         | 43.69                     |
| 1100           | 73.83                       | 150.26         | 50.93                     |
| 1200           | 76.13                       | 156.79         | 58.42                     |
| 1300           | 78.13                       | 162.98         | 66.13                     |
| 1400           | 79.86                       | 168.84         | 74.03                     |
| 1500           | 81.36                       | 174.41         | 82.08                     |
| 1600           | 82.68                       | 179.71         | 90.28                     |
| 1700           | 83.83                       | 184.76         | 98.59                     |
| 1800           | 84.84                       | 189.59         | 107.02                    |
| 1900           | 85.74                       | 194.21         | 115.54                    |
| 2000           | 86.53                       | 198.63         | 124.15                    |
| 2500           | 89.37                       | 218.30         | 168.14                    |
| 3000           | 91.06                       | 234.78         | 213.24                    |
| 3500           | 92.14                       | 248.92         | 259.01                    |
| 4000           | 92.87                       | 261.29         | 305.23                    |
| 4500           | 93.38                       | 272.28         | 351.75                    |
| 5000           | 93.75                       | 282.15         | 398.49                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol



**Table 2.53 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CCD<sub>2</sub>H<sub>2</sub> at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 18.67                       | 67.74          | 3.43                      |
| 300            | 18.80                       | 67.87          | 3.47                      |
| 400            | 25.11                       | 74.15          | 5.66                      |
| 500            | 30.80                       | 80.39          | 8.46                      |
| 600            | 35.61                       | 86.45          | 11.79                     |
| 700            | 39.66                       | 92.26          | 15.55                     |
| 800            | 43.11                       | 97.79          | 19.69                     |
| 900            | 46.08                       | 103.05         | 24.15                     |
| 1000           | 48.64                       | 108.05         | 28.89                     |
| 1100           | 50.87                       | 112.80         | 33.86                     |
| 1200           | 52.81                       | 117.32         | 39.04                     |
| 1300           | 54.51                       | 121.62         | 44.41                     |
| 1400           | 55.99                       | 125.72         | 49.93                     |
| 1500           | 57.28                       | 129.63         | 55.59                     |
| 1600           | 58.41                       | 133.37         | 61.37                     |
| 1700           | 59.41                       | 136.94         | 67.25                     |
| 1800           | 60.29                       | 140.37         | 73.23                     |
| 1900           | 61.07                       | 143.66         | 79.30                     |
| 2000           | 61.76                       | 146.81         | 85.43                     |
| 2500           | 64.24                       | 160.90         | 116.96                    |
| 3000           | 65.73                       | 172.77         | 149.45                    |
| 3500           | 66.69                       | 183.00         | 182.54                    |
| 4000           | 67.33                       | 191.96         | 216.02                    |
| 4500           | 67.78                       | 199.92         | 249.77                    |
| 5000           | 68.10                       | 207.09         | 283.71                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.54 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CCDCOH<sub>2</sub> at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 16.80                       | 68.30          | 3.26                      |
| 300            | 16.91                       | 68.41          | 3.29                      |
| 400            | 21.98                       | 73.98          | 5.23                      |
| 500            | 26.60                       | 79.40          | 7.67                      |
| 600            | 30.54                       | 84.61          | 10.53                     |
| 700            | 33.86                       | 89.58          | 13.75                     |
| 800            | 36.69                       | 94.30          | 17.28                     |
| 900            | 39.11                       | 98.77          | 21.07                     |
| 1000           | 41.19                       | 103.01         | 25.08                     |
| 1100           | 42.99                       | 107.02         | 29.29                     |
| 1200           | 44.55                       | 110.84         | 33.66                     |
| 1300           | 45.90                       | 114.46         | 38.18                     |
| 1400           | 47.07                       | 117.91         | 42.83                     |
| 1500           | 48.09                       | 121.20         | 47.58                     |
| 1600           | 48.99                       | 124.33         | 52.43                     |
| 1700           | 49.77                       | 127.33         | 57.37                     |
| 1800           | 50.46                       | 130.20         | 62.37                     |
| 1900           | 51.07                       | 132.95         | 67.45                     |
| 2000           | 51.61                       | 135.59         | 72.58                     |
| 2500           | 53.54                       | 147.34         | 98.88                     |
| 3000           | 54.69                       | 157.23         | 125.94                    |
| 3500           | 55.43                       | 165.73         | 153.46                    |
| 4000           | 55.92                       | 173.17         | 181.27                    |
| 4500           | 56.27                       | 179.79         | 209.30                    |
| 5000           | 56.52                       | 185.74         | 237.47                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.55 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CCOCTH2 at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 18.33                       | 70.23          | 3.62                      |
| 300            | 18.41                       | 70.35          | 3.65                      |
| 400            | 22.34                       | 76.20          | 5.70                      |
| 500            | 25.66                       | 81.56          | 8.10                      |
| 600            | 28.42                       | 86.50          | 10.81                     |
| 700            | 30.75                       | 91.06          | 13.76                     |
| 800            | 32.73                       | 95.31          | 16.94                     |
| 900            | 34.44                       | 99.27          | 20.30                     |
| 1000           | 35.92                       | 102.98         | 23.81                     |
| 1100           | 37.19                       | 106.47         | 27.47                     |
| 1200           | 38.30                       | 109.76         | 31.24                     |
| 1300           | 39.26                       | 112.87         | 35.12                     |
| 1400           | 40.10                       | 115.81         | 39.08                     |
| 1500           | 40.83                       | 118.61         | 43.13                     |
| 1600           | 41.47                       | 121.27         | 47.24                     |
| 1700           | 42.04                       | 123.80         | 51.41                     |
| 1800           | 42.53                       | 126.22         | 55.64                     |
| 1900           | 42.97                       | 128.53         | 59.91                     |
| 2000           | 43.35                       | 130.75         | 64.22                     |
| 2500           | 44.74                       | 140.60         | 86.25                     |
| 3000           | 45.57                       | 148.85         | 108.83                    |
| 3500           | 46.10                       | 155.92         | 131.74                    |
| 4000           | 46.46                       | 162.11         | 154.86                    |
| 4500           | 46.71                       | 167.61         | 178.13                    |
| 5000           | 46.89                       | 172.54         | 201.51                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.56 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CCT2H2 at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 21.49                       | 71.55          | 4.10                      |
| 300            | 21.58                       | 71.70          | 4.15                      |
| 400            | 25.60                       | 78.49          | 6.51                      |
| 500            | 28.72                       | 84.55          | 9.23                      |
| 600            | 31.21                       | 90.02          | 12.23                     |
| 700            | 33.30                       | 95.00          | 15.46                     |
| 800            | 35.08                       | 99.57          | 18.88                     |
| 900            | 36.64                       | 103.80         | 22.46                     |
| 1000           | 38.00                       | 107.74         | 26.19                     |
| 1100           | 39.20                       | 111.42         | 30.05                     |
| 1200           | 40.25                       | 114.89         | 34.02                     |
| 1300           | 41.18                       | 118.15         | 38.09                     |
| 1400           | 41.99                       | 121.23         | 42.24                     |
| 1500           | 42.71                       | 124.16         | 46.48                     |
| 1600           | 43.34                       | 126.94         | 50.78                     |
| 1700           | 43.89                       | 129.59         | 55.13                     |
| 1800           | 44.39                       | 132.11         | 59.54                     |
| 1900           | 44.82                       | 134.53         | 64.00                     |
| 2000           | 45.21                       | 136.84         | 68.50                     |
| 2500           | 46.62                       | 147.11         | 91.47                     |
| 3000           | 47.48                       | 155.70         | 114.99                    |
| 3500           | 48.02                       | 163.07         | 138.85                    |
| 4000           | 48.39                       | 169.52         | 162.94                    |
| 4500           | 48.65                       | 175.24         | 187.18                    |
| 5000           | 48.84                       | 180.38         | 211.53                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.57 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CDCBCT at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 33.81                       | 85.02          | 5.47                      |
| 300            | 34.03                       | 85.24          | 5.54                      |
| 400            | 44.35                       | 96.50          | 9.47                      |
| 500            | 52.81                       | 107.35         | 14.33                     |
| 600            | 59.58                       | 117.62         | 19.96                     |
| 700            | 65.04                       | 127.24         | 26.20                     |
| 800            | 69.54                       | 136.24         | 32.92                     |
| 900            | 73.31                       | 144.66         | 40.07                     |
| 1000           | 76.50                       | 152.57         | 47.55                     |
| 1100           | 79.24                       | 160.00         | 55.34                     |
| 1200           | 81.59                       | 167.01         | 63.37                     |
| 1300           | 83.63                       | 173.63         | 71.63                     |
| 1400           | 85.40                       | 179.90         | 80.07                     |
| 1500           | 86.94                       | 185.86         | 88.68                     |
| 1600           | 88.28                       | 191.52         | 97.44                     |
| 1700           | 89.46                       | 196.91         | 106.31                    |
| 1800           | 90.49                       | 202.06         | 115.30                    |
| 1900           | 91.41                       | 206.99         | 124.39                    |
| 2000           | 92.22                       | 211.71         | 133.56                    |
| 2500           | 95.14                       | 232.66         | 180.42                    |
| 3000           | 96.88                       | 250.19         | 228.42                    |
| 3500           | 98.00                       | 265.24         | 277.11                    |
| 4000           | 98.75                       | 278.39         | 326.25                    |
| 4500           | 99.27                       | 290.07         | 375.72                    |
| 5000           | 99.65                       | 300.57         | 425.40                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.58 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CDCDCT at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 23.51                       | 75.14          | 4.21                      |
| 300            | 23.64                       | 75.30          | 4.25                      |
| 400            | 29.60                       | 82.96          | 6.92                      |
| 500            | 34.45                       | 90.11          | 10.13                     |
| 600            | 38.37                       | 96.76          | 13.78                     |
| 700            | 41.60                       | 102.93         | 17.78                     |
| 800            | 44.33                       | 108.67         | 22.07                     |
| 900            | 46.67                       | 114.04         | 26.62                     |
| 1000           | 48.69                       | 119.07         | 31.39                     |
| 1100           | 50.46                       | 123.80         | 36.34                     |
| 1200           | 52.00                       | 128.26         | 41.46                     |
| 1300           | 53.35                       | 132.49         | 46.73                     |
| 1400           | 54.53                       | 136.49         | 52.12                     |
| 1500           | 55.57                       | 140.29         | 57.62                     |
| 1600           | 56.48                       | 143.91         | 63.21                     |
| 1700           | 57.28                       | 147.37         | 68.90                     |
| 1800           | 57.99                       | 150.67         | 74.66                     |
| 1900           | 58.62                       | 153.82         | 80.48                     |
| 2000           | 59.18                       | 156.85         | 86.37                     |
| 2500           | 61.21                       | 170.31         | 116.48                    |
| 3000           | 62.43                       | 181.60         | 147.39                    |
| 3500           | 63.21                       | 191.30         | 178.78                    |
| 4000           | 63.74                       | 199.79         | 210.49                    |
| 4500           | 64.11                       | 207.33         | 242.43                    |
| 5000           | 64.38                       | 214.10         | 274.52                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.59 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CDCT2 at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 24.87                       | 75.73          | 4.53                      |
| 300            | 24.98                       | 75.89          | 4.58                      |
| 400            | 29.82                       | 83.79          | 7.33                      |
| 500            | 33.39                       | 90.85          | 10.50                     |
| 600            | 36.15                       | 97.20          | 13.98                     |
| 700            | 38.41                       | 102.95         | 17.71                     |
| 800            | 40.31                       | 108.22         | 21.64                     |
| 900            | 41.95                       | 113.07         | 25.75                     |
| 1000           | 43.38                       | 117.57         | 30.02                     |
| 1100           | 44.63                       | 121.77         | 34.41                     |
| 1200           | 45.73                       | 125.70         | 38.93                     |
| 1300           | 46.70                       | 129.41         | 43.55                     |
| 1400           | 47.55                       | 132.91         | 48.26                     |
| 1500           | 48.29                       | 136.22         | 53.05                     |
| 1600           | 48.95                       | 139.36         | 57.90                     |
| 1700           | 49.54                       | 142.35         | 62.82                     |
| 1800           | 50.05                       | 145.20         | 67.80                     |
| 1900           | 50.51                       | 147.92         | 72.82                     |
| 2000           | 50.92                       | 150.52         | 77.89                     |
| 2500           | 52.41                       | 162.08         | 103.73                    |
| 3000           | 53.31                       | 171.73         | 130.15                    |
| 3500           | 53.88                       | 180.00         | 156.93                    |
| 4000           | 54.27                       | 187.23         | 183.95                    |
| 4500           | 54.55                       | 193.65         | 211.14                    |
| 5000           | 54.75                       | 199.42         | 238.44                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.60 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CCO<sub>2</sub>H<sub>2</sub> at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 15.11                       | 66.62          | 3.14                      |
| 300            | 15.19                       | 66.73          | 3.17                      |
| 400            | 19.03                       | 71.63          | 4.88                      |
| 500            | 22.54                       | 76.26          | 6.96                      |
| 600            | 25.58                       | 80.65          | 9.37                      |
| 700            | 28.16                       | 84.80          | 12.06                     |
| 800            | 30.35                       | 88.71          | 14.98                     |
| 900            | 32.21                       | 92.40          | 18.11                     |
| 1000           | 33.81                       | 95.88          | 21.41                     |
| 1100           | 35.17                       | 99.18          | 24.86                     |
| 1200           | 36.34                       | 102.29         | 28.43                     |
| 1300           | 37.34                       | 105.24         | 32.11                     |
| 1400           | 38.21                       | 108.05         | 35.89                     |
| 1500           | 38.96                       | 110.71         | 39.75                     |
| 1600           | 39.61                       | 113.25         | 43.67                     |
| 1700           | 40.17                       | 115.67         | 47.66                     |
| 1800           | 40.67                       | 117.98         | 51.70                     |
| 1900           | 41.11                       | 120.20         | 55.78                     |
| 2000           | 41.49                       | 122.32         | 59.91                     |
| 2500           | 42.86                       | 131.75         | 81.01                     |
| 3000           | 43.67                       | 139.65         | 102.64                    |
| 3500           | 44.18                       | 146.43         | 124.59                    |
| 4000           | 44.53                       | 152.37         | 146.76                    |
| 4500           | 44.77                       | 157.63         | 169.06                    |
| 5000           | 44.94                       | 162.36         | 191.47                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol



