A COMPUTATIONAL STUDY OF CYCLIC ALKYNES AND THE SEARCH FOR SELECTIVITY IN THE CYCLOADDITIONS OF SUBSTITUTED CYCLOALKYNES

by

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“In science one tries to tell people, in such a way as to be understood by everyone, something that no one ever knew before. But in the case of poetry, it's the exact opposite.”- Paul Dirac

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Abstract

In this work, the geometric and electronic properties of five- to twelve-membered cyclic alkynes have been studied computationally. The data reveal two regimes that have a transition point at a ring size of eight. The data suggest that as the ring size decreases, the occupancy of the π orbitals contributing to the triple bond decreases while the occupancy of the σ bond increases.

The difficulties in organic synthesis with extremely reactive molecules such as cyclohexyne are twofold. They readily engage in unwanted side reactions, and substitution on the molecule imparts little selectivity in its reactions. A major side reaction with cyclohexyne is its tetramerization, and density functional calculations indicate that this occurs through a reaction of cyclohexyne with an anionic starting material. The regiochemistry of [4+2]-cycloadditions of many substituted cycloalkynes has been studied. While in most instances selectivity would be negligible, the calculations have identified selective reactions involving 3,3-dimethylcycloalkynes and 2-*tert*-butylfuran.

List of Abbreviations and Symbols Used

Abbreviations

AO	Atomic Orbital
CGTO	Contracted Gaussian-type Orbital
DFT	Density-Functional Theory
GGA	Generalized Gradient Approximation
GTO	Gaussian-type Orbital
HOMO	Highest Occupied Molecular Orbital
HF	Hartree-Fock theory
IRC	Intrinsic Reaction Coordinate
LCAO	Linear Combination of Atomic Orbitals
LDA	Local-Density Approximation
LSDA	Local-Spin-Density Approximation
LUMO	Lowest Unoccupied Molecular Orbital
MO	Molecular Orbital
QTAIM	Quantum Theory of Atoms in Molecules
SCF	Self-consistent Field
STO	Slater-type Orbital
STQN	Synchronous Transit-guided Quasi-Newton method
TS	Transition State

Symbols

Ψ	Molecular wavefunction
$\mathbf{r}$	Vector describing the positions of all electrons
$\mathbf{R}$	Vector describing the positions of all nuclei
$\hat{H}$	Hamiltonian operator
E	of Schrödinger equation, total atomic or Eigenvalues molecular energy
$\hat{T}$	Kinetic energy operator
$\hat{V}$	Potential energy operator
$\hbar$	Reduced Planck's constant
m_e	Mass of an electron
e	Charge of an electron
ϵ_o	Permittivity of free space
m_i	Mass of particle i
∇^2	Laplacian: $\left(\frac{\partial^2}{\partial_{x^2}}+\frac{\partial^2}{\partial_{y^2}}+\frac{\partial^2}{\partial_{z^2}}\right)$
Z_A	Nuclear charge of nucleus A
r_{ij}	Distance between electron i and j
r_{iA}	Distance between electron i and nucleus A
R_{AB}	Distance between nucleus A and B
χ	One-electron spin orbital
$\varphi(r)$	Atomic orbital
c_{ki}	Atomic orbital expansion coefficient
ζ	Orbital exponent

θ,ϕ	Polar angles
g_{ijk}	Primitive Gaussian function
F	Fock matrix
C	Orbital coefficient matrix
S	Overlap matrix
ε	Orbital energy matrix or dielectric constant
P	Charge density matrix
λ	Perturbation parameter or diagonal term of Hessian matrix
$v_{nuc}(r)$	Nuclear potential of a molecular system
$\rho(r)$	Electron density
$T(\rho)$	Kinetic energy functional
$V_{ee}(\rho)$	Electron-electron potential energy functional
$T_0(\rho)$	Non-interacting kinetic energy functional
$J(\rho)$	Classical Coulomb repulsion energy
$\Delta G^\ddagger$	Gibbs energy barrier for reaction
$\Delta\Delta G_{A,B}{}^\ddagger$	Change in Gibbs energy between TS A and B

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Chapter 1

Introduction

The ability to predict chemical observables using only mathematics is a very worthwhile pursuit. Determining any property of a molecule without ever needing to interact with it has obvious benefits, but the thought of having such a complete understanding of the laws that govern molecular and atomic scales to the point where we are able to fully predict meaningful properties makes it seem hard to believe.

It was the work of Erwin Schrödinger that provided a mathematical description for the interactions of electrons and nuclei in atomic systems. Although Schrödinger's equation offers a description for atomic and molecular systems, the solutions to the equation become incredibly complex for many-electron atoms, even if there are only two electrons. To overcome this problem, theoretical methods were developed to obtain approximate solutions for Schrödinger's equation, allowing chemists to model larger systems. With the explosive increase in computational power and the development of methods to obtain accurate approximations of Schrödinger's equation, it was natural for the evolution of efficient computer programs to emerge. The work of Walter Kohn on the development of density-functional theory, as well as John Pople's work on methods in quantum chemistry, was acknowledged with the 1998 Nobel Prize in chemistry.

Computational chemistry is limited in its effectiveness by two main factors, theory and computing power. In the beginning, performing electronic structure calculations on a small multi-electron system could entail months of work, but with the development of more efficient methods, and the exponential growth in computing power, one can perform a highly accurate calculation on a system containing a half-dozen atoms in an afternoon. Not only do modern calculations take less time, but it is now possible to model a variety of different systems and events. With some researchers focused on highly accurate gas-phase single molecule calculations, and others focusing solid state materials calculations, the application portfolio for computational chemistry has become very diverse.

This thesis will highlight the results of applying modern electronic structure methods to the five- to twelve-membered cyclic alkynes with the primary focus being on the six-membered ring compound, cyclohexyne, and some substituted analogues.

Chapter Two serves as an introduction to cyclic alkyne chemistry and is intended for readers who may be unfamiliar with this area. This section presents the relevant chemistry of the small-ring cyclic alkynes, with an emphasis on the current data available for these species, and from this section the motivation for the studies presented in this thesis will emerge.

Chapter Three contains the theoretical background for the key computational methods used throughout this study, such as density-functional theory (DFT) and quantum theory of atoms in molecules (QTAIM). Furthermore, this section will give an introduction to optimization and other computational algorithms used to find points of interest on the potential energy surface (PES).

Given the lack of a comprehensive study of the electronic and geometric structures of the cycloalkynes, Chapter Four reports the results of a systematic study of the five- to twelve-membered cycloalkynes with contemporary methods within the framework of Kohn-Sham density functional theory (DFT). As a check on the reliability of the computationally efficient DFT calculations, this chapter also reports calculations on the five- to eight-membered rings with the coupled-cluster method and MP2 methods.

Chapter Five will present the results of a regiochemical study of many unsymmetrically substituted cycloalkynes. The chapter will begin with the investigation of unsymmetrically substituted cyclohexyne and then compare these with the results obtained for the seven and eight-membered ring alkynes.

A major side reaction with cyclohexyne is its tetramerization, and the mechanism of how this might occur is elucidated in Chapter Six. Three possible pathways to the tetramer product are explored and their energy profiles are determined using density functional theory. In collaboration with experiment, a mechanism for tetramer formation is proposed.

The thesis ends with some final conclusions of this study and a section dedicated to discussing some possible extensions and future work for the research presented.

Chapter 2

Chemical Background

This Chapter presents the important background information on the chemistry of cycloalkynes. Although limited, an overview of previous experimental research, mainly focused on the characterization of cycloalkynes, will be discussed. Previous computational research on cycloalkynes will also be summarized, and this will lead to the motivation of the studies presented in this thesis.

2.1 Cycloalkyne Stability

The generation of cyclopentyne through methods such as matrix photolysis[1] has led to the suggestion that a five-membered ring is the smallest cyclic structure able to accommodate a carbon-carbon triple bond. There is currently no evidence for the generation of cyclobutyne and cyclopropyne in the literature, but the intermediacy of cyclohexyne[2] and cycloheptyne[3] has been deduced in various experiments. While the existence of cyclopentyne, cyclohexyne and cycloheptyne can at present only be inferred through monitoring the products of reactions and time-resolved infrared spectroscopy, cyclooctyne[4] and cyclononyne[5] are stable and isolable. Figure 2.1 summarizes the stabilities of the small-ring cycloalkynes.

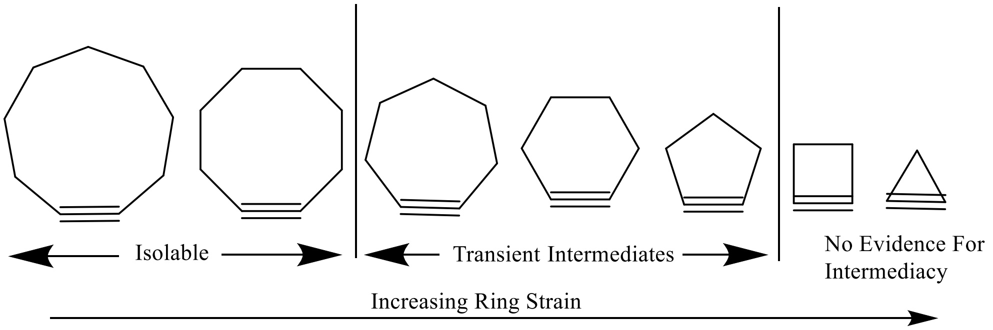


Figure 2.1: As ring strain increases with decreasing ring size, the isolability decreases.

With cyclooctyne being the smallest isolable cycloalkyne, experimentalists have looked at introducing additional unsaturation into the eight-membered ring to monitor ring strain as a function of level of unsaturation.[6,7] As shown in Figure 2.2, it was determined that the additional unsaturation leads to an increase in ring strain, along with reactivity, depending on the relative position and the number of double bonds introduced into the ring.

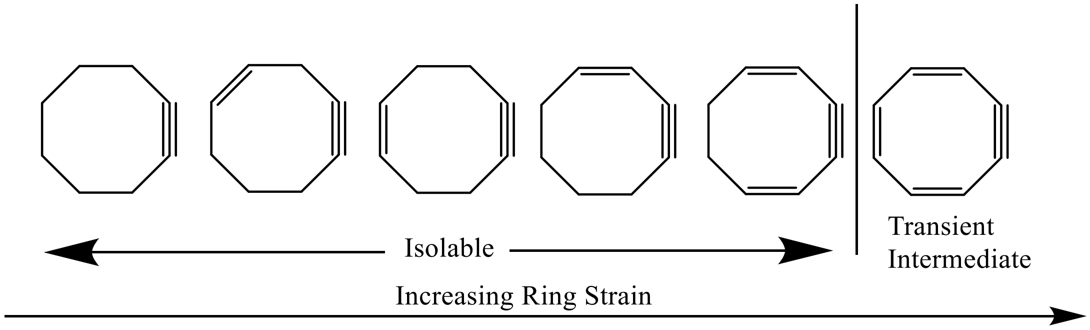


Figure 2.2: The introduction of additional unsaturation in leads to an increase in reactivity and ring strain.

2.2 Oligomerization

In the absence of an additional reagent, cycloalkynes can react with another cycloalkyne. In the event that two cycloalkynes come within close enough contact with one another, oligomerization can occur. For example, cyclooctyne trimerizes to give a benzene derivative when heated.[8,9]

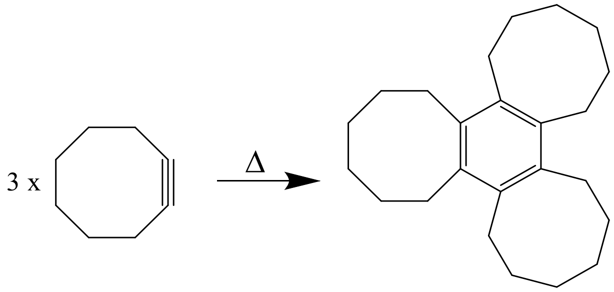


Figure 2.3: As an example of cycloalkyne oligomerization, cyclooctyne will trimerize to give a benzene derivative.

2.3 Experimental Studies on Cycloalkynes

Early experimental research on cycloalkyne chemistry has focused on the generation and detection of small-ring cycloalkynes or cycloalkyne derivatives.[2,3,8,10-12] Furthermore, experimentalists have probed the molecular structure of some angle strained cyclic alkynes by means of electron diffraction; there is structural information for both cyclooctyne[4] and cyclononyne.[5] The concept of cycloalkyne ring strain has been further probed by introducing additional unsaturation into the smallest isolable cycloalkyne, cyclooctyne, revealing that the relative position and number of double bonds will increase ring strain and reactivity.[6,7] Due to the inherent ring strain in cycloalkynes, many experimental studies include investigating the reactivity of inorganic angle-strained cycloalkyne derivatives.[13,14] In a 1983 review on angle strained cycloalkynes[15], Krebs and Wilke focused their discussion on cycloalkynes with a C-C≡C-bond angle deformation larger than 10° from the preferred 180° angle. In this review, Krebs and Wilke discussed the molecular structure, thermochemical properties, and theoretical and experimental data for angle strained cycloalkynes and various derivatives.

2.4 Theoretical Studies on Cycloalkynes

Previous theoretical studies have examined the electronic structure of singlet state cycloalkynes,[16-19] although there have been studies investigating cycloaddition reactions involving simple cycloalkynes, such as 1,3-dipolar cycloadditions of seven- through ten-membered cycloalkynes with triazoles.[20] Electronic structure calculations have shown that for cycloalkynes containing less than six carbons there is a considerable amount of diradical character due to the distortion of one of the equivalent carbon-carbon π-bonds.[16,19] This suggests that one should take caution when trying to model the strained cycloalkyne regime and that the borderline between strained and unstrained may not be as clear cut as previously mentioned. Olivella *et al.* published the first theoretical comparison of the four smallest cycloalkynes in terms of geometric, energetic, and vibrational properties.[17] They reported that the triplet state lies 42 kcal/mol above the singlet ground state. There have been studies that further investigated cycloalkynes of ring sizes four through six, looking at the interconversion of these compounds to their corresponding cycloalkylidenecarbenes.[21] Additionally, studies have aimed at calculating structures, heats of formation, dipole moments, and conformational equilibria for larger members of the cycloalkyne series, specifically cyclooctyne, cyclononyne, and cyclodecyne, using molecular mechanics calculations (MM3).[22] Few ab initio molecular orbital studies have covered the mid-sized cycloalkynes, namely cyclohexyne through cyclooctyne. Nonetheless, there has been a study exploring the conformational properties of cyclohexyne, cycloheptyne, and cyclooctyne.[23]

Chapter 3

Theoretical Background

The main goal of quantum chemistry is to describe the electronic structure of a given chemical system. Methods have been developed that can be used to solve this problem, but it is important to choose a method appropriate for the system under investigation. Further details are available in a standard quantum chemistry textbook.[24-26]

This chapter contains an outline of the methods used to perform quantum chemical calculations on cycloalkyne systems, of which the results will be presented in the following chapters. To begin, an outline of the basic concepts needed for a general understanding of quantum chemistry will be provided followed by a discussion of a few relevant electronic structure theories. A large emphasis will be put on density functional theory (DFT), because much of the work presented in this thesis utilized DFT methods. To conclude this chapter, methods for geometry optimization and a brief introduction to the quantum theory of atoms in molecules (QTAIM) will be presented.

3.1 The Schrödinger Equation

The birth of quantum chemistry can be attributed to Erwin Schrödinger, who in 1926 published his famous eigenvalue problem termed the Schrödinger equation.[27] Many applications of quantum mechanics to chemistry make use of the time-independent Schrödinger equation, shown below.

$$\hat{\mathrm{H}}\Psi(\mathbf{r},\mathbf{R}) = \mathrm{E}\Psi(\mathbf{r},\mathbf{R}) \tag{3.1}$$

The Hamiltonian operator, Ĥ, is a differential operator that represents the total energy of the system under study. The eigenfunctions of the Schrödinger equation are functions of **r**, and **R**, the spatial coordinates of the electrons and nuclei, respectively. For each particular eigenfunction, there is a corresponding eigenvalue, E, representing the total atomic or molecular energy. One of the most important states to look at in chemistry is the ground state, Ψ_0, which is the state with the lowest eigenvalue, E_0.

As mentioned above, the operator associated with a system's energy is the Hamiltonian. This operator contains the mathematical operations associated with the kinetic and potential energy. The energy arising from the momentum of the particles is accounted for in the kinetic operator. The second term, the potential energy operator, accounts for the energy associated with the three classical Coulombic interactions in a molecular system. These three interactions are electron-electron repulsion, nucleus-nucleus repulsion, and electron-nucleus attraction. The kinetic energy operator, $\hat{T}$, and the potential energy operator, $\hat{V}$, are shown below:

$$\hat{T} = \sum_{i}^{N+M} -\frac{1}{2m_i} \nabla_i^2 \tag{3.2}$$

$$\hat{V} = -\sum_{i}^{N}\sum_{A}^{M}\left(\frac{Z_A}{r_{iA}}\right) + \sum_{i}^{N}\sum_{J>i}^{N}\left(\frac{1}{r_{ij}}\right) + \sum_{A}^{M}\sum_{B>A}^{M}\left(\frac{Z_A Z_B}{R_{AB}}\right) \tag{3.3}$$

where Z_A and Z_B are the nuclear charges of nuclei A and B, m_i is the mass of particle i, r_{ij} is the distance between electron i and j, r_{iA} is the distance between electron i and nucleus A, and R_{AB} is the distance between nuclei A and B.

An analytical solution to the Schrödinger equation is not possible for systems containing more than one electron. To improve the utility of the Schrödinger equation, and ultimately apply it to larger systems, approximations must be made. Fortunately, a simplifying first approximation exists.

3.1.1 The Born-Oppenheimer Approximation

The first approximation arises from the fact that the masses of nuclei are much larger than the mass of an electron. Due to such a large difference in mass, the velocity of the nuclei with respect to the electrons will be significantly smaller.[28] Considering the nuclei as fixed in space, the term associated with the kinetic energy of the nuclei can be omitted, leaving the Schrödinger equation for electronic motion. In this approximation, the position of the nuclei are fixed while position coordinate of each electron, $\mathbf{r}_i$, can change.

$$\hat{H}_{el}\Psi(\boldsymbol{r},\boldsymbol{R}) = E_{el}\Psi(\mathbf{r},\mathbf{R}) \tag{3.4}$$

For any set of nuclear coordinates, the electronic Hamiltonian operator can be used to calculate an electronic energy. To obtain the total energy of the system, the classical Coulombic repulsion of the nuclei is added to the electronic energy.

$$E_{tot} = E_{el} + \sum_{A}^{M}\sum_{B>A}^{M}\left(\frac{Z_A Z_B}{R_{AB}}\right) \tag{3.5}$$

The Born-Oppenheimer approximation is not a major source of error. In fact, the approximation only breaks down when nuclear motion must be included for an accurate description of a certain property, such as electronic spectra.

3.1.2 The Orbital Approximation

The electronic wavefunction is a 3N-dimensional function of the position of all, N, electrons in the system. To approximate $\Psi(\mathbf{r})$, a product of one-electron functions is used. These one-electron functions depend only on the Cartesian coordinates of a single electron and are called molecular orbitals (MO), $\Psi_i(x_i, y_i, z_i)$. The probability distribution of the electron in space is the square modulus of its corresponding MO, $|\Psi_i(x_i, y_i, z_i)|^2$. However, to obtain a total description of the electron, the electron spin must be included. Commonly referred to as spin up and spin down, an electron's spin is denoted α and β, respectively. The product of a spatial function and a spin function (α or β) gives the spin orbital, $\chi_i(\mathbf{r},s)$.

To form the total electronic wavefunction the spin orbitals must be chosen to satisfy the Pauli Exclusion Principle, which states that no two electrons of the same spin can occupy the same orbital. Thus, the wavefunction must be antisymmetric with respect to interchanging the coordinates of any two electrons. That is, interchanging the coordinates of two electrons must result in a sign change of the total electronic wavefunction. Due to the uncertainty principle, interchanging two electrons should not change the total electronic distribution, $|\Psi(\mathbf{r})|^2$.

$$|\Psi(1,2,\ldots,i,\ldots,j,\ldots,N-1,N)|^2 = |-\Psi(1,2,\ldots,j,\ldots,i,\ldots,N-1,N)|^2 \qquad (3.6)$$

Slater introduced a convenient determinant form in 1929 now known as a Slater determinant.[29,30] The determinant satisfies the requirements discussed above and has the form seen below:

$$\Psi(1,2,\ldots,N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \ldots & \chi_N(N) \end{vmatrix} \qquad (3.7)$$

In the Slater determinant, all elements in a given column represent one spin orbital and all elements in a given row represent one electron. The properties of the determinant innately invoke the requirements mentioned above. The interchange of any two rows corresponds to the interchange of the coordinates of any two electrons which changes the sign of the determinant. Furthermore, if any two columns have the same value the determinant will vanish, which corresponds to any two electrons of the same spin occupying the same orbital.

3.1.3 Linear Combination of Atomic Orbitals (LCAO)

The MOs mentioned above, $\Psi(\mathbf{r})$, are further approximated as linear combinations of atomic orbitals (AO). These AOs are atom-centered functions, $\phi(\mathbf{r})$, and are commonly referred to as basis functions when expanded with their associated coefficients, c_{ki}. A basis set is a set of K basis functions used to produce the MOs through the following expression:

$$\Psi_i(\boldsymbol{r}) = \sum_{k}^{K} c_{ki}\phi_k(\boldsymbol{r}) \tag{3.8}$$

This approach is called a linear combination of atomic orbitals (LCAO). To compute accurate MOs for a system using the LCAO approach, a sufficiently flexible basis set must be used.

3.2 Basis Sets

As mentioned above, to further approximate the molecular wavefunction, molecular orbitals are approximated by a basis set of atom-centered functions called atomic orbitals. Basis functions contain three components: a normalization constant, an angular component, and a radial component. The normalization constant is used to ensure that the atomic orbital is normalized. The angular component describes the shape and type of orbital (e.g. s, p, etc.), while the radial component describes the spatial separation away from the nucleus (e.g. 2p, 3p, etc.). The most straightforward basis set is a minimal basis set that is composed only of a single basis function for each inner-shell and outer-shell atomic orbital for each atom. An extended basis set is any basis set larger than the minimal basis set. Extended basis sets have multiple basis functions describing each orbital and allow for more orbital flexibility of the atomic orbitals. While minimal basis sets allow for shorter calculation times, calculations with extended basis sets are more time consuming, but always provide more accurate results due to the variational principle.

3.2.1 Slater Type and Gaussian Type Orbitals

In 1930, Slater proposed Slater-type orbitals (STOs) for modeling atomic orbitals.[31] These STOs use exponential functions for the radial component that result in a cusp being formed at the nucleus. The STOs contain a parameter, ζ, called the orbital exponent that determines the size of the orbital. The form of a STO centered on an atom a is shown below:

$$\phi(\mathbf{r}) = \mathrm{N} r_a^{(n-1)} e^{-\zeta r_a} Y_l^m(\theta_a \phi_a) \tag{3.9}$$

where N is the normalization constant and is a product of the radial component, $r_a^{(n-1)} e^{-\zeta r_a}$, and the angular component, $Y_l^m(\theta_a \phi_a)$, which determines the shape of the orbital. In practice, one can obtain accurate results by using only a few strategically chosen STOs. The downside of using STOs is that the calculations can become very time consuming due to computational demand of performing multi-centre integrations.

In 1950 Boys proposed the use of Gaussian-type functions (GTFs), or Gaussian-type orbitals (GTOs), to describe the atomic orbitals and ultimately speed up the molecular integral evaluations.[32] A Cartesian Gaussian centered on an atom has the form,

$$g_{ijk} = N x_a^i y_a^j z_a^k e^{-\zeta r_a^2} \tag{3.10}$$

where N is the normalization constant, i, j, and k are nonnegative integers, ζ is a positive orbital exponent, x_a, y_a, z_a are Cartesian coordinates relative to nucleus a, and r_a is the distance to nucleus a. Instead of a cusp at the nucleus, as described by STOs, GTOs are smooth and continuous at the nucleus and are easier to handle in the integral evaluations. Due to the smoothness and loss of the cusp at the nucleus, the description of the orbitals at the nucleus is incorrect. To overcome this deficiency, a sum of GTOs, each with a different orbital exponent, is used to describe each atomic orbital, $\phi(\mathbf{r})$. Introducing a contraction coefficient, d_p, into the sum produces basis functions known as contracted GTOs (CGTO), which resemble more closely the STOs than a single GTO.

$$\phi(\mathbf{r}) = \sum_p d_p g_p \tag{3.11}$$

3.2.2 Split-Valence Basis Set

Split-valence basis sets have two or more basis functions describing each valence orbital and only one basis function describing each core orbital. Experience has shown that the valence orbitals require more than one basis function in order to achieve accurate results in terms of energy, whereas for many purposes the core orbitals can be described with just a minimal basis set.

3.2.3 Polarization Functions

Atomic orbitals become distorted when interacting in a molecular environment. To model this distortion effect, basis functions with an angular momentum quantum number one higher than the orbitals occupied in a given atom are added. An example of this for the carbon atom would be the addition of d-type orbitals to the basis set. To gain more orbital angular flexibility, it is possible to add more polarization functions to the basis set. For example, a carbon atom could be described with both d- and f-type orbitals. It is common to add these polarization functions to all non-hydrogen atoms as hydrogen is less prone to polarization, except in a minority of cases where the polarization of hydrogen is important.

3.2.4 Pople and Dunning Basis Sets

The most common basis sets used today fall into two regimes, Pople and Dunning. Pople[33] and Dunning[32,34,35] basis sets are both split-valence and make use of contracted Gaussian functions to model the atomic orbitals.

The Dunning basis sets use the naming convention cc-pVnZ, where n is the number of basis functions used to represent each valence orbital in a given atom. Polarization functions are included in the Dunning basis sets and designated by ‘p’ in the naming convention. These basis sets were designed for high level *ab initio* calculations due to the very large range of basis sets that have been developed. The ‘cc’ in the naming convention stands for correlation consistent, coming from the fact that these basis sets were designed to have consistent changes in the correlation energy as the basis set is increased.

The Pople basis sets are comprised of both minimal and split-valence basis sets. Minimal basis sets are composed of CGTOs and are denoted by STO-nG[36], where n is the number of primitive Gaussians used to describe each atomic orbital. The naming convention used for the split-valence Pople basis sets is X-YZG, where X represents the number of primitive GTOs used to produce each core orbital, Y is the number of GTOs used for the firsts set of valence orbitals, and Z for number used in the second set. Along with double-zeta basis sets, there are also valence triple-zeta seta basis sets, e.g. 6-311G(d,p). Pople basis sets can also include polarization functions; the naming convention is to include the orbitals used in brackets after the ‘G’ in the basis set definition. Using the previous example of 6-311G(d,p), this basis set is a valence triple-zeta basis set that includes a set d-type orbitals on all non-hydrogen atoms and one set of p-type orbitals on all hydrogens.

3.3 The Hartree-Fock Method

Today, the most basic *ab initio* electronic structure method is the Hartree-Fock (HF) method. In 1927, Hartree proposed a method for solving the atomic many-body Schrödinger equation.[37] Hartree assumed that each electron moves in an electric field generated from the nuclei and the averaged charge distribution of all other electrons; this assumption is called the mean field approximation. Gaunt[38] and Slater[39] showed that the method proposed by Hartree could be solved using a Slater determinant to construct the many electron wavefunction. Shortly thereafter, Slater[40] and Fock[41] showed that the variational principle should be used to obtain the wavefunction comprised of the product of one electron functions. Hartree developed a determinant form for the HF method in 1935.[42] The modern HF method known today uses atomic basis functions to approximate the one electron functions.[31,43]

3.3.1 The Variational Principle

The variational theorem states that given a system whose Hamiltonian operator, $\hat{H}$, is time independent and whose lowest energy eigenvalue is E_1, and if ϕ is any normalized, well-behaved function that satisfies the boundary conditions of the problem, then,

$$\int \phi^* \hat{\mathrm{H}}\phi d\tau \geq E_1 \tag{3.12}$$

The function ϕ is called a trial wave function. The trial wave function, unless equal to the exact wave function, Ψ, will always yield an energy greater than the exact wavefunction. The variational theorem allows one to calculate an upper bound for a system's ground–state energy. As mentioned above, Slater[40] and Fock[41] proposed this method for solving the wavefunction under the infrastructure put forth by Hartree. The components of the trial wavefunction can be varied to give the lowest energy and better approximate the exact wavefunction. Since the spin orbitals that construct the Slater determinant are defined through a linear combination of atomic orbitals, the expansion coefficients, c_{ki}, can be varied to yield the lowest energy wavefunction. This process gives the best MO description for a given basis set.

3.3.2 Roothaan-Hall Equations

In 1951, Roothaan[44] and Hall[45] separately developed the Roothaan-Hall equations that make the solution of the Hartree-Fock method more computationally manageable. To do this, they transform the Hartree-Fock method into a linear algebra problem.

$$\boldsymbol{FC} = \boldsymbol{FS}\epsilon \tag{3.13}$$

They define a Fock matrix, **F**, whose elements, F_{ij}, are equal to the addition of the core Hamiltonian and an electron-electron repulsion term. The core Hamiltonian, H_{ij}^{core}, only accounts for kinetic energy and the electron-nuclear interaction; it does not include an electron-electron repulsion term.

$$F_{ij} = H_{ij}^{core} + \sum_{k=1}^{K}\sum_{l=1}^{K} P_{kl}\left[(ij|kl) - \frac{1}{2}(ik|jl)\right] \tag{3.14}$$

$$(ij|kl) = \iint \frac{\phi_i(1)\phi_j(1)\phi_k(2)\phi_l(2)}{r_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \tag{3.15}$$

The second term in F_{ij} accounts for the Coulombic electron-electron repulsion and electron exchange. P_{kl} is an element of **P**, the charge density matrix and the summations are over all basis functions, K. **S** is the overlap matrix, whose elements, S_{ij}, account for the overlap between pairs of basis functions, ϕ_i and ϕ_j.

$$S_{ij} = \langle \phi_i | \phi_j \rangle \tag{3.16}$$

C is a matrix constructed from the coefficients of the molecular orbitals and ϵ is a diagonal matrix of one-electron orbital energies.

The Roothaan-Hall equations must be solved iteratively due to the charge density matrix, **P**, being dependent on the orbital coefficients which have to be solved by the total equation itself. Using a procedure known as self-consistent field (SCF), the best values for the coefficients can be obtained in order to yield the lowest energy wavefunction. Initial guesses for **P** and **S**, are used as input to construct the Fock matrix, which is then used to calculate new **C** and **P** matrices. The process is self-consistent when the new charge density matrix, **P**, is equal to the previous one (or close to equal depending on the convergence criteria). The orbital energies, ϵ, and optimized molecular orbital coefficients, **C**, are obtained from the self-consistent charge density matrix, **P**.

3.4 Multi-Configurational Methods

The correlation energy is defined as the difference between the exact energy and the Hartree-Fock energy. The Hartree-Fock method uses the mean field approximation which simplifies the calculations and allows the entire wavefunction to be described using a single determinant. Although convenient, using the single determinant in the Hartree-Fock method does not account for the correlated motions of electrons. To describe the correlation, more than one determinant must be used.

With N electrons and M basis functions, a solution to the ground state HF wavefunction produces 0.5N occupied MOs and M-0.5N virtual MOs. Excited states can be obtained by swapping one or more of the occupied MOs with one or more of the virtual MOs to generate an excited wavefunction that is represented as a determinant.

Two types of multi-configurational methods, Møller-Plesset perturbation and coupled cluster perturbation, are briefly described below.

3.4.1 Møller-Plesset Perturbation

In 1934, Møller and Plesset proposed that electron correlation could be viewed as a perturbation to the HF Hamiltonian.[46] They decomposed the total Hamiltonian into the Hamiltonian from the SCF calculation, $\hat{\mathrm{H}}_0$, and a perturbation that includes electron correlation, $\hat{V}$. In order to improve the eigenfunctions and eigenvalues of the SCF Hamiltonian, a perturbation parameter, λ, is added to the perturbation term.

$$\hat{\mathrm{H}} = \hat{\mathrm{H}}_0 + \lambda\hat{V} \tag{3.17}$$

The eigenfunctions, Ψ_i, and eigenvalues, E_i, can be represented as Taylor expansions containing the perturbation parameter.

$$\Psi_i = \Psi_i^{(0)} + \lambda\Psi_i^{(1)} + \lambda^2\Psi_i^{(2)} + \cdots \tag{3.18}$$

$$E_i = \mathrm{E}_i^{(0)} + \lambda\mathrm{E}_i^{(1)} + \lambda^2\mathrm{E}_i^{(2)} + \cdots$$

The energy corrections are evaluated using the following expressions where the sum of the two lowest-order energies is equal to the HF ground state energy.

$$\begin{aligned}
\mathrm{E}_i^{(0)} &= \left\langle \Psi_i^{(0)} \middle| \hat{\mathrm{H}}_0 \middle| \Psi_i^{(0)} \right\rangle \\
\mathrm{E}_i^{(1)} &= \left\langle \Psi_i^{(0)} \middle| \hat{V} \middle| \Psi_i^{(0)} \right\rangle \\
\mathrm{E}_i^{(2)} &= \left\langle \Psi_i^{(0)} \middle| \hat{V} \middle| \Psi_i^{(0)} \right\rangle
\end{aligned} \tag{3.19}$$

In order to improve upon the HF energy, at least the second order perturbation must be applied. The highest perturbation applied in a calculation is termed n, where the general name for the method is MPn. The MP2 method has a second-order energy defined by

$$E_0^{(2)} = \sum_{a<b,r<s} \frac{\left| \left\langle \Psi_0 \middle| \sum \frac{1}{r_{ij}} \middle| \Psi_{ab}^{rs} \right\rangle \right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \tag{3.20}$$

where a and b are occupied orbitals, r and s are virtual orbitals, and i and j are electrons. The ε terms in the denominator are the energies of the orbitals, a, b, r, and s.[47]

3.4.2 Coupled Cluster

Another multi-configurational method is known as the coupled cluster method.[48,49] This method also produces a linear combination of excited determinants from the HF reference wavefunction. The coupled cluster wavefunction is shown below,

$$|\Psi\rangle = e^{T}|\phi_0\rangle \tag{3.21}$$

where $|\phi_0\rangle$ is a Slater determinant constructed from HF molecular orbitals and T is the cluster operator. The Schrödinger equation can be written using the coupled cluster wave function as,

$$H|\Psi_0\rangle = He^{T}|\phi_0\rangle = Ee^{T}|\phi_0\rangle \tag{3.22}$$

The cluster operator is usually written in the form,

$$T = T_1 + T_2 + T_3 + \cdots \tag{3.23}$$

where T_n is the operator of all n excitations. Common types of coupled cluster methods include CCS, CCSD, and CCSD(t). In CCS, T would only contain T_1 where in CCSD(t) T would contain T_1, T_2, and T_3.

The theory behind evaluating the coupled cluster equations is complex and is beyond the scope of this work.

3.5 Density-Functional Theory

The wavefunction of a many-electron molecule contains more information than is required to describe the properties of the molecule. Density-functional theory (DFT) aims to calculate properties of a system using functions that involve fewer variables than the wavefunction. DFT methods are the most widely used electronic structure methods in computational chemistry. The main attraction of using DFT is that it is accurate but about as computationally demanding as HF. The formulation of DFT started in 1964 with Pierre Hohenberg and Walter Kohn.[50]

3.5.1 The Hohenberg-Kohn Theorem

The theory proposed by Hohenberg and Kohn simply states that the properties of a multi-electron system can be uniquely determined by its electron density, $\rho(\mathbf{r})$. The "functional" term in DFT comes from the fact that the ground state electronic energy, E_0, is a functional of the ground-state electron density, ρ_0.

$$E_0 = E[\rho_0] \tag{3.24}$$

Hohenberg and Kohn showed that an energy expression can be written, shown below, that depends only on an external potential, ν, and the electron density, $\rho(\mathbf{r})$. We have,

$$E_0 = E_\nu[\rho] = \int \rho\,(\boldsymbol{r})\nu(\boldsymbol{r})d\boldsymbol{r} + F[\rho] \tag{3.25}$$

where $F[\rho]$ is defined by $F[\rho] \equiv T[\rho] + V_{ee}[\rho]$. This can be solved variationally using ρ as the trial function. However, although Hohenberg and Kohn proved that the energy functionals in $F[\rho]$ exist, they offered no tangible expressions for them.

3.5.2 Kohn-Sham Theory

The Hohenberg-Kohn theorem does not state how to calculate E_0 from ρ_0 without first finding the wavefunction. In 1965, Kohn and Sham[51] devised a practical method for finding ρ_0, and even better, finding E_0 from ρ_0. The Kohn-Sham (KS) formulation of DFT is only able to give approximate results due to the unknown functional contained in their equations. Kohn and Sham considered a system of N non-interacting electrons, which has the same density as the real N-electron density. The non-interacting density is as follows for a closed-shell system,

$$\rho(\boldsymbol{r}) = 2\sum_{i}^{\frac{N}{2}} \Psi_i^2(\boldsymbol{r}) \tag{3.26}$$

The orbitals, $\Psi_i(\mathbf{r})$, satisfy a Schrödinger equation, seen below, whose Hamiltonian does not include an explicit term for the electron-electron repulsion and where ν_0 is the external potential that yields the non-interacting density.

$$-\frac{1}{2}\nabla^2\Psi_i(\boldsymbol{r}) + \nu_0\Psi_i = \epsilon_i\Psi_i(\boldsymbol{r}) \tag{3.27}$$

To approximate the kinetic energy of the interacting system, Kohn-Sham theory states that it is approximately equal to the kinetic energy of the non-interacting system, $T_0(\rho)$, which is given by,

$$T_0(\rho) = -\frac{1}{2}\sum_i 2\int \Psi_i\,(\boldsymbol{r})\nabla^2\Psi_i(\boldsymbol{r})d\boldsymbol{r} \tag{3.28}$$

To approximate the electron-electron repulsion term, a classical expression for the electrostatic interelectronic repulsion energy as if the electrons formed a continuous distribution of charge with electron density ρ is used; we can define this repulsion energy as a function of density as $J_{ee}(\rho)$.

$$J_{ee}(\rho) = \frac{1}{2}\iint \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}d\boldsymbol{r}_1\,d\boldsymbol{r}_2 \tag{3.29}$$

Using the two approximations, a relationship between the kinetic energy and electron-electron repulsion energy of the interacting system can be related to $T_0(\rho)$ and $J_{ee}(\rho)$ by,

$$T(\rho) + V_{ee}(\rho) = T_0(\rho) + J_{ee}(\rho) + E_{XC}(\rho) \tag{3.30}$$

where $E_{XC}(\rho)$ is called the exchange-correlation energy. This equation can be substituted into the equation proposed by Hohenberg and Kohn for F[ρ] to give,

$$E_{\mathrm{v}}(\rho) = T_0(\rho) + J_{ee}(\rho) + E_{XC}(\rho) + \int \mathrm{v}\rho(\mathbf{r})\mathrm{d}\mathbf{r} \tag{3.31}$$

This equation contains only one unknown term, $E_{XC}(\rho)$.