**Table 2.61 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CDCB2 at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 42.65                       | 90.92          | 6.46                      |
| 300            | 42.98                       | 91.20          | 6.54                      |
| 400            | 58.77                       | 105.79         | 11.64                     |
| 500            | 72.16                       | 120.42         | 18.20                     |
| 600            | 82.95                       | 134.58         | 25.97                     |
| 700            | 91.64                       | 148.06         | 34.71                     |
| 800            | 98.74                       | 160.79         | 44.23                     |
| 900            | 104.65                      | 172.79         | 54.39                     |
| 1000           | 109.62                      | 184.10         | 65.10                     |
| 1100           | 113.84                      | 194.76         | 76.27                     |
| 1200           | 117.46                      | 204.84         | 87.83                     |
| 1300           | 120.57                      | 214.38         | 99.72                     |
| 1400           | 123.25                      | 223.43         | 111.90                    |
| 1500           | 125.58                      | 232.03         | 124.33                    |
| 1600           | 127.61                      | 240.21         | 136.98                    |
| 1700           | 129.39                      | 248.01         | 149.82                    |
| 1800           | 130.94                      | 255.46         | 162.83                    |
| 1900           | 132.32                      | 262.59         | 175.98                    |
| 2000           | 133.53                      | 269.42         | 189.26                    |
| 2500           | 137.88                      | 299.77         | 257.14                    |
| 3000           | 140.47                      | 325.19         | 326.70                    |
| 3500           | 142.12                      | 347.01         | 397.31                    |
| 4000           | 143.22                      | 366.09         | 468.58                    |
| 4500           | 144.00                      | 383.03         | 540.32                    |
| 5000           | 144.56                      | 398.25         | 612.39                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.62 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CDCBCD at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(0K)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 34.32                       | 86.25          | 5.58                      |
| 300            | 34.56                       | 86.48          | 5.65                      |
| 400            | 46.02                       | 98.04          | 9.69                      |
| 500            | 55.79                       | 109.40         | 14.79                     |
| 600            | 63.73                       | 120.32         | 20.77                     |
| 700            | 70.18                       | 130.65         | 27.47                     |
| 800            | 75.52                       | 140.40         | 34.76                     |
| 900            | 80.00                       | 149.57         | 42.53                     |
| 1000           | 83.80                       | 158.21         | 50.72                     |
| 1100           | 87.06                       | 166.37         | 59.26                     |
| 1200           | 89.86                       | 174.08         | 68.10                     |
| 1300           | 92.28                       | 181.38         | 77.20                     |
| 1400           | 94.38                       | 188.30         | 86.53                     |
| 1500           | 96.21                       | 194.89         | 96.05                     |
| 1600           | 97.81                       | 201.16         | 105.74                    |
| 1700           | 99.20                       | 207.14         | 115.58                    |
| 1800           | 100.44                      | 212.85         | 125.55                    |
| 1900           | 101.52                      | 218.32         | 135.64                    |
| 2000           | 102.48                      | 223.56         | 145.83                    |
| 2500           | 105.94                      | 246.87         | 197.97                    |
| 3000           | 108.00                      | 266.41         | 251.44                    |
| 3500           | 109.32                      | 283.18         | 305.74                    |
| 4000           | 110.20                      | 297.86         | 360.57                    |
| 4500           | 110.82                      | 310.90         | 415.78                    |
| 5000           | 111.27                      | 322.62         | 471.25                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.63 Translation, Vibration and External Rotation contribution to Entropy and Heat Capacity for CDCD2 at different temperatures**