3.5.3 Density-Functional Approximation

The main problem with DFT is that E_{XC} is unknown. However, approximations have been developed to allow DFT to be useful in chemistry. The local-density approximation (LDA) is the first approximation that provides fairly accurate results. [51] The LDA functional depends only on the density at the coordinates where it is evaluated, hence it is local. Successful local approximations are those that have been derived from the uniform electron gas model. The local-density approximation for the exchange-correlation energy is shown below as,

$$E_{xc}^{LDA}(\rho) = \int \rho(\boldsymbol{r})\epsilon_{xc}(\rho)d\boldsymbol{r} \tag{3.25}$$

where ϵ_{xc} is the exchange-correlation energy per particle in the uniform electron gas of charge density ρ. Decomposing the exchange-correlation energy into separate expressions for exchange and correlation allows them to be evaluated separately. The exchange term is analytical for a uniform electron gas, leaving expressions for the correlation term to be approximated. The LDA method has been extended to depend on the spin-dependent uniform electron gas model; this method is known as the local-spin-density approximation (LSDA). Using LSDA, the atomization energies overestimate bond strengths by ~160 kJ/mol, which is about half of the absolute error using HF.[52]

To improve on the LSDA method, functionals that depend on both the electron density and the gradient of the electron density have been developed. These functionals are known as GGAs, or generalized gradient approximated functionals.[53,54] The exchange correlation energy dependent on the gradient of the density is usually shown as a correction factor to E_{XC} from LSDA,

$$E_{XC} = E_{XC}^{LSDA}(\rho_\sigma) + bE_{XC}^{GGA}(\rho_\sigma, \nabla\rho_\sigma) \tag{3.26}$$

where b is fit to theoretical atomic data to yield results that improve the error by about an order of magnitude compared to LSDA. There are also functionals that depend on the density, gradient of the density, Laplacian of the density, and the kinetic energy density; these are called meta-GGA methods.

Some DFT methods mix in some HF exchange energy into E_{XC} giving a hybrid method.[55] The exchange-correlation energy equation for hybrid methods takes the form of,

$$E_{XC}^{hybrid} = E_{XC}^{GGA} + \alpha_0(E_X^{HF} - E_X^{GGA}) \tag{3.27}$$

where α_0 is similar to the b parameter mentioned above.

3.5.4 Relevant DFT Methods

A common exchange-correlation hybrid functional is B3LYP, which is composed of the Becke 88 exchange functional and the Lee, Yang, and Parr correlation functional.[55,56] B3LYP has the form shown below,

$$E_{XC}^{B3LYP} = E_x^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + E_c^{LDA} + a_c(E_c^{GGA} - E_c^{LDA}) \tag{3.28}$$

where a_0=0.20, a_x=0.72, and a_c=0.81. B3LYP has proven to be the most popular functional for organic chemistry applications due to its efficiency and accuracy.

The non-Coulomb term of exchange functionals are shown to die off too quickly making them inaccurate at long range. Long-range corrected hybrid density functionals employ 100% HF exchange for long-range electron-electron interactions. In addition, there have also been efforts to devise frameworks that account for long-range dispersion effects. ωB97XD, developed by Head-Gordon in 2008, is a long-range corrected hybrid functional that also includes empirical dispersion.[57] ωB97XD shows significantly superior performance for non-bonded interactions when compared to previous functionals, such as B3LYP or ωB97X.

Another relevant DFT functional is M06-2X.[58] This functional developed by the Truhlar group is part of a larger group of meta-GGA functionals termed the Minnesota Functionals. M06-2X contains 54% Hartree-Fock exchange. It was shown to perform well when dealing with main group thermochemistry, kinetics, and non-covalent interactions.

3.6 Optimization of Geometry and NBO Analysis

Since the molecular wavefunction is dependent on the coordinates of the nuclei of a given system, the energy for a given molecule is dependent on the geometry of the system. The energy of different molecular confirmations can be used to construct a multi-dimensional potential energy surface (PES). The PES is searched by optimization algorithms to find chemically relevant stationary points. The minima represent low energy conformations of the system while first-order saddle points refer to transition states. This information is very valuable when studying chemical reactions as it gives insight to the mechanisms of reactions.

3.6.1 The Berny Optimization Algorithm

The default algorithm for geometry optimization in *Gaussian* is the Berny optimization algorithm.[59] The Berny algorithm attempts to optimize the geometry of the system closer to the nearest local minimum. It does this by using the forces acting on the atoms together with the Hessian matrix to predict lower energy structures. To calculate the explicit Hessian matrix is costly, so an approximate matrix is constructed by the Berny algorithm as the starting point during the first step in the optimization. This matrix is updated as the optimization proceeds and new energies and first derivatives are obtained.

3.6.2 Synchronous Transit-Guided Quasi-Newton Method

The transition states found in the studies contained in this thesis use the Synchronous Transit-Guided Quasi-Newton (STQN) method for locating transition states.[60] This method only uses the coordinates of the reactant and product, although a guess may be added as additional input. As the efficiency of this method is dependent on the starting geometry of the reactants and products, it is important to have previously optimized the reactants and products to their corresponding minima. More information on the exact algorithm and more technical information for this method can be found elsewhere.[60]

3.6.3 Intrinsic Reaction Coordinate

The intrinsic reaction coordinate (IRC) method provides a tool to trace the path of a chemical reaction.[61] The method uses a transition state geometry as input and attempts to locate the adjacent local minima on either side. The calculation begins by taking steps of controlled length and the algorithm attempts to follow the line of steepest decent towards a minimum. The calculation consists of a sequence of constrained optimizations that only terminates when the local minima on both sides of the input transition state geometry is found.

The IRC method allows for full determination of a reaction path given a transition state and is used to verify mechanisms. In addition to providing the barrier of a reaction and thermodynamic information, it is extremely valuable when determining whether a mechanism takes part in multiple steps. If the local minima found correspond to the reactants and product, then it suggests that there is no intermediate in the reaction pathway. However, if the IRC detects a local minimum that does not have the geometry of the product, then it is eluding to a multistep pathway and there is an intermediate. A second calculation is then performed to try and locate a TS connecting the intermediate to the desired product.

3.6.4 Natural Bonding Orbital Analysis

The idea of natural orbitals is attributed to Per-Olov Löwdin, who in 1955 used them to describe a set of orthonormal 1-electron functions that are intrinsic to the N-electron wavefunction.[62] A natural bonding orbital (NBO) is a calculated bonding orbital with maximum electron density. In some cases, such as determining the amount of delocalization, it is of interest to determine the distribution of electron density in atoms and the bonds between them. For example, in aromatic systems such as benzene, one would find that the bond order is 1.5 due to delocalization. Although the example of benzene may be intuitive, performing an NBO analysis on systems that are not well studied provides useful information on the electronic structure and the population of orbitals.

3.7 Quantum Theory of Atoms in Molecules (QTAIM)

Developed by Bader and coworkers, the quantum theory of atoms in molecules uses a topological analysis of the electron density to partition a molecule into regions that define an atom. As use of QTAIM in the studies presented in this thesis is limited, the reader is directed to resources with complete reviews of the subject.[63,64]

Chapter 4

Investigation of the Five- to Twelve-Membered Cyclic Alkynes

In this chapter, the results of a systematic study on the cycloalkyne series comprised of cyclopentyne through cyclododecyne are presented. The electronic and geometric structure of both the singlet and triplet states of ring sizes five- to twelve-membered cyclic alkynes were investigated using DFT methods. For comparison to the computationally efficient DFT calculations, the results are also reported for the five- to eight-membered rings using the coupled cluster method. Although ring sizes larger than eight were not investigated using the coupled-cluster method, it was found that the wavefunction method MP2 closely matched the coupled cluster results for the singlet state five- to eight-membered rings in terms of the triple bond lengths. These results provide the first systematic study of the small-ring cyclic alkynes using modern computational methods.

4.1 Motivation

Wittig published many experimental papers on the small-ring cycloalkynes, discussing their stability, reactions, and structural characteristics.[9,65-69] However, there have been few computational studies on the small-ring cycloalkyne family of molecules. There have been propositions on how these species may behave and what is likely to occur as smaller and smaller rings try to accommodate the triple bond, but there has yet been a systematic study on the properties of the cycloalkynes as a function of ring size. Most studies of cycloalkynes are specific in nature, and look at only one cycloalkyne without comparison with others. The motivation for the study presented in this chapter is based on the lack of information of the cycloalkynes studied in sequence. This chapter presents the first systematic study of cycloalkynes of rings sizes five- through twelve.

4.2 Computational Methods

Geometry optimizations were carried out for the singlet state cyclic alkynes of ring sizes five through twelve at the B3LYP/6-311G(d,p)[55,56] level of theory and for ring sizes of five through eight at the CCSD/cc-PVDZ[70] level of theory. All optimized structures were local minima on their corresponding potential energy surfaces (no imaginary frequencies). The electrostatic potential mapped onto the electron density isosurface was obtained for cyclic alkynes of ring sizes five through twelve at the B3LYP/6-311G(d,p) level of theory. In addition to the restricted calculations on the singlet states, geometry optimizations were carried out for the triplet state cyclic alkynes of ring sizes five through twelve at the UB3LYP/6-311G(d,p) level of theory. Furthermore, ring sizes of five through seven were also optimized at the UCCSD/cc-PVDZ level of theory. Finally, frequency calculations were carried out for ring sizes of five through twelve at the same level of theory as the geometry optimizations to ensure a given geometry was a true minimum on the potential energy surface. Natural bonding orbital (NBO) analyses were carried out for singlet cycloalkynes of ring sizes five through twelve at the B3LYP/6-311G(d,p) level of theory. Harmonic frequency calculations for ring sizes of five and six were carried out at the UCCSD/cc-PVDZ level of theory. The geometry, harmonic frequency, and NBO calculations mentioned above were performed using the electronic structure modeling program Gaussian 09[71] in tandem with GaussView 5 visualization software.[72]

The singlet cyclohexyne molecule was further investigated at the ωB97XD/6-311G(d,p)[57], M06-2X/6-311G(d,p)[58], and MP2/6-311G(d,p)[47,73] levels of theory.

The electron density at the triple bond critical point (BCP) was computed using the QTAIM software package AIMALL.[74] The wavefunction files were generated using Gaussian 09 and used as input for the AIMALL software package. The electron density at the BCP was obtained for singlet state cyclic alkynes of ring sizes five through twelve at the B3LYP/6-311G(d,p) level of theory and for ring sizes of five through eight at the CCSD/cc-PVDZ level of theory.

4.3 Results and Discussion

4.3.1 Geometric and Electronic Structure of the Singlet State Cycloalkynes

Geometry. Figure 4.1 shows the carbon-carbon triple bond lengths for the singlet states of ring sizes five through twelve. Note that cyclopentyne through cyclododecyne were also investigated at the HF/3-21G level of theory to draw comparisons to early work done by Olivella *et al.*[17,18] on cyclopentyne and cyclohexyne. The new data confirm the values obtained with HF/3-21G by Olivella *et al.* and also shows the relationship of the calculated bond lengths with the rest of the cycloalkyne series. As mentioned previously, X-ray crystallographic data for both cyclooctyne and cyclononyne has been reported in the literature.[4,5] The value we obtained for the triple bond length in cyclooctyne using the CCSD/cc-PVDZ level of theory (1.225 Å) was in good agreement with the experimental value (1.23 Å). Cyclononyne was reported to have bond length of 1.21 Å by X-ray crystallography, which is in moderate agreement with the value we obtained using the B3LYP/6-311G(d,p) level of theory (1.204 Å). We expected the CCSD/cc-PVDZ value for cyclononyne to be closer to the experimental result than the B3LYP/6-311G(d,p) value, but due to computational cost only ring sizes up to eight were computed at the CCSD/cc-PVDZ level of theory. The MP2/6-311G(d,p) level of theory matches closely to the CCSD results, suggesting that for cyclononyne both CCSD and MP2 would predict a length longer than the length determined crystallographically. Taking the coupled cluster results as the most accurate, one can see that the B3LYP/6-311G(d,p) and HF/3-21G levels of theory seem to predict a bond length that is shorter than from the CCSD/cc-PVDZ level of theory by about 0.025 Å and 0.042 Å, respectively. Each method shared a common trend as ring size is increased and showed a clear inflection point occurring at a ring size of eight. Figure 4.2 shows the average bond length adjacent to the C_1-C_2 bond as a function of ring size calculated at the B3LYP/6-311G(d,p) level of theory. The adjacent bond length follows the same general trend as the ring size is increased, that is, the average adjacent bond length decreases until a ring size of eight is reached, followed by a plateau through the larger ring sizes.

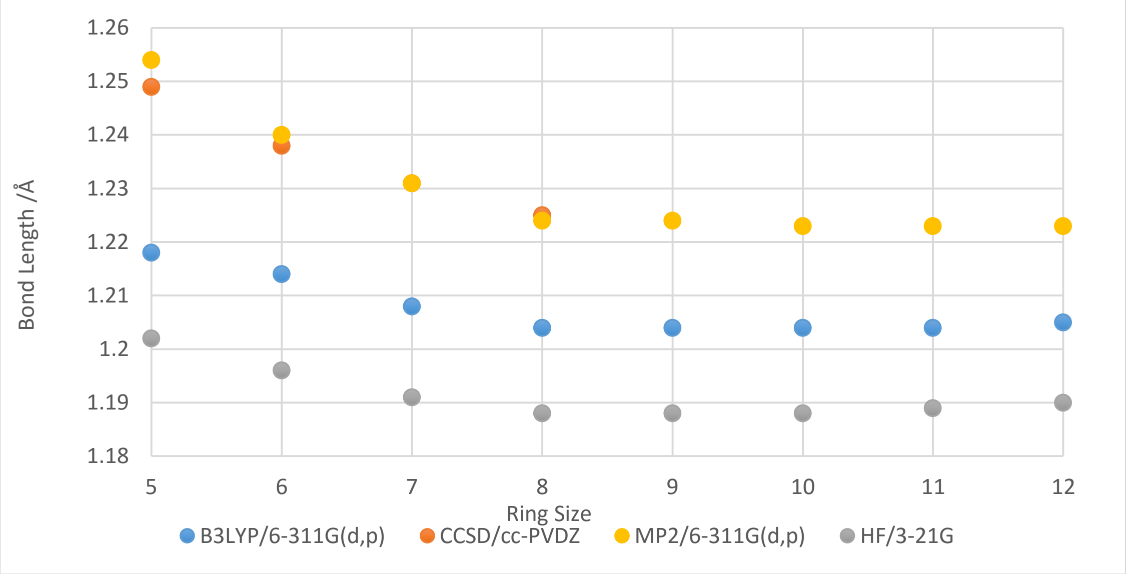


Figure 4.1: Singlet state carbon-carbon triple bond lengths as a function of ring size at the B3LYP/6-311G(d,p), HF/3-21G, MP2/6-311G(d,p), and CCSD/cc-PVDZ levels of theory.

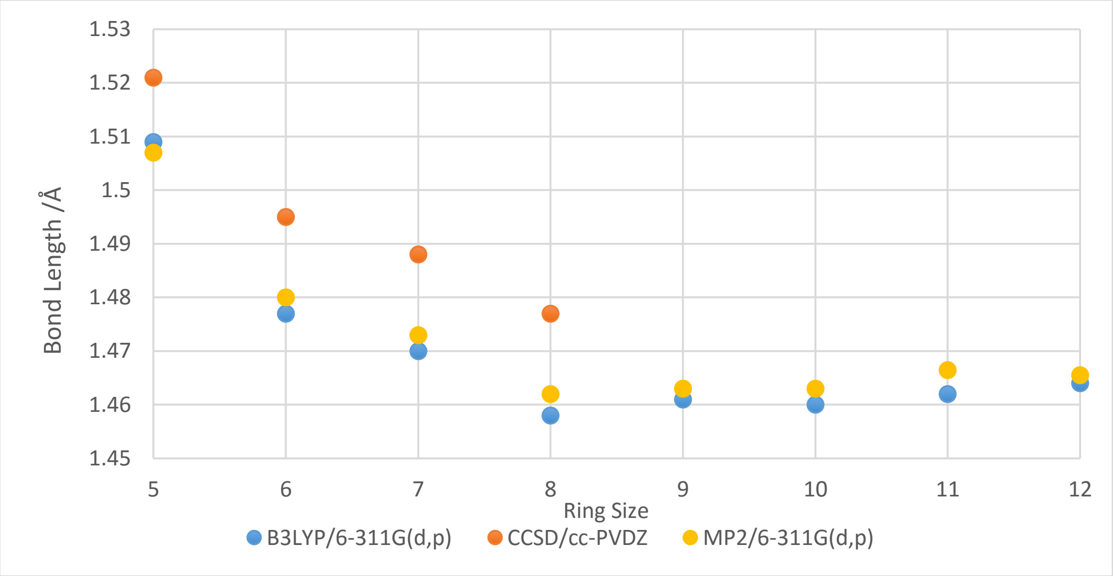


Figure 4.2: Average bond length adjacent to the C_1-C_2 as a function of ring size calculated at the B3LYP/6-311G(d,p), MP2/6-311G(d,p), and CCSD/cc-PVDZ levels of theory for the singlet states of cyclopentyne through cyclododecyne.

Early work on cycloalkynes used the deformation of the C-C≡C-angle as an indicator to determine whether a cycloalkyne is strained or unstrained.[15] Figure 4.3 shows the C-C≡C-angle for the optimized singlet state structures plotted as a function of ring size. One can see excellent agreement between the CCSD/cc-PVDZ, MP2/6-311G(d,p), and B3LYP/6-311G(d,p) levels of theory and a clearly linear relationship between the C-C≡C-bond angle and ring size from cyclopentyne to cyclooctyne. As the ring size increases past cyclooctyne, and the C-C≡C-bond angle approaches the ideal 180°, the linear relationship is lost. The MP2 and CCSD results are similar, while the B3LYP results seem to be in less agreement when compared to the results obtained for the smaller ring sizes. It has been previously proposed that there is a linear relationship between the carbon-carbon triple bond stretching frequency and experimental or calculated C-C≡C-bond angles as ring size increases.[6] Figure 4.4 shows the results for wavenumber as a function of C-C≡C-bond angle for ring sizes five through twelve. The calculations suggest that as ring size increases from five through eight there is a linear relationship between the triple bond harmonic stretching frequency and C-C≡C-bond angle, suggesting that the proposition is correct. Although, as the ring sizes increases past a ring size of eight the linear relationship is lost and starts to plateau.