| T <sup>a</sup> | C <sub>p</sub> <sup>b</sup> | S <sup>c</sup> | [H(T)-H(OK)] <sup>d</sup> |
|----------------|-----------------------------|----------------|---------------------------|
| 298            | 22.12                       | 71.75          | 3.87                      |
| 300            | 22.26                       | 71.90          | 3.91                      |
| 400            | 29.33                       | 79.30          | 6.50                      |
| 500            | 35.45                       | 86.53          | 9.74                      |
| 600            | 40.53                       | 93.47          | 13.55                     |
| 700            | 44.75                       | 100.05         | 17.81                     |
| 800            | 48.31                       | 106.27         | 22.47                     |
| 900            | 51.36                       | 112.15         | 27.45                     |
| 1000           | 53.99                       | 117.70         | 32.72                     |
| 1100           | 56.28                       | 122.97         | 38.23                     |
| 1200           | 58.27                       | 127.96         | 43.95                     |
| 1300           | 60.00                       | 132.70         | 49.86                     |
| 1400           | 61.52                       | 137.21         | 55.93                     |
| 1500           | 62.85                       | 141.50         | 62.15                     |
| 1600           | 64.01                       | 145.60         | 68.48                     |
| 1700           | 65.04                       | 149.52         | 74.93                     |
| 1800           | 65.94                       | 153.27         | 81.47                     |
| 1900           | 66.74                       | 156.86         | 88.10                     |
| 2000           | 67.45                       | 160.31         | 94.81                     |
| 2500           | 70.02                       | 175.68         | 129.20                    |
| 3000           | 71.56                       | 188.61         | 164.59                    |
| 3500           | 72.54                       | 199.73         | 200.59                    |
| 4000           | 73.20                       | 209.48         | 237.01                    |
| 4500           | 73.67                       | 218.14         | 273.69                    |
| 5000           | 74.01                       | 225.93         | 310.58                    |

<sup>a</sup> Temperature in Kelvin

<sup>b</sup> Heat Capacity in cal/mol/K

<sup>c</sup> Entropy in cal/mol/K

<sup>d</sup> Enthalpy in kcal/mol

**Table 2.64 Internal Rotor Contributions to Entropy and Heat Capacity for Each Species**

| Species             | Rotor           | $S^{\circ}_{298}$ <sup>a</sup> | $Cp_{300}$ <sup>b</sup> | $Cp_{400}$ | $Cp_{500}$ | $Cp_{600}$ | $Cp_{800}$ | $Cp_{1000}$ | $Cp_{1500}$ |
|---------------------|-----------------|--------------------------------|-------------------------|------------|------------|------------|------------|-------------|-------------|
| CCB2H2              |                 | 16.34                          | 3.35                    | 2.97       | 2.71       | 2.53       | 2.32       | 2.21        | 2.09        |
|                     | C6H5-CH2C6H5    | 8.52                           | 1.24                    | 1.14       | 1.09       | 1.06       | 1.03       | 1.02        | 1.00        |
|                     | C6H5-CH2C6H5    | 7.83                           | 2.12                    | 1.84       | 1.62       | 1.47       | 1.29       | 1.19        | 1.09        |
| CCBCDH2             |                 | 12.81                          | 4.51                    | 4.36       | 4.08       | 3.79       | 3.29       | 2.94        | 2.48        |
|                     | C6H5-CH2C2H3    | 7.09                           | 2.26                    | 2.04       | 1.82       | 1.65       | 1.42       | 1.29        | 1.13        |
|                     | C2H3-CH2C6H5    | 5.72                           | 2.25                    | 2.32       | 2.26       | 2.14       | 1.87       | 1.66        | 1.35        |
| CCBCOH2             |                 | 12.15                          | 4.35                    | 4.21       | 4.07       | 3.95       | 3.72       | 3.47        | 2.93        |
|                     | C6H5-CH2CHO     | 5.77                           | 2.10                    | 2.19       | 2.27       | 2.32       | 2.31       | 2.19        | 1.81        |
|                     | CHO-CH2C6H5     | 6.38                           | 2.25                    | 2.02       | 1.80       | 1.63       | 1.41       | 1.28        | 1.13        |
| CCBCTH2             |                 | 8.07                           | 1.10                    | 1.05       | 1.03       | 1.02       | 1.01       | 1.00        | 1.00        |
|                     | C6H5-CH2C2H     | 8.07                           | 1.10                    | 1.05       | 1.03       | 1.02       | 1.01       | 1.00        | 1.00        |
| CCD2H2              |                 | 12.63                          | 4.38                    | 3.92       | 3.51       | 3.18       | 2.75       | 2.51        | 2.23        |
|                     | CH2(C2H3)-C2H3  | 6.12                           | 2.29                    | 2.12       | 1.91       | 1.73       | 1.48       | 1.33        | 1.15        |
|                     | CH2(C2H3)-C2H3  | 6.51                           | 2.09                    | 1.80       | 1.60       | 1.45       | 1.28       | 1.18        | 1.08        |
| CCDCOH2             |                 | 12.23                          | 4.54                    | 4.21       | 3.80       | 3.44       | 2.95       | 2.66        | 2.31        |
|                     | CHO-CH2C2H3     | 6.17                           | 2.25                    | 2.05       | 1.84       | 1.66       | 1.43       | 1.30        | 1.14        |
|                     | C2H3-CH2CHO     | 6.06                           | 2.29                    | 2.16       | 1.96       | 1.78       | 1.52       | 1.37        | 1.17        |
| CCO2H2              |                 | 14.31                          | 2.43                    | 2.25       | 2.16       | 2.11       | 2.06       | 2.04        | 2.01        |
|                     | CHO-CH2CHO      | 7.13                           | 1.26                    | 1.15       | 1.10       | 1.07       | 1.04       | 1.02        | 1.01        |
|                     | CHO-CH2CHO      | 7.18                           | 1.18                    | 1.10       | 1.06       | 1.04       | 1.02       | 1.01        | 1.00        |
| CCOCTH2             |                 | 5.97                           | 2.31                    | 2.17       | 1.97       | 1.79       | 1.53       | 1.37        | 1.18        |
|                     | CHO-CH2C2H      | 5.97                           | 2.31                    | 2.17       | 1.97       | 1.79       | 1.53       | 1.37        | 1.18        |
| CDCB2 <sup>c</sup>  |                 | 7.40                           | 2.30                    | 2.15       | 1.95       | 1.76       | 1.51       | 1.35        | 1.17        |
|                     | C6H5-C(CH2)C6H  | 7.40                           | 2.30                    | 2.15       | 1.95       | 1.76       | 1.51       | 1.35        | 1.17        |
| CDCBCD <sup>c</sup> |                 | 6.95                           | 2.31                    | 2.18       | 1.99       | 1.81       | 1.54       | 1.38        | 1.18        |
|                     | C6H5-C(CH2)C2H3 | 6.95                           | 2.31                    | 2.18       | 1.99       | 1.81       | 1.54       | 1.38        | 1.18        |
| CDCBCT              |                 | 6.77                           | 2.34                    | 2.26       | 2.09       | 1.91       | 1.63       | 1.45        | 1.22        |
|                     | C6H5-C(CH2)C2H  | 6.77                           | 2.34                    | 2.26       | 2.09       | 1.91       | 1.63       | 1.45        | 1.22        |
| CDCD2               |                 | 10.37                          | 4.20                    | 4.47       | 4.61       | 4.61       | 4.35       | 3.96        | 3.19        |
|                     | C2H3-C(CH2)C2H  | 5.24                           | 2.17                    | 2.28       | 2.33       | 2.31       | 2.13       | 1.92        | 1.54        |
|                     | C2H3-C(CH2)C2H  | 5.13                           | 2.03                    | 2.18       | 2.27       | 2.31       | 2.22       | 2.04        | 1.65        |
| CDCDCT              |                 | 5.06                           | 2.12                    | 2.23       | 2.31       | 2.33       | 2.24       | 2.06        | 1.66        |
|                     | C2H3-C(CH2)C2H  | 5.06                           | 2.12                    | 2.23       | 2.31       | 2.33       | 2.24       | 2.06        | 1.66        |

<sup>a</sup> Units in kcal/mol<sup>b</sup> Units in cal/mol/K<sup>c</sup> Only one Internal Rotor considered here, the second internal rotor was found to have a very high Rotation Barrier during calculations, which are suspected to be erroneous. The torsion frequency for this rotor has been used instead of the internal rotation contribution.