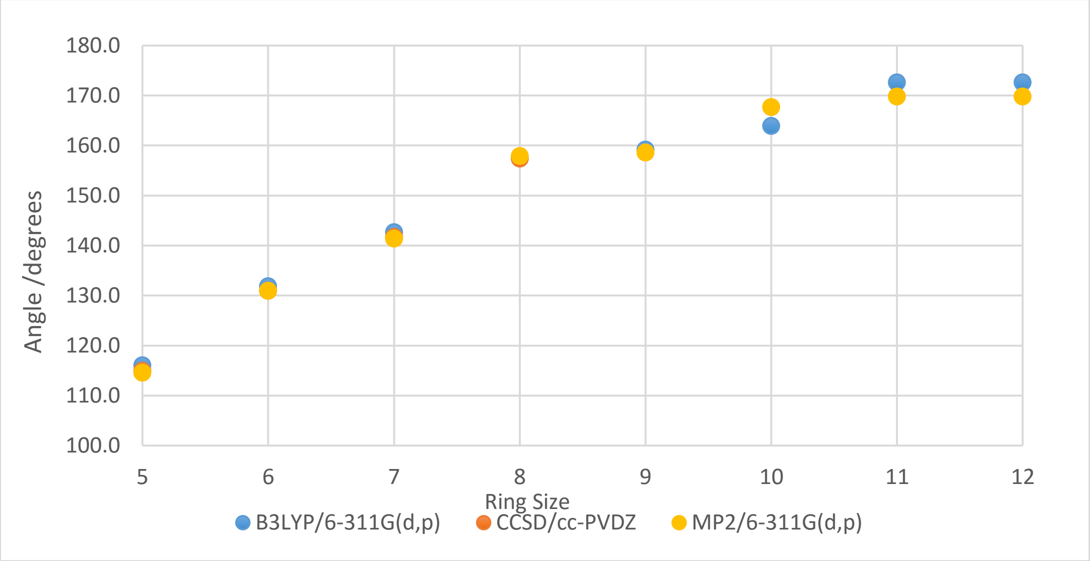


Figure 4.3: Singlet state C-C≡C-bond angles as a function of ring size at the B3LYP/6-311G(d,p), MP2/6-311G(d,p), and CCSD/cc-PVDZ levels of theory.

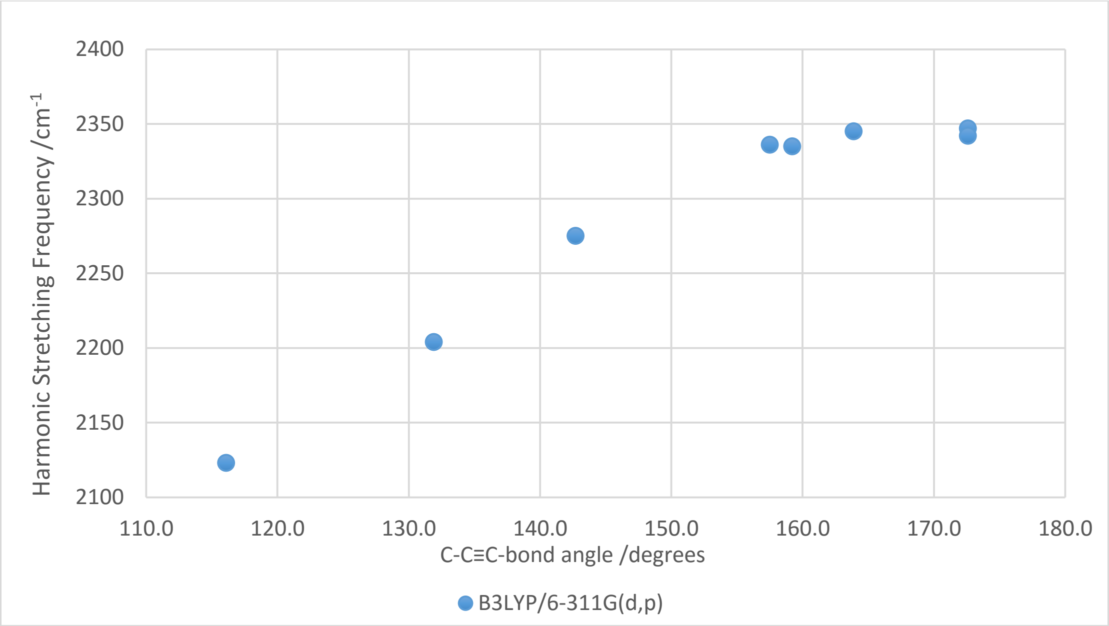


Figure 4.4: Unscaled Singlet state harmonic stretching frequencies as a function of the corresponding C-C≡C-bond at the B3LYP/6-311G(d,p).

Electronic structure. To investigate whether there is an obvious electronic reason for the inflection point at a ring size of eight as seen in the Figures 4.1 and 4.2, the LUMO, HOMO, and HOMO-1 were obtained at the B3LYP/6-311G(d,p) level of theory, and can be seen in Figure 4.5. The molecular orbitals for the LUMO, HOMO, and HOMO-1 stay in the relative order in terms of energy as the ring size increases, but for cyclooctyne and cyclononyne the LUMO is positive in energy, unlike cycloheptyne and cyclohexyne. Additionally, the LUMO increases in energy from the six-membered ring to the eight-membered ring. The lobes of the LUMO located at the triple bond seem to be reduced as the ring size is decreased. The decrease in ring size seems to cause the LUMO lobes at the triple bond to become less hindered with respect to the corresponding out of phase lobes of the triple bond.

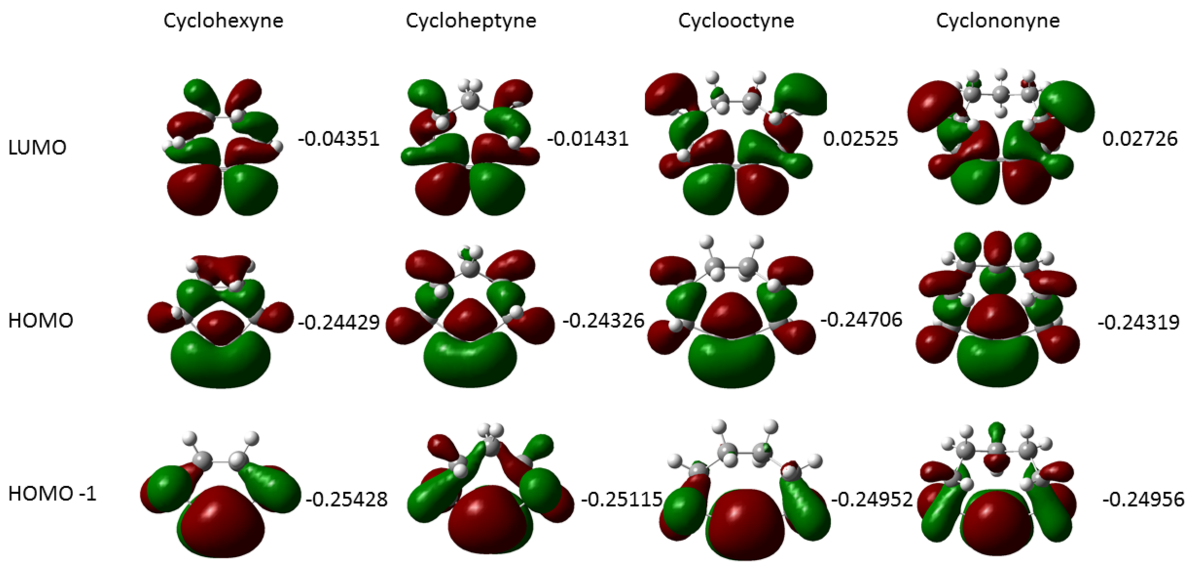


Figure 4.5: The LUMO, HOMO, and HOMO-1 obtained at the B3LYP/6-311G(d,p) level of theory for the singlet states of cyclohexyne through cyclononyne. Energy in units of hartrees.

To determine the electron density at the bond critical point[75] QTAIM analyses were performed for the singlet state optimized geometries at the B3LYP/6-311G(d,p) and CCSD/cc-PVDZ levels of theory. The electron density at the bond critical point (BCP) for ring sizes five through twelve can be seen in Figure 4.7. The electron density and the electrostatic potential cubes were generated from the total SCF density in preparation for generating the mapped surface. The electrostatic potential isosurface was mapped onto the electron density with an isovalue of 0.05 electrons/Å^3. The surfaces for cycloalkynes of ring size five through twelve can be seen in Figure 4.6. The electron density at the bond critical point should decrease when going from a conventional triple bond, to a double bond, to a single bond due to the change in length. In this case, the triple bond under investigation is not in a standard system. Figure 4.7 suggests the electron density at the bond critical point increases as the ring size decreases. This is likely due to the decreasing bond length. It should be noted that the smallest ring, cyclopentyne, has a predicted electron density at the triple bond critical bond point of roughly 0.439 electrons; this value is higher than the electron density reported for general triple bonds. The common inflection point between previous figures at a ring size of eight is also seen in this plot.

Looking now at Figure 4.8, the NBO analyses show that the in-plane and out-of-plane π-orbitals decrease in electron occupation while the σ bond increases in electron occupation as the ring size decreases. Comparing both Figure 4.6 and Figure 4.7, the results suggest that the electron density at the BCP of the triple bond is increasing as ring size decreases due to the donation from the π-orbitals to the σ bond; Figure 4.6 is a pictorial representation of this trend. At a ring size of eight, the red electrostatic potential "hot spot" around the triple bond is fully connected. Below a ring size of eight, the "hot spot" begins to diminish only on the out-of-plane portion of the isosurface and the electrostatic potential at the two carbons of the triple bond decreases.

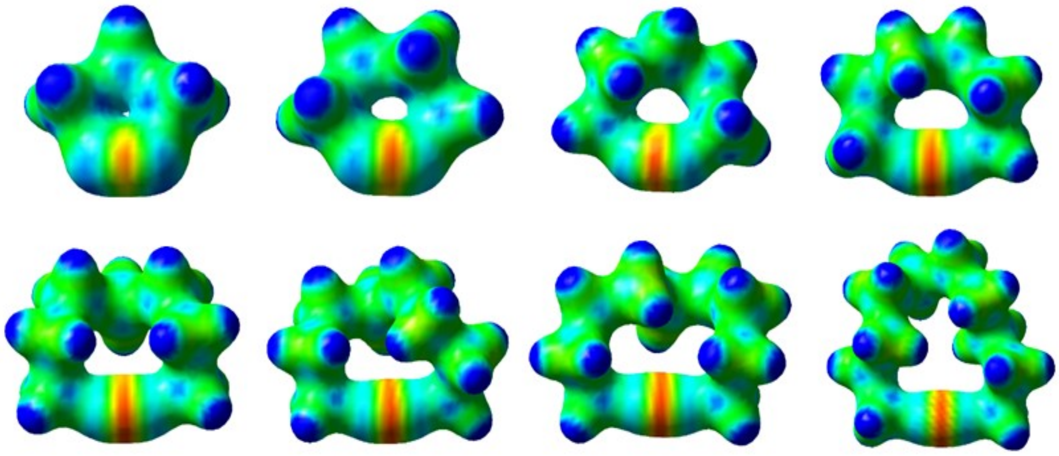


Figure 4.6: The surface generated from mapping the electrostatic potential onto the electron density for the cycloalkynes cyclopentyne, cyclohexyne, cycloheptyne, cyclooctyne, cyclononyne, cyclodecyne, cycloundecyne, and cyclododecyne. The surface was created with an isovalue of 0.05 electrons/Å^3 and an electrostatic potential range of 0.02-0.250 J/C.

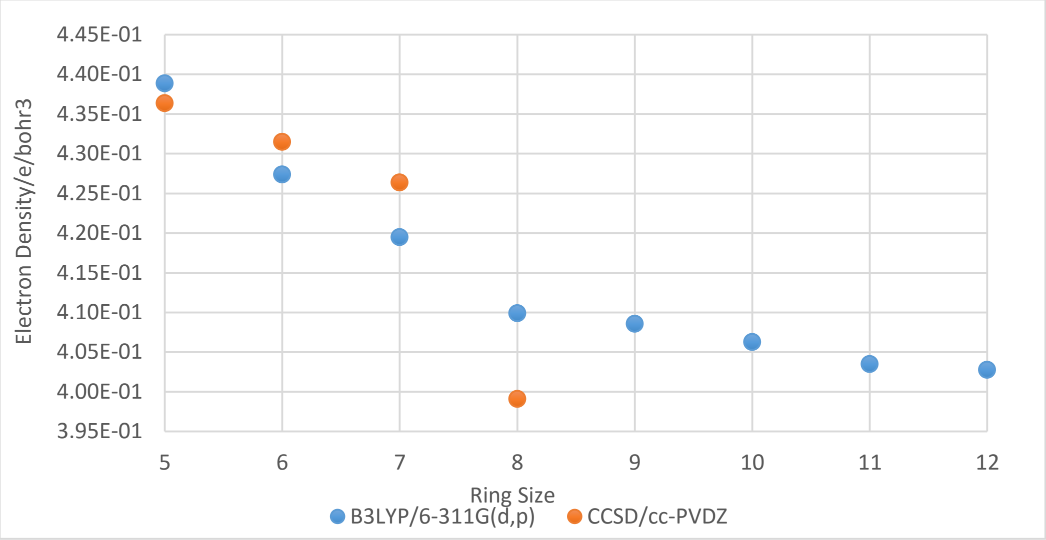


Figure 4.7: Singlet state electron density at the triple bond critical points (BCP) as a function of ring size at the B3LYP/6-311G(d,p) and CCSD/cc-PVDZ levels of theory.

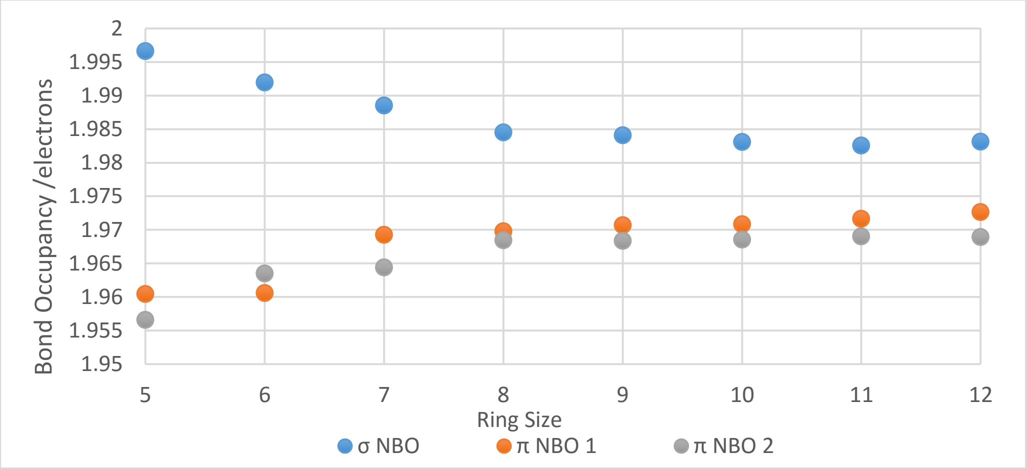


Figure 4.8: Singlet state triple bond occupancy as a function of ring size at the B3LYP/6-311G(d,p) level of theory.

4.3.2 A Closer Look at Singlet State Cyclohexyne

The singlet state cyclohexyne molecule, Figure 4.9, was further investigated by means of geometry optimizations at the CCSD/cc-PVDZ, B3LYP/6-311G(d,p), ωB97XD/6-311G(d,p), MP2/6-311G(d,p), and M06-2X/6-311G(d,p) levels of theory

(Table 4.1). It should be noted that the optimized structure of ring sizes five through eight all are in a twist-chair conformation whereas ring sizes nine through twelve take on a boat-like conformation. The cyclohexyne molecule was chosen to be examined more closely due to previous literature on this molecule.[2,21,76,77] The C_1-C_2 bond length is the first point of interest in cyclohexyne. Taking the CCSD value as the most accurate value, Table 4.1 shows that ωB97XD, B3LYP, and M06-2X all undershoot the CCSD value. The ωB97XD/6-311G(d,p) and M06-2X/6-311G(d,p) levels of theory both predict a C_1-C_2 bond length of 1.209 Å. The value calculated using the MP2 method is larger than the CCSD value by 0.002 Å. Olivella *et al.*[17] has previously calculated the C_1-C_2 bond length to be 1.196 Å and 1.219 Å using HF/3-21G and GVB/3-21G, respectively. The two adjacent bonds to the C_1-C_2 triple bond, C_1-C_3 and C_2-C_4, are predicted to be 1.495 Å with the coupled cluster method. All other functionals/methods undershot the coupled cluster value. Unlike the C_1-C_2 bond, the MP2 method predicted a value, 1.480 Å, closest to the coupled cluster prediction; Olivella *et al.* had reported values of 1.484 Å and 1.488 Å at the HF/3-21G and GVB/3-21G levels of theory, respectively. The C_3-C_5 and C_4-C_6 bond lengths were predicted to be 1.570 Å using the coupled cluster method. With the exception of B3LYP, the other density functionals/methods predicted a shorter bond length, with the ωB97XD value being the closest to the CCSD value at 1.569 Å. Olivella *et al.* obtained longer bond lengths of 1.590 Å and 1.577 Å using HF/3-21G and GVB/3-21G, respectively. The C_5-C_6 bond length was predicted to be 1.542 Å by all methods/functions except B3LYP, which predicted a length of 1.546 Å and CCSD, which predicted 1.551 Å. Olivella reported values of 1.562 Å and 1.558 Å using HF/3-21G and GVB/3-21G, respectively. The important C_2-C_1-C_3 bond angle was predicted to be 131.0° by CCSD. B3LYP, ωB97XD, and M06-2X predicted larger angles of 131.8°, 131.8°, and 131.9°, respectively. The MP2 method predicted the same angle as CCSD of 131.0° while Olivella *et al.* report values of 132.8° and 131.0° using HF/3-21G and GVB/3-21G, respectively.

Olivella *et al.*[17] report the triplet state (^{3}B) of cyclohexyne as lying 42 kcal/mol above the singlet ground state (^{1}A) using the GVB/UHF/3-21G level of theory. The calculations at the CCSD/cc-PVDZ level of theory are in agreement with the earlier results, predicting the triplet state of cyclohexyne to lie 43 kcal/mol above the ground state. The ^{1}A-^{3}B energy gap for cyclopentyne was reported to be 20.6 kcal/mol at the GVB/ROHF/3-

21G level of theory and 25 kcal/mol at the CISD/6-31G(d) level of theory. For the ^{1}A-^{3}B energy gap we obtained a value of 15 kcal/mol at the CCSD/cc-PVDZ level of theory. It was proposed that due to the change in ^{1}A-^{3}B energy gap seen for cyclopentyne when using a higher level of theory that the value obtained for the ^{1}A-^{3}B energy gap cyclohexyne gap would also change if calculated at a higher level of theory. The results show that there is only 1 kcal/mol change in the ^{1}A-^{3}B energy gap for cyclohexyne comparing the GVB/UHF/3-21G and CCSD/cc-PVDZ levels of theory.

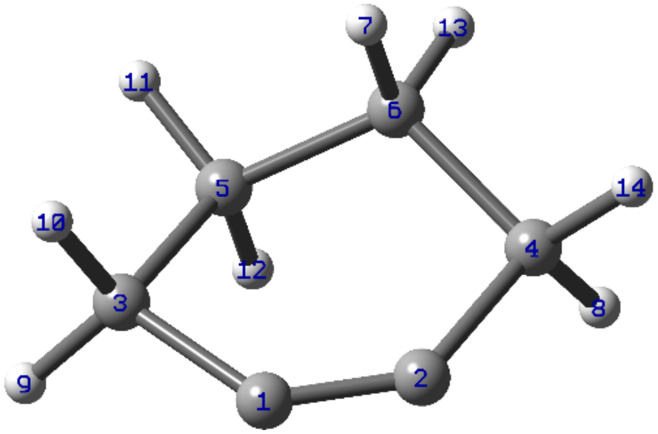


Figure 4.9: Optimized structure for the singlet ground state of cyclohexyne at CCSD/cc-PVDZ.

Table 4.1. Relevant Geometrical Parameters[a,b] of the Optimized Molecular Structure of Cyclohexyne Calculated at the CCSD/cc-PVDZ, ωB97XD/6-311G(d,p), M06-2X/6-311G(d,p), and MP2/6-311G(d,p) Levels of Theory.