**Table 2.65 Ideal Gas-phase Thermodynamic Properties<sup>a,m</sup>**

| Species             | Symmetry | $\Delta H_f^\circ$ <sup>b</sup> | $S^\circ$ <sup>c</sup> | $C_p^{300^\circ}$ <sup>c</sup> | $C_p^{400}$ | $C_p^{500}$ | $C_p^{600}$ | $C_p^{800}$ | $C_p^{1000}$ | $C_p^{1500}$ |
|---------------------|----------|---------------------------------|------------------------|--------------------------------|-------------|-------------|-------------|-------------|--------------|--------------|
| CCB2H2              | 8        | 42.41                           | 105.48                 | 42.71                          | 57.42       | 70.13       | 80.49       | 95.81       | 106.44       | 122.09       |
| TVR <sup>d</sup>    |          |                                 | 89.14                  | 39.36                          | 54.45       | 67.42       | 77.96       | 93.49       | 104.23       | 120.00       |
| I.R. <sup>e</sup>   |          |                                 | 16.34                  | 3.35                           | 2.97        | 2.71        | 2.53        | 2.32        | 2.21         | 2.09         |
| Literature          |          | 39.39 <sup>g</sup>              | 104 <sup>h</sup>       |                                |             |             |             |             |              |              |
| CCBCDH2             | 2        | 34.70                           | 92.18                  | 33.58                          | 44.14       | 53.19       | 60.58       | 71.60       | 79.38        | 91.12        |
| TVR <sup>d</sup>    |          |                                 | 79.37                  | 29.07                          | 39.78       | 49.11       | 56.79       | 68.31       | 76.44        | 88.64        |
| I.R. <sup>e</sup>   |          |                                 | 12.81                  | 4.51                           | 4.36        | 4.08        | 3.79        | 3.29        | 2.94         | 2.48         |
| CCBCOH2             | 2        | -13.35                          | 92.15                  | 31.52                          | 40.87       | 48.99       | 55.67       | 65.61       | 72.45        | 82.38        |
| TVR <sup>d</sup>    |          |                                 | 80.00                  | 27.17                          | 36.66       | 44.92       | 51.72       | 61.89       | 68.99        | 79.45        |
| I.R. <sup>e</sup>   |          |                                 | 12.15                  | 4.35                           | 4.21        | 4.07        | 3.95        | 3.72        | 3.46         | 2.93         |
| CCBCTH2             | 2        | 74.70                           | 89.54                  | 31.64                          | 41.14       | 49.15       | 55.65       | 65.33       | 72.14        | 82.36        |
| TVR <sup>d</sup>    |          |                                 | 81.47                  | 30.54                          | 40.09       | 48.12       | 54.63       | 64.32       | 71.14        | 81.36        |
| I.R. <sup>e</sup>   |          |                                 | 8.07                   | 1.10                           | 1.05        | 1.03        | 1.02        | 1.01        | 1.00         | 1.00         |
| CCD2H2              | 2        | 27.08                           | 80.37                  | 23.18                          | 29.03       | 34.31       | 38.79       | 45.86       | 51.15        | 59.52        |
| TVR <sup>d</sup>    |          |                                 | 67.74                  | 18.80                          | 25.11       | 30.80       | 35.61       | 43.11       | 48.64        | 57.28        |
| I.R. <sup>e</sup>   |          |                                 | 12.63                  | 4.38                           | 3.92        | 3.51        | 3.18        | 2.75        | 2.51         | 2.24         |
| Literature          |          | 25.41 <sup>i</sup>              | 79.821 <sup>j</sup>    | 23.6 <sup>k</sup>              | 30.09       | 35.83       | 40.66       | 48.16       | 53.61        | 62.00        |
| CCDCOH2             | 1        | -20.68                          | 80.53                  | 21.45                          | 26.19       | 30.40       | 33.98       | 39.64       | 43.85        | 50.40        |
| TVR <sup>d</sup>    |          |                                 | 68.30                  | 16.91                          | 21.98       | 26.60       | 30.54       | 36.69       | 41.19        | 48.09        |
| I.R. <sup>e</sup>   |          |                                 | 12.23                  | 4.54                           | 4.21        | 3.80        | 3.44        | 2.95        | 2.66         | 2.31         |
| CCO2H2              | 2        | -64.88                          | 80.93                  | 17.61                          | 21.28       | 24.70       | 27.69       | 32.41       | 35.85        | 40.97        |
| TVR <sup>d</sup>    |          |                                 | 66.62                  | 15.18                          | 19.03       | 22.54       | 25.58       | 30.35       | 33.81        | 38.96        |
| I.R. <sup>e</sup>   |          |                                 | 14.31                  | 2.43                           | 2.25        | 2.16        | 2.11        | 2.06        | 2.04         | 2.01         |
| CCOCTH2             | 1        | 19.72                           | 76.20                  | 20.72                          | 24.51       | 27.63       | 30.21       | 34.26       | 37.29        | 42.01        |
| TVR <sup>d</sup>    |          |                                 | 70.23                  | 18.41                          | 22.34       | 25.66       | 28.42       | 32.73       | 35.92        | 40.83        |
| I.R. <sup>e</sup>   |          |                                 | 5.97                   | 2.31                           | 2.17        | 1.97        | 1.79        | 1.53        | 1.37         | 1.18         |
| CCT2H2              | 2        | 112.43                          | 71.55                  | 21.58                          | 25.60       | 28.72       | 31.21       | 35.08       | 38.00        | 42.71        |
| TVR <sup>d</sup>    |          |                                 | 71.55                  | 21.58                          | 25.60       | 28.72       | 31.21       | 35.08       | 38.00        | 42.71        |
| CDCB2               | 8        | 60.86                           | 102.67                 | 47.25                          | 62.90       | 76.09       | 86.69       | 102.23      | 112.95       | 128.74       |
| TVR <sup>d</sup>    |          |                                 | 95.27                  | 44.95                          | 60.75       | 74.14       | 84.93       | 100.72      | 111.60       | 127.57       |
| I.R. <sup>e,l</sup> |          |                                 | 7.40                   | 2.30                           | 2.15        | 1.95        | 1.76        | 1.51        | 1.35         | 1.17         |
| CDCBCD              | 2        | 53.41                           | 93.20                  | 36.87                          | 48.20       | 57.78       | 65.53       | 77.06       | 85.18        | 97.39        |
| TVR <sup>d</sup>    |          |                                 | 86.25                  | 34.56                          | 46.02       | 55.79       | 63.72       | 75.52       | 83.80        | 96.21        |
| I.R. <sup>e,l</sup> |          |                                 | 6.95                   | 2.31                           | 2.18        | 1.99        | 1.81        | 1.54        | 1.38         | 1.18         |
| CDCBCT              | 2        | 94.96                           | 91.79                  | 36.37                          | 46.61       | 54.90       | 61.49       | 71.17       | 77.95        | 88.15        |
| TVR <sup>d</sup>    |          |                                 | 85.02                  | 34.03                          | 44.35       | 52.81       | 59.58       | 69.54       | 76.50        | 86.93        |
| I.R. <sup>e</sup>   |          |                                 | 6.77                   | 2.34                           | 2.26        | 2.09        | 1.91        | 1.63        | 1.45         | 1.22         |

**Table 2.65 Ideal Gas-phase Thermodynamic Properties<sup>a,e</sup> (Continued)**

| Species           | Symmetry | $\Delta H_f^\circ$ <sup>b</sup> | $S^\circ$ <sup>c</sup> | Cp300 <sup>e</sup> | Cp400 | Cp500 | Cp600 | Cp800 | Cp1000 | Cp1500 |
|-------------------|----------|---------------------------------|------------------------|--------------------|-------|-------|-------|-------|--------|--------|
| CDCD2             | 2        | 48.68                           | 82.12                  | 26.46              | 33.80 | 40.06 | 45.14 | 52.66 | 57.95  | 66.04  |
| TVR <sup>d</sup>  |          |                                 | 71.75                  | 22.26              | 29.33 | 35.45 | 40.53 | 48.31 | 53.99  | 62.85  |
| I.R. <sup>e</sup> |          |                                 | 10.37                  | 4.20               | 4.47  | 4.61  | 4.61  | 4.35  | 3.96   | 3.19   |
| CDCDCT            | 1        | 85.45                           | 80.20                  | 25.76              | 31.83 | 36.76 | 40.70 | 46.56 | 50.75  | 57.23  |
| TVR <sup>d</sup>  |          |                                 | 75.14                  | 23.64              | 29.60 | 34.45 | 38.37 | 44.32 | 48.69  | 55.57  |
| I.R. <sup>e</sup> |          |                                 | 5.06                   | 2.12               | 2.23  | 2.31  | 2.33  | 2.24  | 2.06   | 1.66   |
| CDCT2             | 2        | 131.68                          | 75.73                  | 24.98              | 29.82 | 33.39 | 36.15 | 40.31 | 43.38  | 48.29  |
| TVR <sup>d</sup>  |          |                                 | 75.73                  | 24.98              | 29.82 | 33.39 | 36.15 | 40.31 | 43.38  | 48.29  |

<sup>a</sup> Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm.