Method	rC1C2)	r(C1C3)	r(C3C5)	r(C5C6)	∠(C2C1C3)	∠(C1C3C5)	∠(C3C5C6)	∠(C3C1C2C4)	∠(C1C2C4C6)	∠(C3C5C6C4)
CCSD	1.238	1.495	1.570	1.551	131.0	102.0	114.6	-5.9	16.9	60.7
B3LYP	1.214	1.477	1.577	1.546	131.8	102.2	115.0	-5.1	15.6	57.1
ωB97XD	1.209	1.476	1.569	1.542	131.8	101.8	114.8	-5.0	15.8	58.5
M062X	1.209	1.479	1.568	1.542	131.9	101.5	114.6	-4.3	15.7	59.9
MP2	1.240	1.480	1.565	1.542	131.0	102.0	114.1	-0.7	14.0	62.1

[a]Geometrical parameters are defined as in Figure 4.4. [b]Distances (r) are in angstroms and angles are in degrees.

4.3.3 Geometric and Electronic Structure of the Triplet State Cycloalkynes

Geometry. The reported triple bond length of cyclohexyne in the triplet state by Olivella *et al.*[17] agrees with the result obtained in this study using the same level of theory, UHF/3-21G. They made the conclusion that the acetylenic in-plane π–bond is completely broken in the triplet state of cyclohexyne due to the bond length being close to the experimental length of the double bond of cyclohexene, 1.335 Å. The value for the triple bond length calculated using the UCCSD/cc-PVDZ level of theory was 1.352 Å, which is longer than the experimental bond length for cyclohexene. This agrees with Olivella's prediction that the acetylenic in-plane π bond is completely broken in cyclohexyne, and even suggests a further lengthening of the bond past the cyclohexene carbon-carbon double bond length. The C_1-C_2 bond length of cyclopentyne through cyclododecyne shows, as seen in Figure 4.10, an expected lengthening of the bond when compared to the singlet states. The predicted bond lengths for the triplet states follow almost the inverse trend of that of the singlet states except for cyclooctyne, which appears to be an anomaly. Both UB3LYP and UHF predict a larger than expected lengthening of the bond going from cycloheptyne to cyclooctyne with a shortening of the bond proceeding onto cyclononyne.

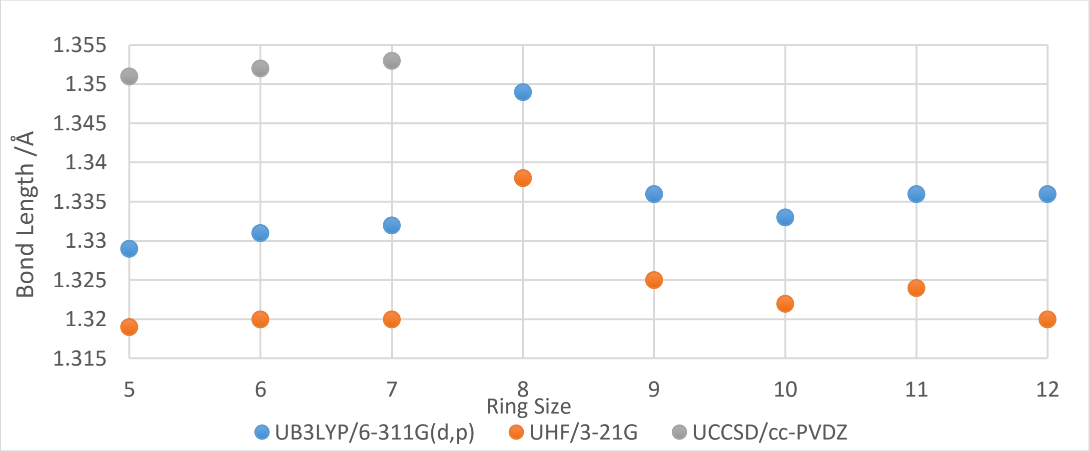


Figure 4.10: Triplet state carbon-carbon triple bond lengths as a function of ring size at the UB3LYP/6-311G(d,p), UHF/3-21G, and UCCSD/cc-PVDZ levels of theory.

The calculations predict the C_1-C_2 bond length in the triplet state of cyclooctyne to be longer than that of any other ring size. To try and explain this from a geometric point of view, analyses of the neighboring C-C bonds were performed. Figure 4.11 shows the average C-C bond lengths adjacent to the C_1-C_2 bond. Together, Figures 4.10 and 4.11 show that as the C_1-C_2 bond distance increases, there is an accompanying decrease in the adjacent C-C bond length, suggesting some delocalization. The sudden increase in bond length from a ring size of seven to eight is also captured in Figure 4.11, where the adjacent bond length is shortened by about the same magnitude. The previous trend is somewhat lost with higher ring sizes, suggesting that the delocalization may be only happening into one of the adjacent bonds, as the Figure 4.11 only shows the average bond length of the two adjacent bonds. The lengthening of the adjacent bonds for cyclooctyne suggests that there is more delocalization in cyclooctyne than other cycloalkynes within the series of interest and helps to explain the lengthening of when proceeding from cycloheptyne to cyclooctyne in the series.

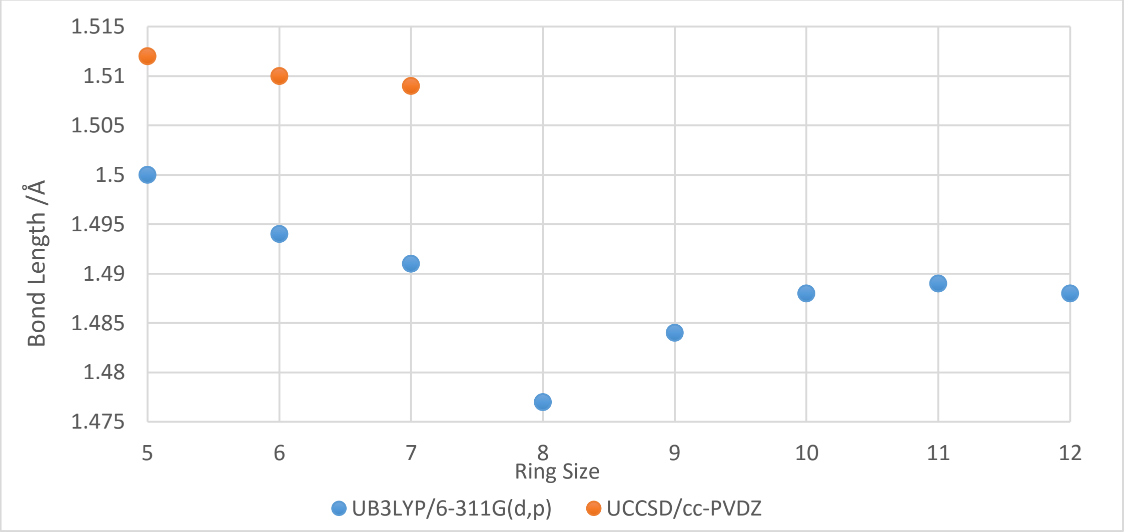


Figure 4.11: Average bond length adjacent to the C_1-C_2 bond as a function of ring size calculated at the UB3LYP/6-311G(d,p) for the triplet states of cyclopentyne through cyclododecyne.

Electronic structure. The alpha HOMO, HOMO-1, and HOMO-2 for cyclohexyne, cycloheptyne, cyclooctyne, and cyclononyne can be seen in Figure 4.12. The anomaly seen in the geometric analyses can also be seen in the molecular orbitals. The HOMO and HOMO-1 are the molecular orbitals of interest as they are housing the two radical electrons. The largest difference in the series is with cyclooctyne. Cyclooctyne has a HOMO-1 resembling that of every other ring's HOMO-2. The HOMO-1 and HOMO-2 for cyclooctyne are relatively close in energy, which could explain the switch in orbitals we see with cyclooctyne compared to the rest of the series. The spin density isosurfaces for cyclohexyne through cyclodecyne can be seen in Figure 4.13. The spin density isosurface for all ring sizes except eight show local spin density on carbons one and two with spin density across the C_1-C_2 bond as well. The spin density profile for cyclooctyne is different from the rest of the series; it seems to be delocalized around carbons one and two, along with the bond joining them, in a more three-dimensional manner compared to that of the other rings. The lengthening followed by contraction of the C_1-C_2 bond seen in Figure 4.10 must be related to the anomalies present in the electronic structure and spin density profiles of cyclooctyne.

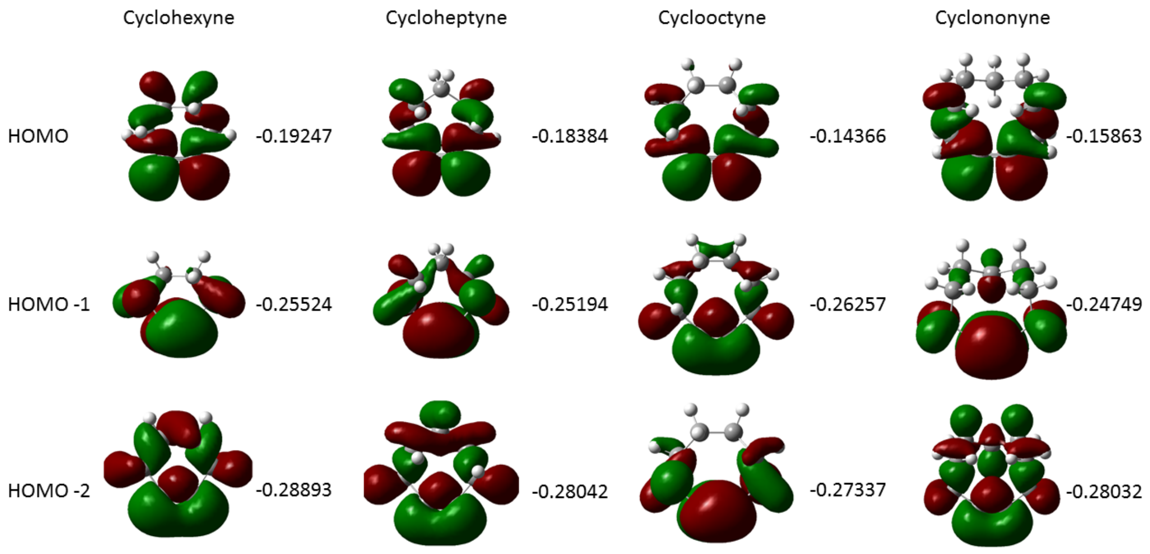


Figure 4.12: The HOMO, HOMO-1 and HOMO-2 molecular orbitals obtained at the UB3LYP/6-311G(d,p) level of theory for the triplet states of cyclohexyne through cyclononyne. Energy is in units of hartrees.

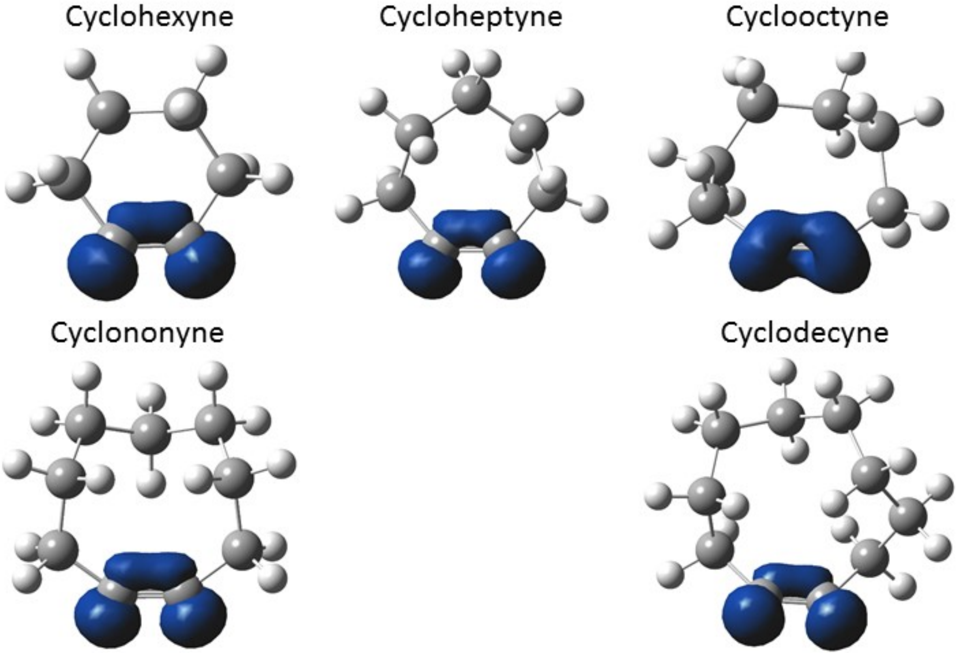


Figure 4.13: Spin density isosurfaces obtained at the UB3LYP/6-311G(d,p) level of theory with an isodensity value of 0.02 for the triplet states of cyclohexyne through cyclodecyne.

4.3.4 Vibrational Frequency Analysis of the Singlet and Triplet State Cycloalkynes

A frequency analysis for cycloalkynes of ring sizes five through twelve was carried out at several levels of theory. The C_1-C_2 stretching frequencies for the singlet states can be seen in Figure 4.14. In addition to the singlet state frequency analysis, the same analysis was performed for the triplet state structures. The C_1-C_2 stretching frequencies of the triplet states can be found in the Figure 4.15. The experimental C_1-C_2 stretching frequency for cyclooctyne was reported to be 2260 cm^{-1} [78]; we obtained 2336 cm^{-1} at the B3LYP/6-311G(d,p) level of theory. Applying the suitable frequency scaling factor for the B3LYP/6-31G(d) level of theory (0.9614) to the B3LYP/6-311G(d,p) results brings the predicted stretching frequency value down to 2246 cm^{-1}, which is in moderate agreement with the experimental value. The experimental C_1-C_2 stretching frequency value reported for cyclononyne is 2230 cm^{-1}.[79] The value we obtained using the B3LYP/6-311G(d,p) level of theory was 2335 cm^{-1}, only one wavenumber off from the frequency calculated for cyclooctyne. Applying the previously mentioned frequency scaling factor brings the result down to an expected experimental frequency of 2245 cm^{-1}, also in moderate agreement with the experimental value. Although the predicted frequencies are in moderate accord with the experimental data, the calculations predict cyclooctyne and cyclononyne to have essentially the same stretching frequency, which was not the case for the experimental values.

For the singlet states, there was once again a linear relationship with ring size up to the eight-membered ring. CCSD/cc-PVDZ and B3LYP/6-311G(d,p) showed moderate agreement while the HF/3-21G seems to overshoot the CCSD- and B3LYP-predicted frequencies, as expected. Cyclopentyne and cyclohexyne were already calculated by Olivella *et al.*[17,18]; to see how this method performs over the series, we calculated the frequencies for ring sizes seven to twelve. Interestingly, the C_1-C_2 stretching frequency obtained by Olivella *et al.* was close to the frequency obtained at CCSD/cc-PVDZ. The intersection of the two methods seems to occur at a ring size of five and deviates as the ring size increases or decreases. The B3LYP/6-311G(d,p) level of theory predicts frequencies close the coupled cluster values when looking at cycloheptyne and cyclooctyne. The values predicted by the HF/3-21G level of theory are much larger than the B3LYP/6-311G(d,p) values for all ring sizes except for where the two levels of theory intersect at a ring size of five. The common inflection point is seen once again at a ring size of eight where the values predicted by the different levels of theory start to plateau.

The frequency analysis for the triplet states is consistent with the electronic and geometric results mentioned previously. There is a linear relationship between the wavenumber and the ring size until a ring size of eight, in which the frequency for the relatively lengthened C_1-C_2 bond is significantly decreased compared to the general trend. Olivella had previously calculated the frequencies for cyclopentyne and cyclohexyne in their triplet states at the UHF/3-21G level of theory. The higher level calculations show a large gap of ~133 cm^{-1} compared to the UHF/3-21G calculations. The coupled cluster results could only be calculated for ring sizes five and six due to computational cost, but the coupled cluster results that were carried out seem to in good agreement with the UB3LYP values.

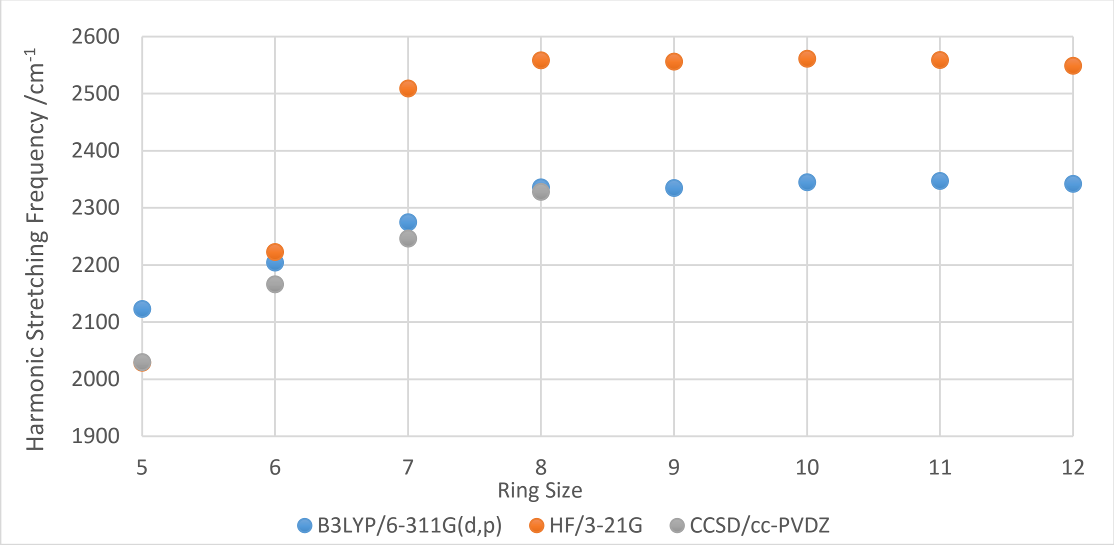


Figure 4.14: Singlet state C_1-C_2 stretching frequencies as a function of ring size at the B3LYP/6-311G(d,p), HF/3-21G, and CCSD/cc-PVDZ levels of theory.

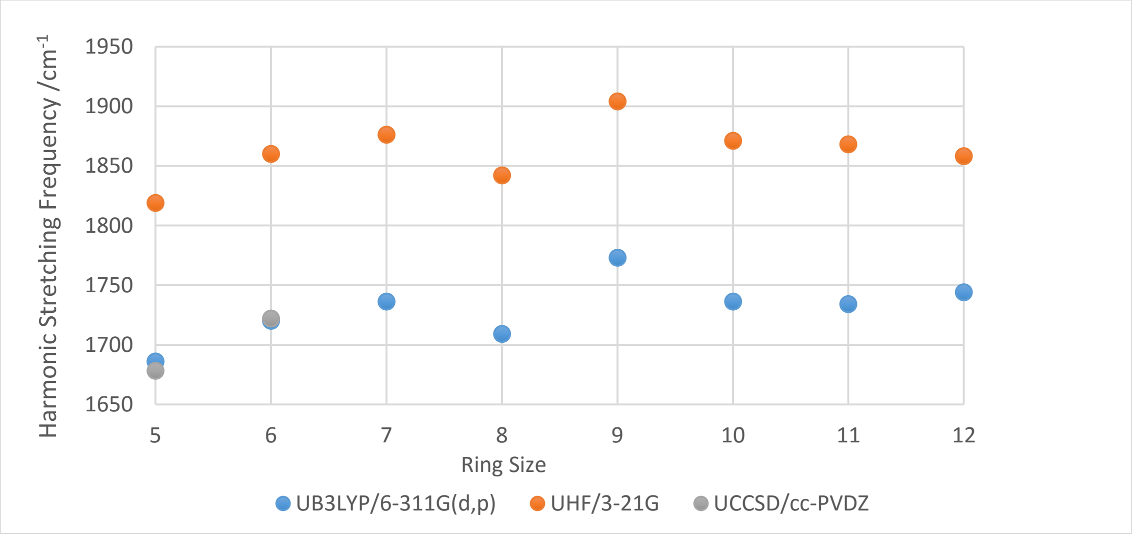


Figure 4.15: Triplet state C_1-C_2 stretching frequencies as a function of ring size at the UB3LYP/6-311G(d,p), UHF/3-21G, and UCCSD/cc-PVDZ levels of theory.