<sup>b</sup> Units in kcal/mol.

<sup>c</sup> Units in cal/mol.K.

<sup>d</sup> The sum of contributions from translations, external rotations, and vibrations.

<sup>e</sup> Contribution from internal rotations.

<sup>f</sup> Symmetry number is taken into account ( $-\text{Rln}(\text{symmetry number})$ ).

<sup>g</sup> Reference 44

<sup>h</sup> Reference 45

<sup>i</sup> Reference 42

<sup>j</sup> Reference 43

<sup>k</sup> Reference 44, for all Cp values, shown as literature reference.

<sup>l</sup> Only one Internal Rotor considered here, the second internal rotor was found to have a very high Rotation Barrier during calculations, which are suspected to be erroneous. The torsion frequency for this rotor has been used instead of the internal rotation contribution.

<sup>m</sup> CDCT2 and CCT2H2 do not have any internal rotors and hence no contributions from Internal Rotors to Entropy and Heat Capacity.

## 2.4.5 Group Additivity Values

Group additivity<sup>27</sup> is a straightforward and reasonably accurate calculation method to estimate thermodynamic properties of hydrocarbons and oxygenated hydrocarbons;<sup>28</sup> modifications have also been reported that make it useful for chlorinated and fluorinated hydrocarbons.<sup>29,30,31,32</sup> In this work a set of hydrocarbon and oxy hydrocarbon groups has been derived from the thermodynamic property data of the calculated species.

For example values are reported for the group C/CB/CD/H2 derived from CCBCDH2.

$\Delta H_f^{\circ}$  <sub>298</sub> and  $C_p$ 's of C/CB/CD/H2 are calculated on the basis of

$$\text{CCBCDH2} = (\text{C/CB/CD/H2}) + (\text{CB/C}) + 5(\text{CB/H}) + (\text{CD/C/H}) + (\text{CD/H2})$$

$S^{\circ}$  <sub>298</sub> of C/CB/CD/H2 is calculated on the basis of

$$\text{CCBCDH2} = (\text{C/CB/CD/H2}) + (\text{CB/C}) + 5(\text{CB/H}) + (\text{CD/C/H}) + (\text{CD/H2}) + R \ln(\sigma) + \text{OI}$$

where  $R = 1.987 \text{ cal/mol.K}$ ,  $\sigma$  is symmetry number, and OI stand for optical isomer group. The group values of other groups are estimated in the same manner, each one derived from one species calculated in this work. Selection of the initial group values is critical to development of group additivity for accurate property estimation. These criteria are fully discussed in reference 29 and 30. The group values for  $\Delta H_f^{\circ}$  <sub>298</sub>,  $S^{\circ}$  <sub>298</sub>, and  $C_p$  (T) of all the groups not calculated in this work are taken from the existing literature value.<sup>28,33</sup> The parameters used in calculating Group Values are shown in Table 2.65. All the group values are derived in this work are listed in Table 2.66.

**Table 2.66 Groups (for Group Additivity<sup>a,b</sup>)  
and Structure Parameters for Species**

| Species | Group # | Group ID   | Quantity | No. of Internal |          |
|---------|---------|------------|----------|-----------------|----------|
|         |         |            |          | Rotors          | Symmetry |
| CCB2H2  | 1       | CB/C       | 2        | 2               | 8        |
|         | 2       | CB/H       | 10       |                 |          |
|         | 3       | C/CB2/H2   | 1        |                 |          |
| CCBCDH2 | 1       | CB/C       | 1        | 2               | 2        |
|         | 2       | CB/H       | 5        |                 |          |
|         | 3       | CD/C/H     | 1        |                 |          |
|         | 4       | CD/H2      | 1        |                 |          |
|         | 5       | C/CB/CD/H2 | 1        |                 |          |
| CCBCOH2 | 1       | CB/C       | 1        | 2               | 2        |
|         | 2       | CB/H       | 5        |                 |          |
|         | 3       | CO/C/H     | 1        |                 |          |
|         | 4       | C/CB/CO/H2 | 1        |                 |          |
| CCBCTH2 | 1       | CB/C       | 1        | 1               | 2        |
|         | 2       | CB/H       | 5        |                 |          |
|         | 3       | CT/C       | 1        |                 |          |
|         | 4       | CT/H       | 1        |                 |          |
|         | 5       | C/CB/CT/H2 | 1        |                 |          |
| CCD2H2  | 1       | CD/H2      | 2        | 2               | 2        |
|         | 2       | CD/C/H     | 2        |                 |          |
|         | 3       | C/CD2/H2   | 1        |                 |          |
| CCDCOH2 | 1       | CD/H2      | 1        | 2               | 1        |
|         | 2       | CD/C/H     | 1        |                 |          |
|         | 3       | CO/C/H     | 1        |                 |          |
|         | 4       | C/CD/CO/H2 | 1        |                 |          |
| CCO2H2  | 1       | CO/C/H     | 2        | 2               | 2        |
|         | 2       | C/CO2/H2   | 1        |                 |          |
| CCOCTH2 | 1       | CT/H       | 1        | 1               | 1        |
|         | 2       | CT/C       | 1        |                 |          |
|         | 3       | CO/C/H     | 1        |                 |          |
|         | 4       | C/CO/CT/H2 | 1        |                 |          |
| CCT2H2  | 1       | CT/C       | 2        | 0               | 2        |
|         | 2       | CT/H       | 2        |                 |          |
|         | 3       | C/CT2/H2   | 1        |                 |          |
| CDCB2   | 1       | CB/CD      | 2        | 2               | 8        |
|         | 2       | CB/H       | 10       |                 |          |
|         | 3       | CD/H2      | 1        |                 |          |
|         | 4       | CD/CB2     | 1        |                 |          |
| CDCBCD  | 1       | CD/H2      | 2        | 1               | 2        |
|         | 2       | CD/CD/H    | 1        |                 |          |
|         | 3       | CB/CD      | 1        |                 |          |
|         | 4       | CB/H       | 5        |                 |          |
|         | 5       | CD/CB/CD   | 1        |                 |          |



**Table 2.66 Groups (for Group Additivity<sup>a,b</sup>)  
and Structure Parameters for Species (Continued)**

| Species | Group # | Group ID | Quantity | No. of Internal |          |
|---------|---------|----------|----------|-----------------|----------|
|         |         |          |          | Rotors          | Symmetry |
| CDCBCT  |         | 1        | CT/H     | 1               | 1 2      |
|         |         | 2        | CT/CD    | 1               |          |
|         |         | 3        | CB/CD    | 1               |          |
|         |         | 4        | CD/H2    | 1               |          |
|         |         | 5        | CB/H     | 5               |          |
|         |         | 6        | CD/CB/CT | 1               |          |
| CDCD2   |         | 1        | CD/H2    | 3               | 2 2      |
|         |         | 2        | CD/CD/H  | 2               |          |
|         |         | 3        | CD/CD2   | 1               |          |
| CDCDCT  |         | 1        | CT/H     | 1               | 1 1      |
|         |         | 2        | CT/CD    | 1               |          |
|         |         | 3        | CD/CD/H  | 1               |          |
|         |         | 4        | CD/H2    | 2               |          |
|         |         | 5        | CD/CD/CT | 1               |          |
| CDCT2   |         | 1        | CT/CD    | 2               | 0 2      |
|         |         | 2        | CT/H     | 2               |          |
|         |         | 3        | CD/H2    | 1               |          |
|         |         | 4        | CD/CT2   | 1               |          |

<sup>a</sup>Multiplicity of all species is 1, Spin of all species is 0, Number of Optical Isomers for all species is 1

<sup>b</sup>The last group for each species is the target group whose group value has been determined in this work. For example the last group shown for CCB2H2 is C/CB2/H2, whose group value has been determined in this work.

**Table 2.66 Group Values**

| Groups                  | $\Delta H_f^\circ_{298}$ <sup>a</sup> | $S^\circ_{298}$ <sup>b</sup> | Cp300 <sup>b</sup> | Cp400 | Cp500 | Cp600 | Cp800 | Cp1000 | Cp1500 |
|-------------------------|---------------------------------------|------------------------------|--------------------|-------|-------|-------|-------|--------|--------|
| C/CB2/H2                | -1.61                                 | 9.69                         | 4.97               | 6.74  | 8.17  | 9.19  | 10.49 | 11.46  | 12.83  |
| Cohen <sup>c</sup>      | -6.3                                  |                              |                    |       |       |       |       |        |        |
| C/CB/CD/H2              | -2.16                                 | 8.02                         | 5.45               | 7.41  | 8.89  | 9.93  | 11.22 | 12.17  | 13.68  |
| Cohen <sup>c</sup>      | -2.5                                  |                              |                    |       |       |       |       |        |        |
| C/CB/CO/H2              | -5.96                                 | 8.66                         | 5.62               | 7.66  | 9.19  | 10.34 | 11.75 | 12.76  | 0      |
| C/CB/CT/H2              | -1.81                                 | 9.9                          | 4.36               | 6.33  | 7.87  | 9.04  | 10.6  | 11.77  | 12.53  |
| C/CD2/H2                | -2.62                                 | 10.59                        | 4.66               | 6.25  | 7.66  | 8.78  | 10.42 | 11.71  | 13.9   |
| Cohen <sup>c</sup>      | -4.3                                  |                              |                    |       |       |       |       |        |        |
| C/CD/CO/H2              | -6.13                                 | 10.05                        | 5.16               | 6.93  | 8.26  | 9.3   | 10.72 | 11.93  | -      |
| C/CO2/H2                | -6.08                                 | 12.51                        | 3.55               | 5.54  | 7.06  | 8.33  | 10.01 | 11.45  | -      |
| Cohen <sup>c</sup>      | -6.6                                  |                              |                    |       |       |       |       |        |        |
| C/CO/CT/H2 <sup>c</sup> | -5.38                                 | 10.25                        | 5.28               | 7.17  | 8.51  | 9.57  | 10.99 | 12.21  | -      |
| Cohen <sup>c</sup>      | -5                                    |                              |                    |       |       |       |       |        |        |
| C/CT2/H2                | 3.43                                  | 10.83                        | 4.76               | 6.66  | 8.12  | 9.29  | 10.94 | 12.24  | 12.31  |
| CD/CB2                  | 10                                    | -19.04                       | 2.66               | 4.32  | 5.38  | 5.98  | 6.53  | 6.72   | 6.89   |
| Cohen <sup>c</sup>      | 8                                     |                              |                    |       |       |       |       |        |        |
| CD/CB/CD                | 11.81                                 | -16.87                       | 2.42               | 3.52  | 4.33  | 4.89  | 5.59  | 5.87   | 6.52   |
| Cohen <sup>c</sup>      | 13                                    |                              |                    |       |       |       |       |        |        |
| CD/CB/CT                | 11.3                                  | -15.42                       | 3.63               | 4.54  | 5.72  | 4.98  | 5.31  | 5.56   | 5.91   |
| CD/CD2                  | 12.19                                 | -12.09                       | 2.24               | 3.14  | 4.03  | 4.8   | 5.75  | 5.92   | 6.29   |
| Cohen <sup>c</sup>      | 6.6                                   |                              |                    |       |       |       |       |        |        |
| CD/CD/CT                | 11.05                                 | -12.53                       | 3.25               | 3.79  | 5     | 4.49  | 5.26  | 5.64   | 6.11   |
| CD/CT2                  | 15.22                                 | -12.76                       | 4.18               | 4.4   | 5.9   | 4.07  | 4.62  | 5.19   | 5.8    |

<sup>a</sup> Units in kcal/mol.<sup>b</sup> Units in cal/mol.K.<sup>c</sup> Reference 28.

## 2.5 Summary

Thermodynamic properties of 12 hydrocarbons and three oxygenated hydrocarbons are calculated using density functional method with isodesmic reaction schemes for cancellation of errors in energy. Standard enthalpies of formation,  $\Delta H_f^\circ$ 's are calculated using only isodesmic reaction schemes based on the B3LYP/6-31G(d). Entropies  $S^\circ_{298}$  and heat capacities ( $C_p(T)$ 's ( $300 \leq T/K \leq 1500$ )) are determined with B3LYP/6-31G(d) optimized geometries and frequencies. Enthalpy, Entropy and  $C_p(T)$  properties are determined for C/CD<sub>2</sub>/H<sub>2</sub>, C/CB<sub>2</sub>/H<sub>2</sub>, C/CD/CT/H<sub>2</sub>, C/CB/CD/H<sub>2</sub>, C/CT<sub>2</sub>/H<sub>2</sub>, C/CB/CT/H<sub>2</sub>, C/CO<sub>2</sub>/H<sub>2</sub>, CD/CD<sub>2</sub>, CD/CD/CT, CD/CB/CT, C/CD/CO/H<sub>2</sub>, C/CO/CT/H<sub>2</sub>, C/CB/CO/H<sub>2</sub>, CD/CB/CD, CD/CT<sub>2</sub>, CD/CB<sub>2</sub> groups for use in group additivity. Intramolecular torsion potentials are determined and used for analysis of  $C_p(T)$  and S.

## CHAPTER 3

### CONCLUSIONS

Thermodynamic Properties of CCB<sub>2</sub>H<sub>2</sub>, CCBCDH<sub>2</sub>, CCBCOH<sub>2</sub>, CCBCTH<sub>2</sub>, CCD<sub>2</sub>H<sub>2</sub>, CCDCOH<sub>2</sub>, CCO<sub>2</sub>H<sub>2</sub>, CCOCTH<sub>2</sub>, CCT<sub>2</sub>H<sub>2</sub>, CDCB<sub>2</sub>, CDCBCD, CDCBCT, CDCD<sub>2</sub>, CDCDCT, CDCT<sub>2</sub> are calculated using density functional methods with isodesmic reaction schemes for cancellation of errors in the Enthalpy calculations. Standard enthalpy of formation,  $\Delta H_f^\circ_{298}$  is calculated using isodesmic reaction schemes based on B3LYP/6-31G(d) calculations level. Entropies  $S^\circ_{298}$  and heat capacities ( $C_p(T)$ 's (300 ≤ T/K ≤ 1500)) are determined by B3LYP/6-31G(d) optimized geometries and frequencies. Evaluation of data from the isodesmic reaction analysis, results in  $\Delta H_f^\circ_{298}$  values for CCB<sub>2</sub>H<sub>2</sub> of 42.41 kcal/mol, CCBCDH<sub>2</sub> of 34.7 kcal/mol, CCBCOH<sub>2</sub> of -13.35 kcal/mol, CCBCTH<sub>2</sub> of 74.7 kcal/mol, CCD<sub>2</sub>H<sub>2</sub> of 27.08 kcal/mol, CCDCOH<sub>2</sub> of -20.68 kcal/mol, CCO<sub>2</sub>H<sub>2</sub> of -64.88 kcal/mol, CCOCTH<sub>2</sub> of 19.72 kcal/mol, CCT<sub>2</sub>H<sub>2</sub> of 112.43 kcal/mol, CDCB<sub>2</sub> of 60.86 kcal/mol, CDCBCD of 53.41 kcal/mol, CDCBCT of 94.96 kcal/mol, CDCD<sub>2</sub> of 48.68 kcal/mol, CDCDCT of 85.45 kcal/mol and CDCT<sub>2</sub> of 131.68 kcal/mol.

Enthalpy, entropy and  $C_p(T)$  properties are determined for C/CB<sub>2</sub>/H<sub>2</sub>, C/CB/CD/H<sub>2</sub>, C/CB/CO/H<sub>2</sub>, C/CB/CT/H<sub>2</sub>, C/CD<sub>2</sub>/H<sub>2</sub>, C/CD/CO/H<sub>2</sub>, C/CO<sub>2</sub>/H<sub>2</sub>, C/CO/CT/H<sub>2</sub>, C/CT<sub>2</sub>/H<sub>2</sub>, CD/CB<sub>2</sub>, CD/CB/CD, CD/CB/CT, CD/CD<sub>2</sub>, CD/CD/CT, CD/CT<sub>2</sub> groups for use in group additivity. Calculations result in Group Values for C/CB<sub>2</sub>/H<sub>2</sub> of -1.61 kcal/mol, C/CB/CD/H<sub>2</sub> of -2.16 kcal/mol, C/CB/CO/H<sub>2</sub> of

- 5.96 kcal/mol, C/CB/CT/H<sub>2</sub> of - 1.81 kcal/mol, C/CD<sub>2</sub>/H<sub>2</sub> of -2.62 kcal/mol, C/CD/CO/H<sub>2</sub> of -6.13 kcal/mol, C/CO<sub>2</sub>/H<sub>2</sub> of -6.08 kcal/mol, C/CO/CT/H<sub>2</sub> of -5.38 kcal/mol, C/CT<sub>2</sub>/H<sub>2</sub> of -3.43 kcal/mol, CD/CB<sub>2</sub> of 10 kcal/mol, CD/CB/CD of 11.81 kcal/mol, CD/CB/CT of 11.3 kcal/mol, CD/CD<sub>2</sub> of 12.19, CD/CD/CT of 11.05 kcal/mol, CD/CT<sub>2</sub> of 15.22 kcal/mol.