4.4 Conclusions

It was found that for cyclopentyne and cyclohexyne the triplet state is higher in energy relative to the singlet state. The results obtained using the coupled cluster method suggest that, relative to the triplet state, the singlet state of cyclohexyne lies 43 kcal/mol lower in energy, while singlet state cyclopentyne lies 15 kcal/mol lower in energy. These data reinforce the previous calculations done by Olivella and coworkers.[17] The limited structural data available for the cycloalkyne series, cyclononyne and cyclooctyne, matches quite well with the calculated data in this study.

The singlet state cycloalkyne series was found to have a smooth trend in geometric and electronic structure properties as a function of ring size. The data we report reveal two regimes that have a transition point at a ring size of eight. The data suggest that as the ring size decreases, the occupancy of the π orbitals contributing to the triple bond decreases while the occupancy of the σ bond increases. Furthermore, it was found that as the ring size decreases, the electron density at the triple bond critical point increases. This change in electron density is thought to be attributed to the change in the triple bond length as the ring size is decreased. The calculations for the triplet state cycloalkynes show an anomaly in the electronic and geometric structure at a ring size of eight at all levels of theory.

Chapter 5

The Search for Selectivity in the Cycloadditions of Substituted Cycloalkynes

In this chapter, the results of a study to explore the regioselectivity in Diels-Alder reactions involving unsymmetrically substituted cycloalkynes are summarized. To do this, unsymmetrically substituted cycloalkynes reacting with various dienes were modelled using the ωB97XD functional.[57] Although many reactions were studied, only the relevant reactions of the search will be shown; these happen to involve 3,3-dimethylcycloalkynes reacting with 2-tert-butylfuran.

5.1 Introduction and Motivation

Although cyclohexyne has seen little synthetic application, it is starting to be utilized in the synthesis of large molecules.[76,80] Many organic chemists are not interested in just bare reagents, but reagents that are unsymmetrically substituted. The advantage of using unsymmetrically substituted reagents is that it allows for more functionality in the final product. However, a potential problem with using unsymmetrically substituted cyclohexynes is regioselectivity. Cyclohexyne is a highly strained molecule and is therefore expected to have extremely low reaction barriers. If cyclohexyne is going to start to be used more by synthetic chemists, there needs to be more knowledge on the energy profiles of unsymmetrically substituted cyclohexyne analogues.

In this chapter, the results of a study modeling the [4π+2π] cycloadditions (Diels-Alder reactions) of many unsymmetrically substituted cycloalkyne analogues with furan analogues are presented. The influence of steric hindrance and ring size on the difference in energy barriers of the regioisomeric pathways is quantified. The question is how bulky would substituents on the cyclohexyne and the diene have to be in order to achieve a reasonable level of regioselectivity.

5.2 Computational Methods and Model Systems

The general reaction scheme followed to investigate the regioselectivity of unsymmetrically substituted cycloalkynes undergoing [4+2]-cycloaddition with unsymmetrically substituted furan derivatives can be seen in Figure 5.1.

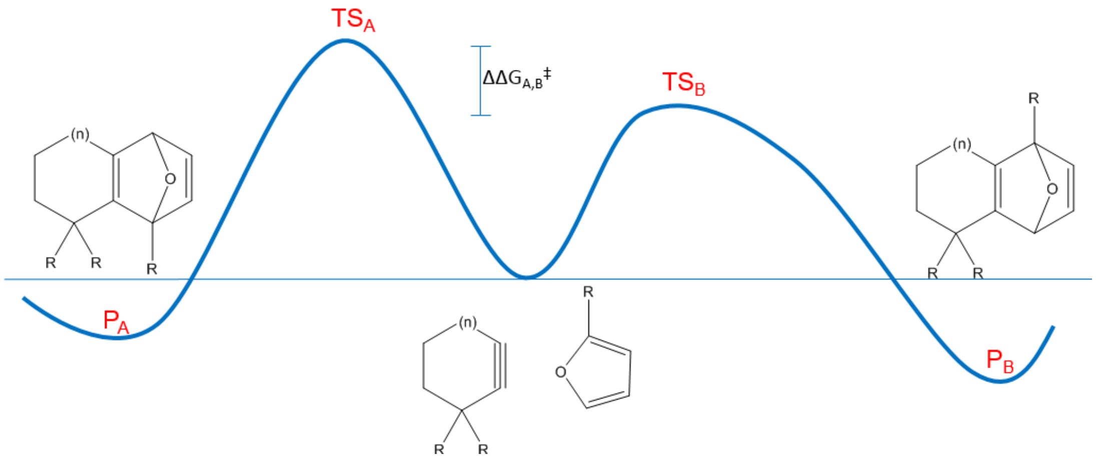


Figure 5.1: The general reaction scheme used to investigate the regioselectivity of unsymmetrically substituted cycloalkynes. The x-axis can be interpreted as reaction coordinate and the y-axis Gibbs energy.

P_A and P_B are the two possible regioisomeric products, TS_A and TS_B are their transition states, respectively, and $\Delta\Delta G_{A,B}^\ddagger$ is the difference in Gibbs energy of TS_A and TS_B. In the case above, P_A is the *syn*-product and P_B is the *anti*-product with respect to the substituents on the dienophile and diene. All calculations were performed using the Gaussian 09 suite of programs[71] at the ωB97XD/6-311G(d,p)[57] level of theory using the STQN method[60] for location of the transition states. Geometry optimizations and frequency calculations were performed for both reactants and products to ensure that the geometries used as input into the STQN calculations were minima on the PES. All transition states using the STQN method were confirmed using frequency analysis to be first-order saddle points on the PES. To calculate $\Delta\Delta G_{A,B}^{\ddagger}$, the sum of electronic and thermal free energies at 298.15 K and 1.0 atm were calculated for both transition states and the smaller of the two was subtracted from the larger.

Furan was chosen as the diene because of its forced *s-cis* conformation as well as its common use in Diels-Alder type reactions. Due to the reactivity of cycloalkynes, bulky substituents were strategically chosen for the diene and dienophile in the hope of making $\Delta\Delta G_{A,B}^{\ddagger}$ large.

5.3 Results and Discussion

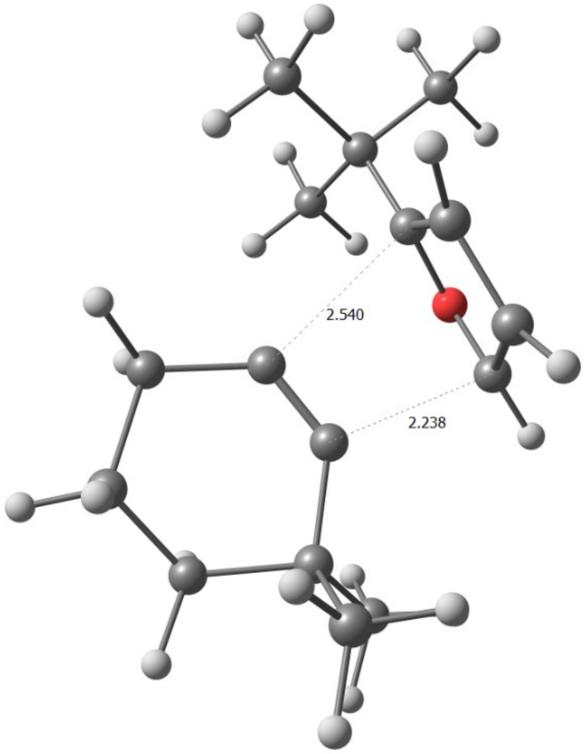
5.3.1 3,3-Dimethylcyclohexyne Diels-Alder Reaction

The results suggest that the largest $\Delta\Delta G_{A,B}^{\ddagger}$ using various cyclohexyne analogues as the dienophile and 2-*tert*-butylfuran as the diene is 0.6 kcal/mol with 3,3-dimethylcyclohexyne. The *anti* and *syn* transition states are shown in Figure 5.2. At room temperature, a $\Delta\Delta G_{A,B}^{\ddagger}$ of 0.6 kcal/mol gives an *anti* to *syn* product ratio of 3:1 according to transition state theory.[81]

The *anti*-TS was found to have incipient bond lengths of 2.540 Å and 2.238 Å and the molecular planes of the two species are perpendicular with respect to one another. The longer incipient bond length was associated with the *tert*-butyl substituted carbon on the diene and the carbon of the triple bond further away from the dimethyl group. The energy barrier for this reaction was determined to be 14.4 kcal/mol. The *syn*-TS was found to have incipient bond lengths of 2.684 Å and 2.142 Å. As expected, the longer incipient bond length was associated with the more sterically hindered carbons, while the shorter one was associated with less hindered carbons.

The distances at the transition states between the bulky substituents on the addends, dimethyl and *tert*-butyl, were recorded because shorter distances were expected to correlate with greater steric hindrance. The question was whether the distances would vary significantly as the ring size of the substituted cyclohexyne increased. At the same time activation energies and thus the regioselectivity of the Diels-Alder reactions were to be assessed. The shortest distance between the two sterically interacting groups in the disfavored *syn*-TS was 2.199 Å. The energy barrier for this reaction was determined to be 15.0 kcal/mol, only 0.6 kcal/mol above that of the *anti*-TS.

Anti-TS



Syn-TS

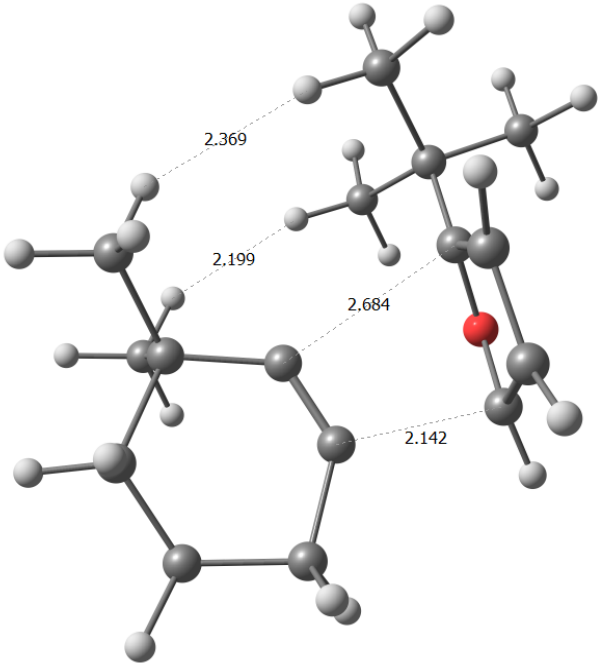


Figure 5.2: The two transition states associated with the Diels-Alder reaction of 3,3-dimethylcyclohexyne and 2-*tert*-butylfuran. The $\Delta\Delta G_{A,B}^{\ddagger}$ for this reaction was calculated to be 0.6 kcal/mol.

5.3.2 3,3-Dimethylcycloheptyne Diels-Alder Reaction

Using the same substituents as the previous reaction but increasing the cycloalkyne ring size by one carbon, the Diels-Alder cycloaddition of 3,3-dimethylcycloheptyne and 2-*tert*-butylfuran was modeled. The transition states for both the *anti* and *syn* additions are shown in Figure 5.3.

The *anti*-TS geometry had shorter incipient bond lengths compared to the six-membered *anti*-TS, with incipient bond distances of 2.182 Å and 2.390 Å. As with the previous reaction, the longer incipient bond length was associated with the *tert*-butyl substituted carbon on the 2-*tert*-butylfuran and the carbon of the triple bond further away from the dimethyl group. However, the difference in the incipient bond lengths were smaller for this reaction when compared to the six-membered *anti*-TS, 0.208 Å and 0.302 Å, respectively. The energy barrier for the *anti*-addition reaction was 20.5 kcal/mol.

The *syn*-TS geometry was found to have incipient bond lengths of 2.621 Å and 2.042 Å, which were shorter than the incipient bond lengths found for the *syn*-TS involving the six-membered ring, but the difference in incipient bond lengths of each structure was almost the same. Like the six-membered ring analogue, the longer incipient bond length was associated with the substituted carbons, while the shorter was associated with the unsubstituted carbons. Comparing the two *syn* transition states, the bulky substituents were slightly closer together in the seven-membered case, with the shortest difference between the *tert*-butyl and dimethyl substituents being 2.117 Å. This distance was 0.082 Å shorter than for the six-membered ring analogue. The energy barrier for this reaction was 22.9 kcal/mol producing a $\Delta\Delta G_{A,B}^{\ddagger}$ of 2.4 kcal/mol, which was a significantly larger than for the six-membered ring analogue reaction.

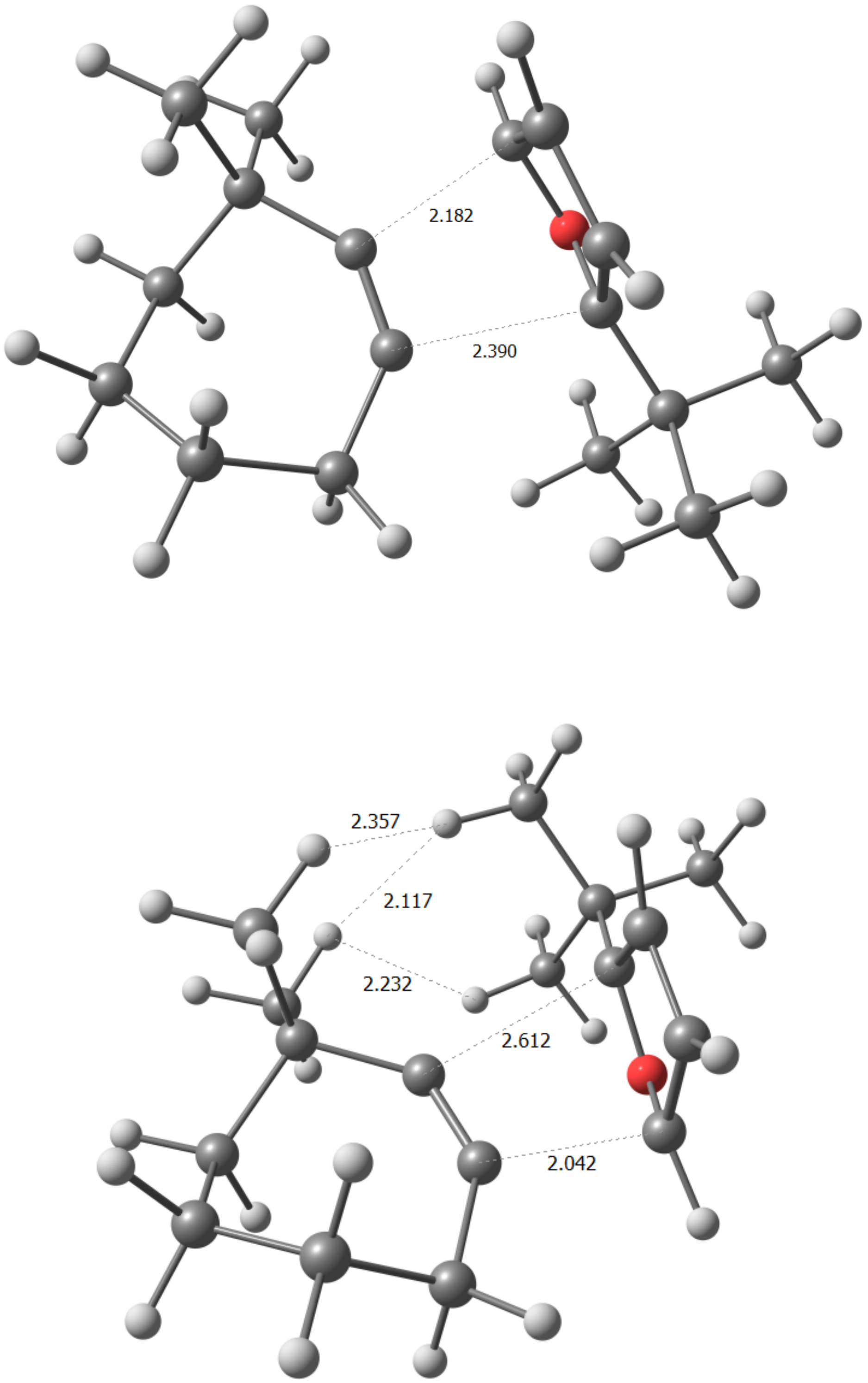


Figure 5.3: The two transition states associated with the Diels-Alder reaction of 3,3-dimethylcycloheptyne and 2-*tert*-butylfuran. The $\Delta\Delta G_{A,B}^{\ddagger}$ for this reaction was calculated to be 2.4 kcal/mol

5.3.3 3,3-Dimethylcyclooctyne Diels-Alder Reaction

Increasing the cycloalkyne ring size again by one more carbon gave the eight-membered analogue, 3,3-dimethylcyclooctyne. The *anti* and *syn* transitions states located for this reaction can be seen in Figure 5.4. A general geometric trend was beginning to form as ring size is increased.

The *anti*-TS geometry was found to have shorter incipient bond lengths, on average, compared to the six- and seven-membered analogues. The incipient bond lengths were 2.350 Å and 2.061 Å. The geometry was similar to the previous analogues in that the incipient bond length associated with the *tert*-butyl substituted carbon was longer than the other incipient bond length. The energy barrier for this reaction was larger than the smaller-ring analogues with an energy barrier of 34.1 kcal/mol.

The *syn*-TS geometry was found to have incipient bond lengths of 2.495 Å and 1.971 Å, which were shorter than the incipient bond lengths found for the *syn*-transition states involving the smaller-ring analogues. Consistent with the previous findings, the longer incipient bond length was associated with the more substituted carbons, while the shorter is associated with the unsubstituted carbons. Again, the bulky substituents were slightly closer together compared with the previous analogues, with the shortest distance between the *tert*-butyl and dimethyl substituents being 2.030 Å, which was 0.087 Å shorter than for the seven-membered ring analogue. The energy barrier for this reaction was 38.1 kcal/mol giving a $\Delta\Delta G_{A,B}^{\ddagger}$ of 4.0 kcal/mol for this system.