## **APPENDIX A**

### **SPREADSHEET FOR CALCULATION OF SPECIES ENTHALPY USING ISODESMIC REACTIONS AND B3LYP/6-31G(d) ENERGY VALUES**

This Appendix demonstrates the calculation of the Enthalpy value for each species using an isodesmic reaction, known Enthalpy Values for other species in the reaction except the target species and B3LYP/6-31G(d) Energy Values for all species in the reaction.

**Spreadsheet<sup>c</sup> for Calculating Species Enthalpy using Isodesmic Reaction and B3LYP/6-31G(d) Energy Values**

| Isodesmic Reaction to find $\Delta H_f^\circ_{298}(\text{CCD2H2})$  |                |          |             |              |                           |
|---|----------------|----------|-------------|--------------|---------------------------|
|   | C7H12(CCD2H2)  | +        | C2H4        | =            | C3H6 + C4H6               |
| E298 <sup>a</sup> →   | -195.0653059   |          | -78.4820544 |              | -117.7440033 -155.8172818 |
| $\Delta H_f^\circ_{298}$ <sup>b</sup> →                             |                |          | 12.5399     |              | 4.878107223 26.00382488   |
| $\Delta H^\circ_{\text{rxn},298}$ <sup>c</sup> →                    | -0.01392484    | hartree  | =           | -8.737976348 | kcal/mol                  |
| ANSWER <sup>d</sup> →   | 27.08000846    | kcal/mol |             |              |                           |
| Isodesmic Reaction to find $\Delta H_f^\circ_{298}(\text{CCB2H2})$  |                |          |             |              |                           |
|   | C13H12(CCB2H2) | +        | C2H4        | =            | C7H8 + C8H8               |
| E298 <sup>a</sup> →   | -502.1876041   |          | -78.4820544 |              | -271.3064366 -309.3757556 |
| $\Delta H_f^\circ_{298}$ <sup>b</sup> →                             |                |          | 12.5399     |              | 11.95028717 35.10994371   |
| $\Delta H^\circ_{\text{rxn},298}$ <sup>c</sup> →                    | -0.01253372    | hartree  | =           | -7.865034637 | kcal/mol                  |
| ANSWER <sup>d</sup> →   | 42.38536552    | kcal/mol |             |              |                           |
| Isodesmic Reaction to find $\Delta H_f^\circ_{298}(\text{CCBCDH2})$ |                |          |             |              |                           |
|   | C9H10(CCBCDH2) | +        | C2H4        | =            | C7H8 + C4H6               |
| E298 <sup>a</sup> →   | -348.6268569   |          | -78.4820544 |              | -271.3064366 -155.8172818 |
| $\Delta H_f^\circ_{298}$ <sup>b</sup> →                             |                |          | 12.5399     |              | 11.95028717 26.00382488   |
| $\Delta H^\circ_{\text{rxn},298}$ <sup>c</sup> →                    | -0.01480716    | hartree  | =           | -9.291640972 | kcal/mol                  |
| ANSWER <sup>d</sup> →   | 34.70585303    | kcal/mol |             |              |                           |
| Isodesmic Reaction to find $\Delta H_f^\circ_{298}(\text{CCT2H2})$  |                |          |             |              |                           |
|   | C5H4(CCT2H2)   | +        | C2H4        | =            | C4H4 + C3H4               |
| E298 <sup>a</sup> →   | -192.6469954   |          | -78.4820544 |              | -154.6072265 -116.5380024 |
| $\Delta H_f^\circ_{298}$ <sup>b</sup> →                             |                |          | 12.5399     |              | 70.50669431 44.31166483   |
| $\Delta H^\circ_{\text{rxn},298}$ <sup>c</sup> →                    | -0.01617914    | hartree  | =           | -10.15257214 | kcal/mol                  |
| ANSWER <sup>d</sup> →   | 112.4310313    | kcal/mol |             |              |                           |

**Spreadsheet<sup>e</sup> for Calculating Species Enthalpy using Isodesmic Reaction and B3LYP/6-31G(d) Energy Values (Continued)**

| Isodesmic Reaction to find $\Delta H_f^\circ_{298}$ (CCBCT)  |                |          |             |                       |                           |
|--|----------------|----------|-------------|-----------------------|---------------------------|
|  | C9H8(CCBCT)    | +        | C2H4        | =                     | C8H8 + C3H4               |
| E298 <sup>a</sup> →  | -347.4202569   |          | -78.4820544 |                       | -309.3757556 -116.5380024 |
| $\Delta H_f^\circ_{298}$ <sup>b</sup> →                      |                |          | 12.5399     |                       | 35.10994371 44.31166483   |
| $\Delta H^\circ_{\text{rxn},298}$ <sup>c</sup> →             | -0.01144678    | hartree  | =           | -7.182968918 kcal/mol |                           |
| ANSWER <sup>d</sup> →  | 74.06467746    | kcal/mol |             |                       |                           |
| Isodesmic Reaction to find $\Delta H_f^\circ_{298}$ (CCO2H2) |                |          |             |                       |                           |
|  | C3H4O2(CCO2H2) | +        | C2H4        | =                     | C2H4O + C3H4O             |
| E298 <sup>a</sup> →  | -267.0036997   |          | -78.4820544 |                       | -153.7147535 -191.784604  |
| $\Delta H_f^\circ_{298}$ <sup>b</sup> →                      |                |          | 12.5399     |                       | -40.7982804 -20.07648245  |
| $\Delta H^\circ_{\text{rxn},298}$ <sup>c</sup> →             | -0.01360344    | hartree  | =           | -8.536294634 kcal/mol |                           |
| ANSWER <sup>d</sup> →  | -64.87836822   | kcal/mol |             |                       |                           |
| Isodesmic Reaction to find $\Delta H_f^\circ_{298}$ (CDCD2)  |                |          |             |                       |                           |
|  | C6H8(CDCD2)    | +        | C2H4        | =                     | C4H6 + C4H6               |
| E298 <sup>a</sup> →  | -233.1444265   |          | -78.4820544 |                       | -155.8172818 -155.8172818 |
| $\Delta H_f^\circ_{298}$ <sup>b</sup> →                      |                |          | 12.5399     |                       | 26.00382488 26.00382488   |
| $\Delta H^\circ_{\text{rxn},298}$ <sup>c</sup> →             | -0.00808276    | hartree  | =           | -5.072012728 kcal/mol |                           |
| ANSWER <sup>d</sup> →  | 44.5397625     | kcal/mol |             |                       |                           |
| Isodesmic Reaction to find $\Delta H_f^\circ_{298}$ (CDCDCT) |                |          |             |                       |                           |
|  | C6H6(CDCDCT)   | +        | C2H4        | =                     | C4H6 + C4H4               |
| E298 <sup>a</sup> →  | -231.9400993   |          | -78.4820544 |                       | -155.8172818 -154.6072265 |
| $\Delta H_f^\circ_{298}$ <sup>b</sup> →                      |                |          | 12.5399     |                       | 26.00382488 70.50669431   |
| $\Delta H^\circ_{\text{rxn},298}$ <sup>c</sup> →             | -0.0023547     | hartree  | =           | -1.477597797 kcal/mol |                           |
| ANSWER <sup>d</sup> →  | 85.44821699    | kcal/mol |             |                       |                           |



**Spreadsheet<sup>e</sup> for Calculating Species Enthalpy using Isodesmic Reaction and B3LYP/6-31G(d) Energy Values (Continued)**

| Isodesmic Reaction to find $\Delta H_f^\circ_{298}$ (CDCBCT) |               |         |             |              |                           |
|--|---------------|---------|-------------|--------------|---------------------------|
|  | C10H8(CDCBCT) | +       | C2H4        | =            | C8H8 + C4H4               |
| E298 <sup>a</sup> →  | -385.4979317  |         | -78.4820544 |              | -309.3757556 -154.6072265 |
| $\Delta H_f^\circ_{298}$ <sup>b</sup> →                      |               |         | 12.5399     |              | 35.10994371 70.50669431   |
| $\Delta H^\circ_{\text{rxn},298}$ <sup>c</sup> →             | -0.00299602   | hartree | =           | -1.88003251  | kcal/mol                  |
| ANSWER <sup>d</sup> →  | 94.95677053   |         |             |              | kcal/mol                  |
| Isodesmic Reaction to find $\Delta H_f^\circ_{298}$ (CCDCO)  |               |         |             |              |                           |
|  | C4H6O(CCDCO)  | +       | C2H4        | =            | C3H6 + C3H4O              |
| E298 <sup>a</sup> →  | -231.0352988  |         | -78.4820544 |              | -117.7440033 -191.784604  |
| $\Delta H_f^\circ_{298}$ <sup>b</sup> →                      |               |         | 12.5399     |              | 4.878107223 -20.07648245  |
| $\Delta H^\circ_{\text{rxn},298}$ <sup>c</sup> →             | -0.01125422   | hartree | =           | -7.062135592 | kcal/mol                  |
| ANSWER <sup>d</sup> →  | -20.67613963  |         |             |              | kcal/mol                  |
| Isodesmic Reaction to find $\Delta H_f^\circ_{298}$ (CCTCO)  |               |         |             |              |                           |
|  | C4H4O(CCTCO)  | +       | C2H4        | =            | C3H4 + C3H4O              |
| E298 <sup>a</sup> →  | -229.8277603  |         | -78.4820544 |              | -116.5380024 -191.784604  |
| $\Delta H_f^\circ_{298}$ <sup>b</sup> →                      |               |         | 12.5399     |              | 44.31166483 -20.07648245  |
| $\Delta H^\circ_{\text{rxn},298}$ <sup>c</sup> →             | -0.01279176   | hartree | =           | -8.026957318 | kcal/mol                  |
| ANSWER <sup>d</sup> →  | 19.7222397    |         |             |              | kcal/mol                  |
| Isodesmic Reaction to find $\Delta H_f^\circ_{298}$ (CCBCO)  |               |         |             |              |                           |
|  | C8H8O(CCBCO)  | +       | C2H4        | =            | C7H8 + C3H4O              |
| E298 <sup>a</sup> →  | -384.5973246  |         | -78.4820544 |              | -271.3064366 -191.784604  |
| $\Delta H_f^\circ_{298}$ <sup>b</sup> →                      |               |         | 12.5399     |              | 11.95028717 -20.07648245  |
| $\Delta H^\circ_{\text{rxn},298}$ <sup>c</sup> →             | -0.01166168   | hartree | =           | -7.317820817 | kcal/mol                  |
| ANSWER <sup>d</sup> →  | -13.34827446  |         |             |              | kcal/mol                  |

**Spreadsheet<sup>c</sup> for Calculating Species Enthalpy using Isodesmic Reaction and B3LYP/6-31G(d) Energy Values (Continued)**

| Isodesmic Reaction to find $\Delta H_f^\circ$ (CDCBCD) |                |          |             |              |                           |
|--|----------------|----------|-------------|--------------|---------------------------|
|  | C10H10(CDCBCD) | +        | C2H4        | =            | C4H6 + C8H8               |
| E298 <sup>a</sup> →                                    | -386.7049815   |          | -78.4820544 |              | -155.8172818 -309.3757556 |
| $\Delta H_f^\circ$ <sub>298</sub> <sup>b</sup> →       |                |          | 12.5399     |              | 26.00382488 35.10994371   |
| $\Delta H^\circ$ <sub>rxn,298</sub> <sup>c</sup> →     | -0.00600158    | hartree  | =           | -3.766051466 | kcal/mol                  |
| ANSWER <sup>d</sup> →                                  | 52.33992006    | kcal/mol |             |              |                           |
| Isodesmic Reaction to find $\Delta H_f^\circ$ (CDCT2)  |                |          |             |              |                           |
|  | C6H4(CDCT2)    | +        | C2H4        | =            | C4H4 + C4H4               |
| E298 <sup>a</sup> →                                    | -230.7272954   |          | -78.4820544 |              | -154.6072265 -154.6072265 |
| $\Delta H_f^\circ$ <sub>298</sub> <sup>b</sup> →       |                |          | 12.5399     |              | 70.50669431 70.50669431   |
| $\Delta H^\circ$ <sub>rxn,298</sub> <sup>c</sup> →     | -0.0051032     | hartree  | =           | -3.202309032 | kcal/mol                  |
| ANSWER <sup>d</sup> →                                  | 131.6757977    | kcal/mol |             |              |                           |
| Isodesmic Reaction to find $\Delta H_f^\circ$ (CDCB2)  |                |          |             |              |                           |
|  | C14H12(CDCB2)  | +        | C2H4        | =            | C8H8 + C8H8               |
| E298 <sup>a</sup> →                                    | -540.2643905   |          | -78.4820544 |              | -309.3757556 -309.3757556 |
| $\Delta H_f^\circ$ <sub>298</sub> <sup>b</sup> →       |                |          | 12.5399     |              | 35.10994371 35.10994371   |
| $\Delta H^\circ$ <sub>rxn,298</sub> <sup>c</sup> →     | -0.00506634    | hartree  | =           | -3.179179013 | kcal/mol                  |
| ANSWER <sup>d</sup> →                                  | 60.85916643    | kcal/mol |             |              |                           |

<sup>a</sup>E298 represents the B3LYP/6-31G(d) energy of the species (ZPVE and thermal correction are considered)

<sup>b</sup> $\Delta H_f^\circ$ <sub>298</sub> represents the Enthalpy of formation of the particular species

<sup>c</sup> $\Delta H^\circ$ <sub>rxn,298</sub> represents the Heat of reaction

<sup>d</sup>Answer in each case is the  $\Delta H_f^\circ$ <sub>298</sub> of the target species.

<sup>e</sup>Note that since 1 Hartree = 627.51 kcal/mol the energy values shown in Hartrees are important to 6 significant figures past the decimal, while the Enthalpy values shown in kcal/mol are important to 2 significant digits after the decimal.

## **APPENDIX B**

### **REFERENCE GROUP VALUES USED TO CALCULATE THE GROUP VALUES FOR TARGET GROUPS**

This Appendix contains the following table:

Table A-1 Reference Group Values

This table gives the group values for different groups used in the Group Additivity calculations to determine Group Values for the target groups in this work.

**Table A-1 Reference Group Values**

| Group   | $\Delta H_f^\circ$ <sup>a</sup> | $S^\circ$ <sup>b</sup> | $Cp_{300}^b$ | $Cp_{400}$ | $Cp_{500}$ | $Cp_{600}$ | $Cp_{800}$ | $Cp_{1000}$ | $Cp_{1500}$ |
|---------|---------------------------------|------------------------|--------------|------------|------------|------------|------------|-------------|-------------|
| CB/C    | 5.51                            | -7.69                  | 2.67         | 3.14       | 3.68       | 4.15       | 4.96       | 5.44        | 5.98        |
| CB/CD   | 5.8                             | -7.8                   | 3.59         | 3.97       | 4.38       | 4.72       | 5.28       | 5.61        | 5.75        |
| CB/H    | 3.3                             | 11.53                  | 3.24         | 4.44       | 5.46       | 6.3        | 7.54       | 8.41        | 9.73        |
| CD/C/H  | 8.59                            | 7.97                   | 4.16         | 5.03       | 5.81       | 6.5        | 7.65       | 8.45        | 9.62        |
| CD/CD/H | 6.78                            | 6.38                   | 4.46         | 5.79       | 6.75       | 7.42       | 8.35       | 9.11        | 10.09       |
| CD/H2   | 6.26                            | 27.61                  | 5.1          | 6.36       | 7.51       | 8.5        | 10.07      | 11.27       | 13.19       |
| CO/C/H  | -29.4                           | 34.9                   | 7.03         | 7.87       | 8.82       | 9.68       | 11.2       | 12.2        | -           |
| CT/C    | 27.3                            | 6.35                   | 3.13         | 3.48       | 3.81       | 4.09       | 4.6        | 4.92        | 6.35        |
| CT/CD   | 27.9                            | 6.43                   | 2.57         | 3.54       | 3.5        | 4.92       | 5.34       | 5.5         | 5.8         |
| CT/H    | 27.2                            | 24.7                   | 5.28         | 5.99       | 6.49       | 6.87       | 7.47       | 7.96        | 8.85        |

<sup>a</sup>Group Values for Enthalpy from Reference 28, Units kcal/mol

<sup>b</sup>Group Values for Entropy and Heat Capacity(300K – 1500K) from Reference 33, Units cal/mol/K

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