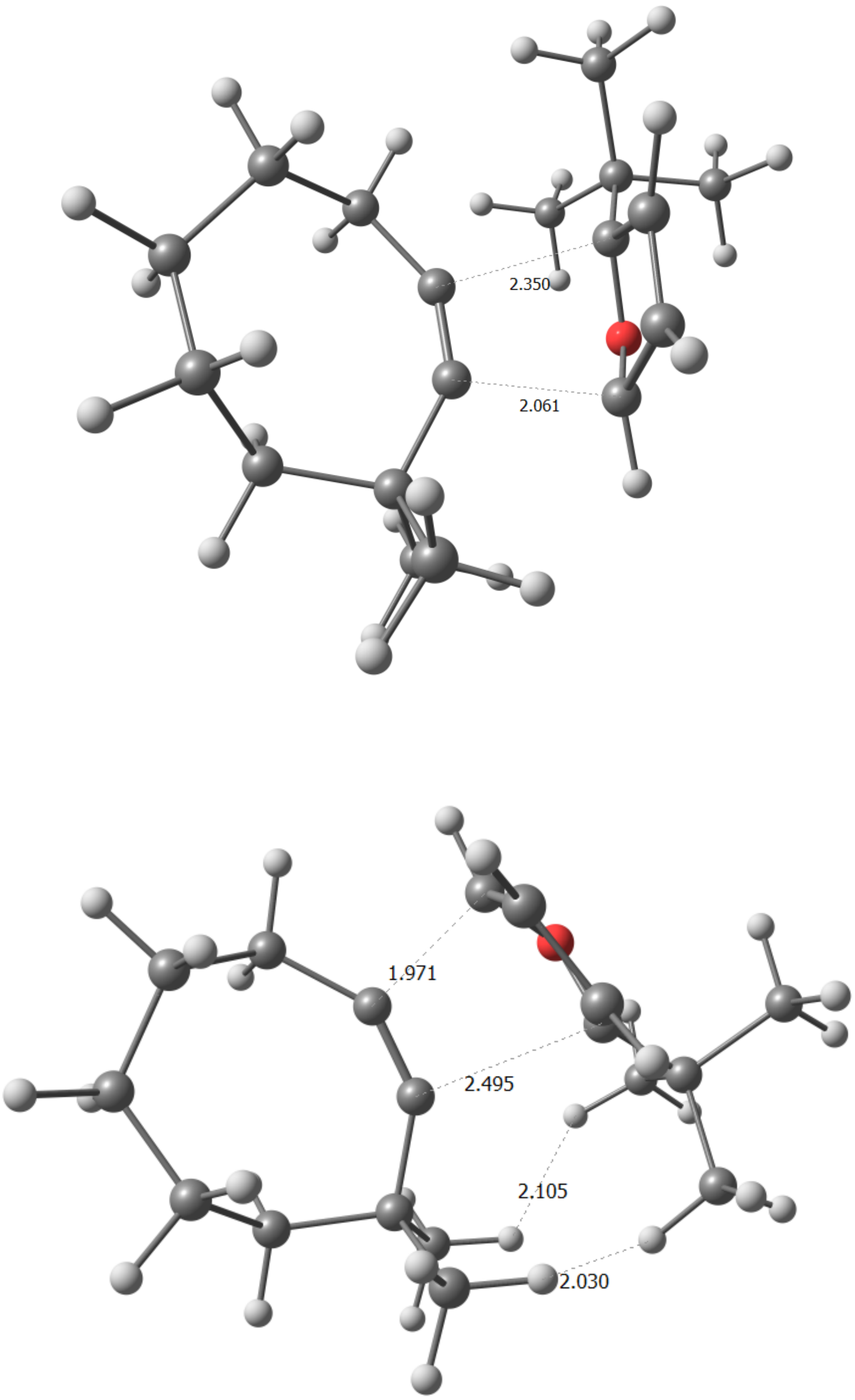


Figure 5.4: The two transition states associated with the Diels-Alder reaction of 3,3-dimethylcyclooctyne and 2-*tert*-butylfuran. The $\Delta\Delta G_{A,B}^{\ddagger}$ for this reaction was calculated to be 4.0 kcal/mol

5.3.4 3,3-Dimethylcyclononyne Diels-Alder Reaction

Finally, increasing the cycloalkyne ring size past the unique ring size of eight, the reaction of 3,3-dimethylcyclononyne and 2-*tert*-butylfuran was modeled. The *anti* and *syn* transitions states found for this reaction can be seen in Figure 5.5.

The *anti*-TS geometry had incipient bond lengths similar (one of them is identical), to the eight-membered analogue; the shortest incipient bond length for the eight- and nine-membered rings were both 2.061 Å and were associated with the unsubstituted carbon on 2-*tert*-butylfuran. The other incipient bond length was determined to be 2.285 Å for the nine-membered ring analogue, which was 0.065 Å shorter than the corresponding incipient bond length determined for the eight-membered analogue. The energy barrier for the *anti*-TS for the nine-membered ring analogue was calculated to be 35.3 kcal/mol, only slightly higher than for the eight-membered analogue.

The *syn*-TS geometry was found to have incipient bond lengths of 2.491 Å and 1.901 Å, which were similar to those for the eight-membered analogue. As with the previous rings, the longer incipient bond length was associated with the substituted carbons, while the shorter was associated with the unsubstituted carbons. The closest distance between the two bulky groups was 1.974 Å, which was 0.036 Å shorter than the eight-membered analogue, making it apparent that the substituents were consistently coming closer together as the ring size increased. The energy barrier for this reaction was determined to be 40.0 kcal/mol giving a $\Delta\Delta G_{A,B}^{\ddagger}$ of 3.7 kcal/mol for this system; this was similar to the $\Delta\Delta G_{A,B}^{\ddagger}$ calculated for the eight-membered analogue.

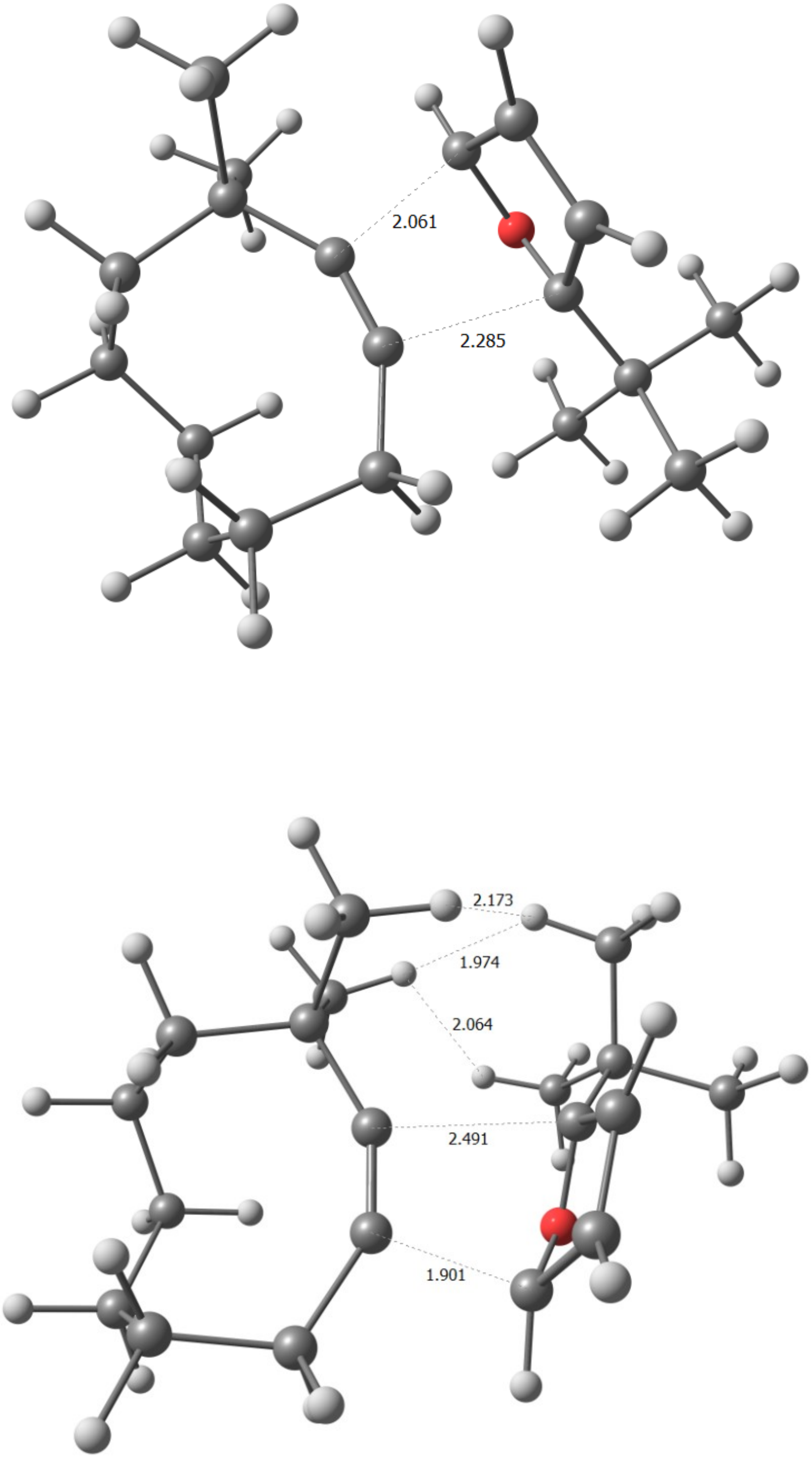


Figure 5.5: The two transition states associated with the Diels-Alder reaction of 3,3-dimethylcyclononyne and 2-*tert*-butylfuran. The $\Delta\Delta G_{A,B}^{\ddagger}$ for this reaction was calculated to be 3.7 kcal/mol.

5.3.5 Comparison of Transition States

Figure 5.6 shows the average incipient bond length as a function of ring size. As ring size decreases, the calculations show that for both the *syn*- and *anti*-transition states the incipient bond length decreases. The *anti*-TS average incipient bond length is smaller than the *syn*-TS for all ring sizes. The triple bond lengths of both *syn*- and *anti*-transition states were found to increase with ring size as shown in Figure 5.7. The data clearly shows that as ring size is decreased the transition state occurs earlier and the geometry looks more like the reactants. To enforce this notion, the average of the angles shown in Figure 5.8, using the six-membered *anti*-TS as an example, was plotted against ring size as well the same average angle for the associated products. In addition to the evidence above, this shows that as ring size is increased, the geometry of the transition state, whether it be *anti* or *syn*, becomes more similar to the product and thus occurs later in the reaction according to Hammond's postulate.

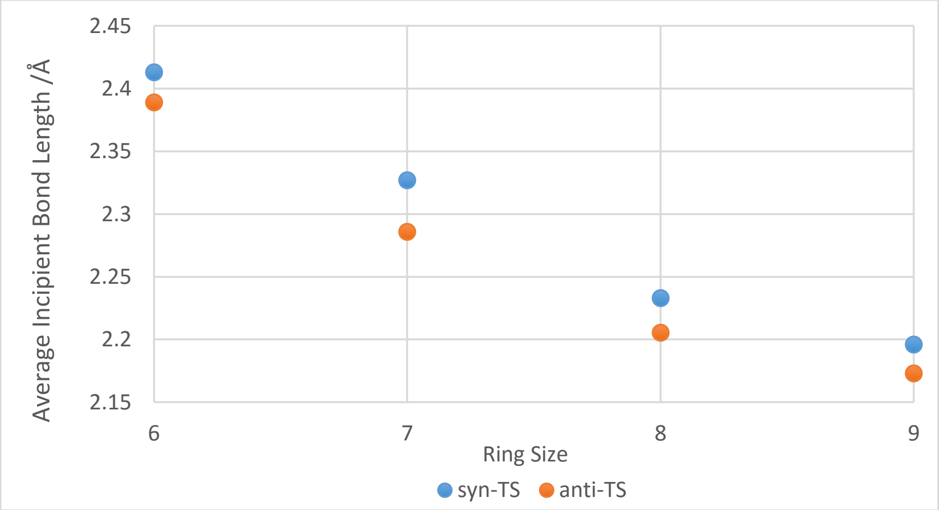


Figure 5.6: Average incipient bond length as a function of ring size for both *anti*- and *syn*-transition states.

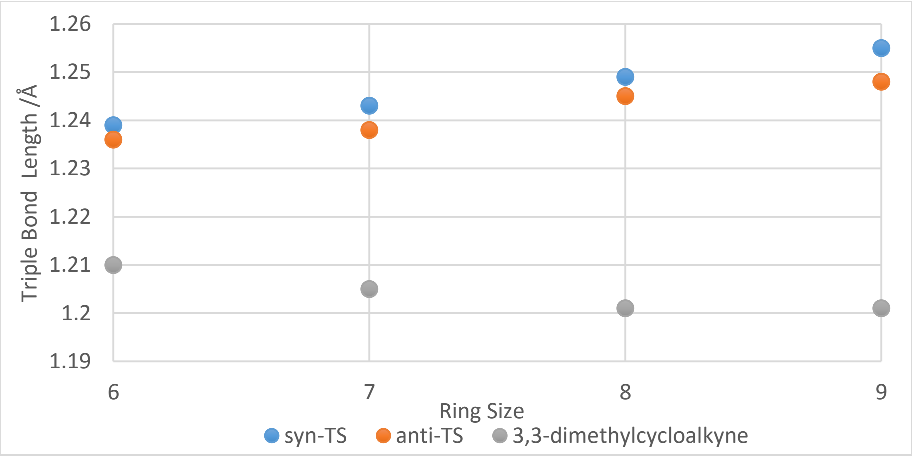


Figure 5.7: Triple bond length as a function of ring size for both *anti*- and *syn*-transition states as well as the 3,3-dimethylcycloalkyne reactant.

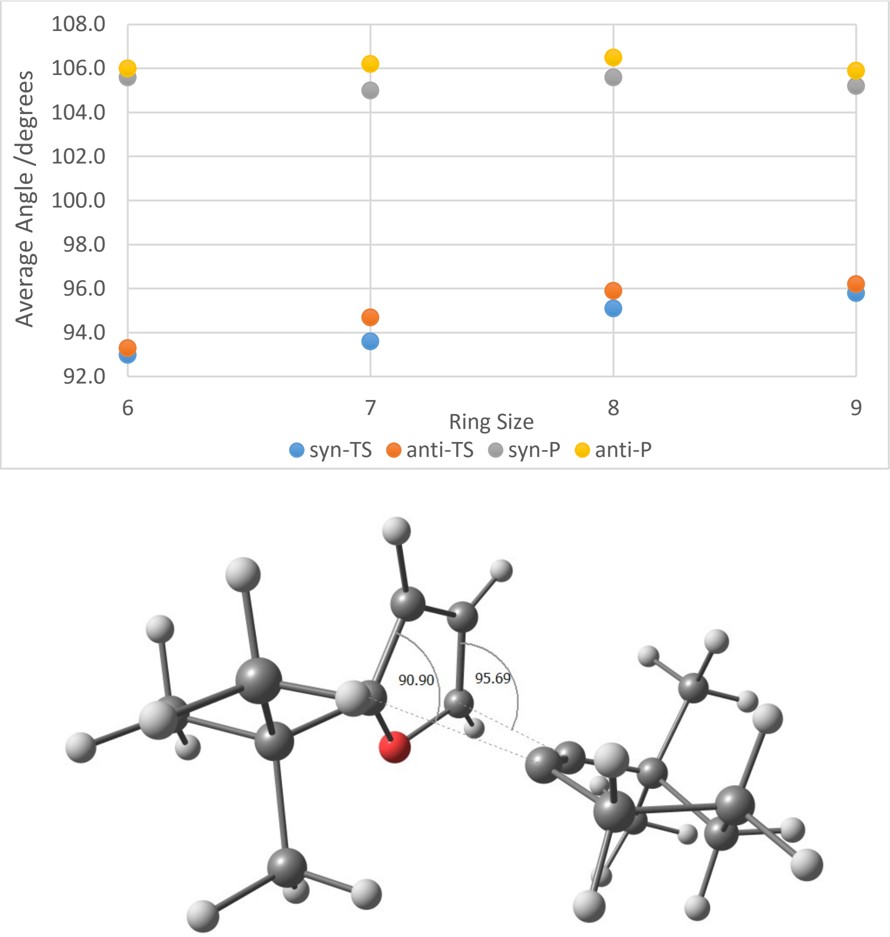


Figure 5.8: Average angle as a function of ring size for the *anti*- and *syn*-transition states and products. The angle is an average of the two angles shown.

Figure 5.9 summarizes the Gibbs energy results presented in the previous section, showing Gibbs energy as a function of ring size for both the *anti*- and *syn*-transition states. It is clearly shown that as the cycloalkyne ring size is increased, the Diels-Alder reaction selectivity also linearly increases until the eight-membered analogue is reached.

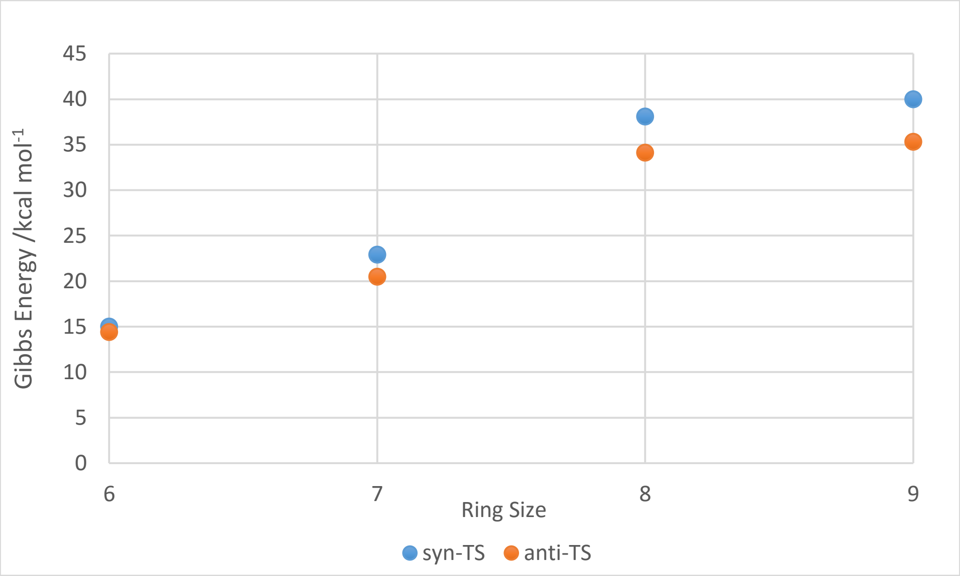


Figure 5.9: Gibbs energy calculated at 1.0 atm and 298.15 K for both the *syn*- and *anti*-transition states for the Diels-Alder reaction between 3,3-dimethylalkynes of ring sizes six through eight and 2-*tert*-butylfuran.

5.4 Conclusions

While in most instances the selectivity of [4+2]-cycloadditions involving cyclohexyne was calculated to be negligible, the reaction of 3,3-dimethylcyclohexyne and 2-*tert*-butylfuran was predicted to be slightly selective with a $\Delta\Delta G_{A,B}^{\ddagger}$ of 0.6 kcal/mol and a predicted 3:1 ratio of *anti* to *syn* products. To determine how the selectivity changes as a function ring size, the seven- through nine-membered cycloalkyne analogues were also modeled undergoing [4+2]-cycloadditions with 2-*tert*-butylfuran.

As expected due to steric hindrance, it was found that the *syn*-TS for all ring sizes was higher in energy than the *anti*-TS. The calculations revealed that as the size of the cycloalkyne ring increased, there was an almost linear increase in $\Delta\Delta G_{A,B}^{\ddagger}$ up until the cyclooctyne analogue with $\Delta\Delta G_{A,B}^{\ddagger}$ calculated to be 0.6 kcal/mol, 2.4 kcal/mol, and 4.0 kcal/mol for the six- through eight-membered analogues, respectively. When the ring size was increased again to the nine-membered analogue, $\Delta\Delta G_{A,B}^{\ddagger}$ was found to decrease relative to the to the eight-membered analogue but by only 0.3 kcal/mol, which suggested that the maximum $\Delta\Delta G_{A,B}^{\ddagger}$ for the cycloalkyne analogues in this particular reaction is around 4.0 kcal/mol.

The geometries of the transition states were similar with differences mostly attributed to incipient bond lengths. All *anti*-transition states showed longer incipient bond lengths between the *tert*-butyl substituted carbon on the 2-*tert*-butylfuran and the carbon of the triple bond further away from the dimethyl group, where all *syn*-transition states showed a longer incipient bond length associated with the substituted carbons, shorter incipient bond lengths associated with the unsubstituted carbons. In general, the incipient bond lengths were longer for the smaller rings, indicative of earlier transition states for lower energy barriers.

The distance between the two bulky substituents, dimethyl and *tert*-butyl, were found to become slightly shorter as ring size increased, but the large jump in $\Delta\Delta G_{A,B}^{\ddagger}$ and $\Delta G^{\ddagger}$ as ring size increased can likely be attributed to the reactivity of the cycloalkyne as a comparison of TS geometries to the reactant and product show a clear trend with ring size.

The results suggest that if unsymmetrically substituted cyclohexyne is to be used in organic synthesis, attention must be given to substituents added. Bulky substituents must be added to both the diene and cyclohexyne to increase the selectivity of the reaction. The study only investigated bulky substituents as a method to driving selectivity, but there may be a significant electronic effect that could also contribute to the selectivity of the cycloalkyne [4+2]-cycloadditions. The effects of electronically biasing cyclohexyne as recently been published by Houk and coworkers.[82]

Chapter 6

The Tetramerization of Cyclohexyne

Although tetramers of cyclohexyne were studied experimentally in 1965 by Wittig,[68] the mechanism for how the oligomerization process occurs has never been studied computationally. In this chapter, the mechanism for the tetramerization of cyclohexyne is examined.

6.1 Motivation and Introduction

The valence isomers of tetrameric cyclohexyne were studied experimentally by Wittig and Weinlich in 1965 as contribution to their series of papers labelled “Zur Existenz niedergliedriger Cycloalkine” or, “The existence of low-membered cycloalkynes”.[68] They alluded to mechanisms for the generation of numerous oligomerization products of cyclohexyne, including the dimer, trimer, and various tetramers. The motivation of this study lies in experimental results where a specific tetramer was generated in 50% yield by François LeFort in the Burnell research group at Dalhousie University through a process shown below:

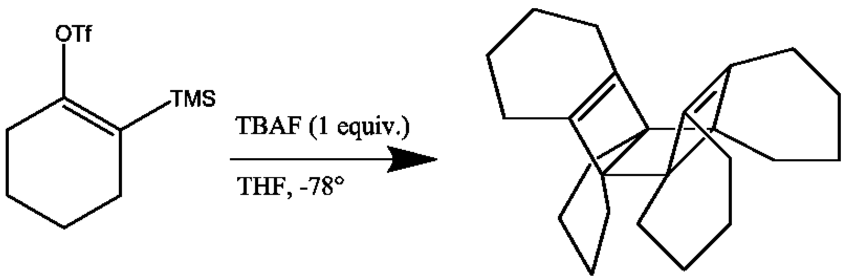


Figure 6.1: The experimental conditions for the formation of a cyclohexyne tetramer.

where cyclohexyne was presumed to be generated from a step-wise elimination and then underwent some oligomerization mechanism to form the tetramer. Wittig and Weinlich had proposed that the tetramer shown in Figure 6.1 can be formed through a Diels-Alder reaction of two cyclohexyne dimers, as shown in Figure 6.2.[68]

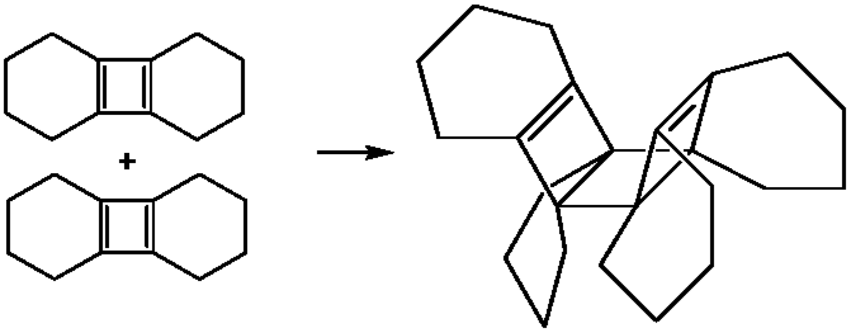


Figure 6.2: The formation of a cyclohexyne tetramer from the Diels-Alder reaction between two cyclohexyne molecules.

The formation of the cyclohexyne dimer was proposed to be the product of a [2+2]-cycloaddition of two cyclohexyne molecules, as seen in Figure 6.3.

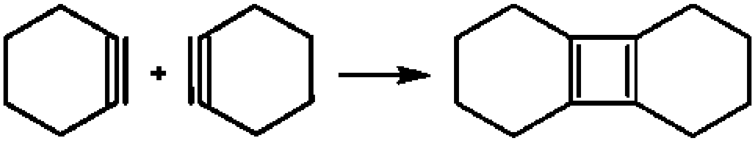


Figure 6.3: The dimerization of cyclohexyne.

In this chapter, the energy reaction profile for two possible mechanisms for the tetramerization pathway of cyclohexyne are studied. The chapter will conclude with a combination of experimental and computational results have led to a proposal of a third pathway that is more likely responsible for the tetramerization of cyclohexyne.

6.2 Computational Methods and Model Systems

All calculations were performed with the Gaussian 09 suite of programs.[71] Geometry optimizations were performed at the ωB97XD/6-311G(d,p)[57] level of theory and transition states were found using the STQN method.[60] The reaction paths were followed using intrinsic reaction coordinate (IRC) calculations.[61,83] Frequency calculations were performed on all structures using the same level theory to ensure either a local minimum or first-order saddle point. All reported energies are the sum of electronic and thermal free energies at 298.15 K and 1.0 atm.

The reaction pathways that were modelled as candidates for the tetramerization are shown in sections 6.2.1-6.2.2. The proposition of a third pathway is presented and examined in section 6.3.4.

6.2.1 Pathway I: Dimerization Followed by Diels-Alder

In the first step of Pathway I, as proposed by Wittig[68], dimerization of cyclohexyne occurs to generate a cyclobutadiene derivative. In turn, the cyclobutadiene derivative dimerizes by a [4+2]-cycloaddition to yield the tetrameric product (Figure 6.4).

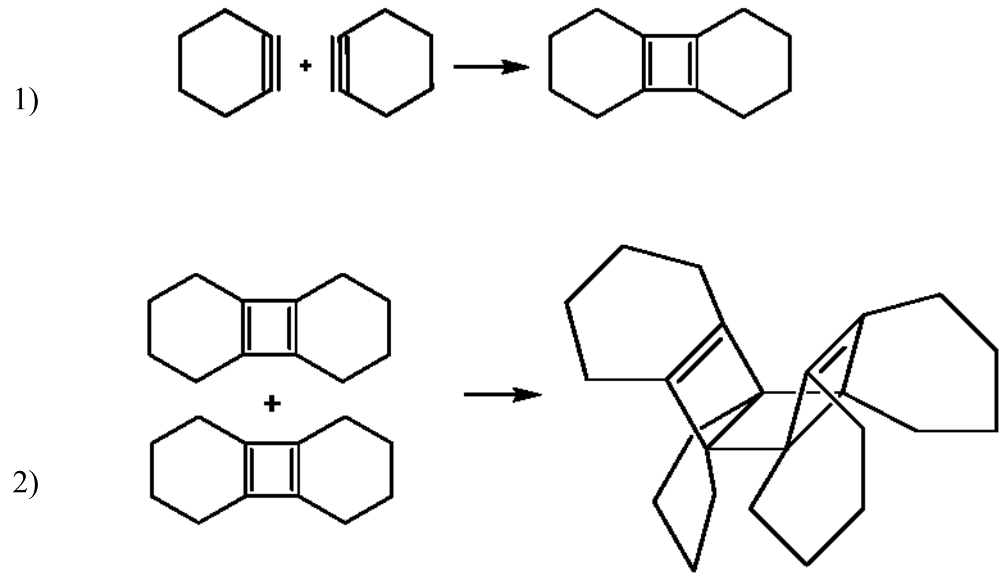


Figure 6.4: A proposed pathway for the generation of a cyclohexyne tetramer.

6.2.2 Pathway II: Building Block Mechanism

A second possible pathway, pathway II, to the tetramer is by consecutive reactions with cyclohexyne (Figure 6.5). In this pathway, a dimer is initially generated as in pathway I by the [2+2]-cycloaddition of two cyclohexyne molecules. This cyclohexyne dimer then undergoes a [4+2]-cycloaddition with another cyclohexyne molecule to yield the trimer, which is a derivative of Dewar benzene. Since the thermal opening of the Dewar benzene to the benzene derivative is symmetry forbidden, the barrier for this conversion would be expected to be high. In the last step, the tetramer is generated from a specific [2+2]-cycloaddition between the Dewar benzene and another molecule of cyclohexyne. There are four possible sites where cyclohexyne can add to the Dewar benzene. Figure 6.5 shows two double bonds, labelled A and B, on the Dewar benzene where a [2+2]-cycloaddition can happen, and this reaction could take place to either face of A or B. Herein these sites are referred to as Bf, Bb, Af, and Ab where lower case f and b indicate “front” or “back” relative to the Dewar benzene as shown in Figure 6.5. The only site of reaction that would yield the observed tetramer is Bf.

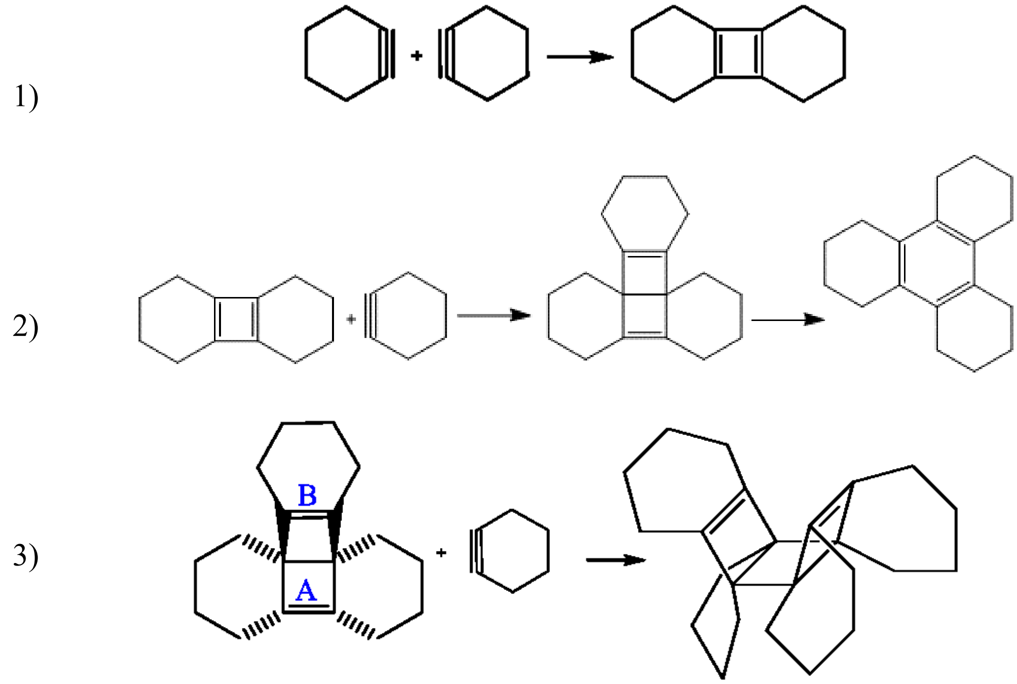


Figure 6.5: A proposed pathway for the formation of a cyclohexyne trimer where the mechanism is comprised of subsequent additions of four cyclohexyne molecules in three steps.

6.3 Results and Discussion

6.3.1 Pathway I: Double Dimerization

The first step in Pathway I was the dimerization of cyclohexyne. A concerted [2+2]-cycloaddition would be thermally antarafacial, and so it was not surprising that the dimerization was stepwise. The initial carbon-carbon bond formed via a barrier of 8.1 kcal/mol, and the second carbon-carbon bond closed the four-membered ring via a transition state with a barrier of 7.1 kcal/mol. These transition states are depicted in Figure 6.6. At the first transition state, TS_1, the two cyclohexyne molecules were arranged with their π-systems *anti* to one another, and the incipient bond, between C_{18} and C_4, had a distance of 2.218 Å. The second step was somewhat surprising. It required rotation by about 90° of one of the cyclohexyne rings, and the IRC revealed that TS_2 proceeded to the cyclobutadiene derivative (dimer) through a mechanism where new bonds formed between C_3 and C_{18} and between C_4 and C_{17} at the same time as the initially formed the C_{18}-C_4 bond was then broken.

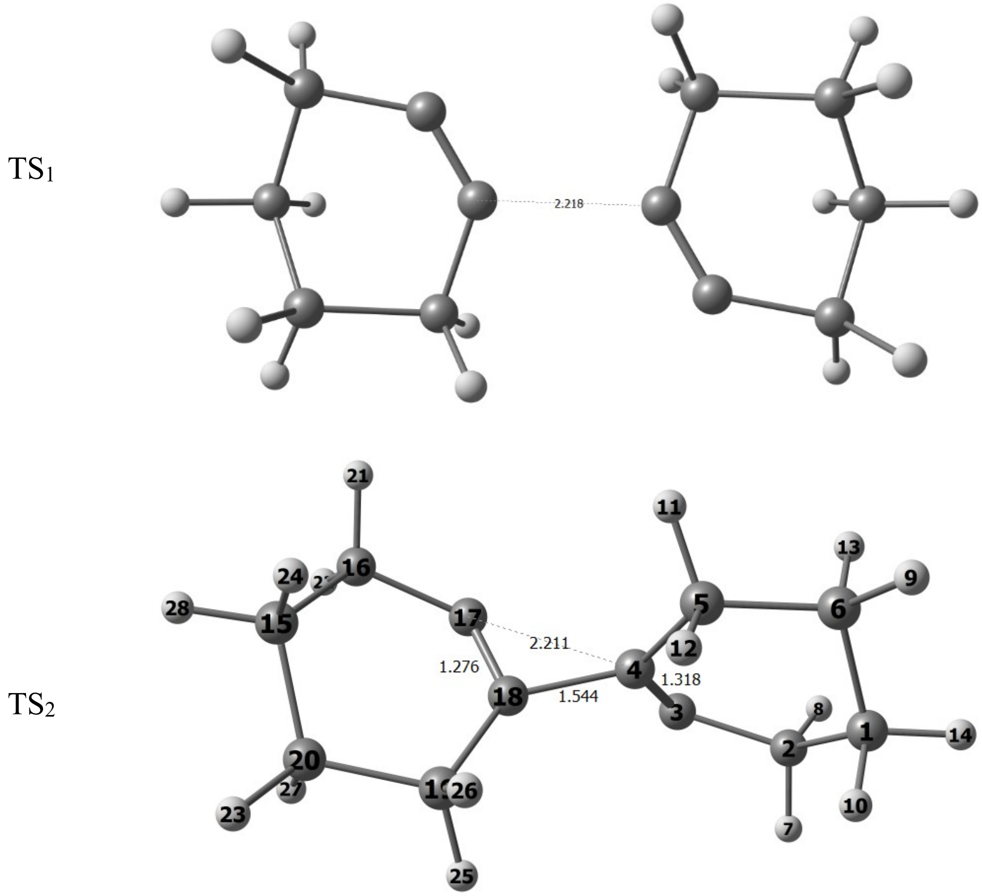


Figure 6.6: The geometries of the transition states, TS_1 and TS_2, corresponding to the first and second step in the dimerization of cyclohexyne. The energy barriers were found to be 8.1 kcal/mol and 7.1 kcal/mol for the first and second step, respectively.

The second step of Pathway I is the Diels-Alder reaction between two molecules of the cyclobutadiene derivative, i.e., the cyclohexyne dimer. This should be a symmetry allowed, concerted [4+2]-cycloaddition between one cyclobutadiene molecule as the diene and the other as the dienophile. The activation barrier was found to lie just 0.8 kcal/mol above the energy of the reactants and so the reaction is almost barrierless. The geometry of transition state (TS) for this reaction, Figure 6.7, showed the expected suprafacial approach. The long incipient bond lengths are indicative of a low-barrier Diels-Alder reaction, but what was extraordinary was that all four pairs of subtended sp^2 carbons were at approximately the same distance, so the primary reacting carbons were indistinguishable from the secondary sites. This transition state has almost C_{4v} symmetry.

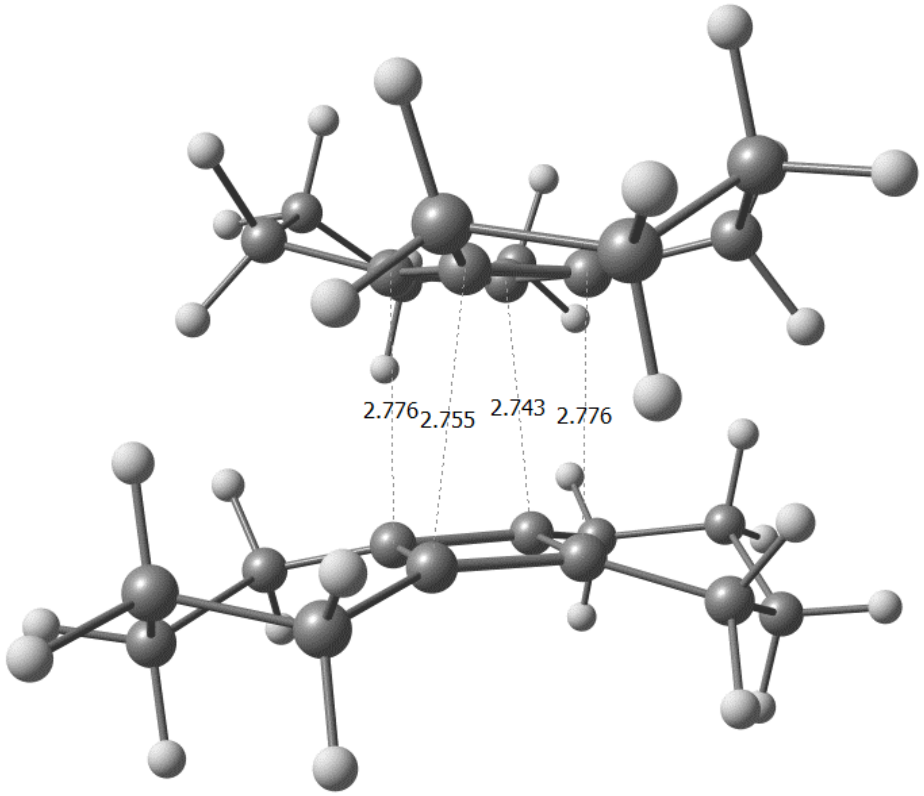


Figure 6.7: The geometry of the transition state associated with the second step in Pathway I; a Diels-Alder reaction between two cyclohexyne dimers.

6.3.2 Pathway II: Building Block Mechanism

The first step of Pathway II is the same as Pathway I, i.e., the [2+2] dimerization of cyclohexyne. The second step in Pathway II is the addition of a molecule of cyclohexyne to the cyclohexyne dimer, the cyclobutadiene derivative, to form the Dewar benzene trimer.

This was expected to be a concerted [4+2]-cycloaddition. The TS for this reaction, shown in Figure 6.8, was found to lie 6.4 kcal/mol above the energy of the reactants. The formation of the trimer was confirmed to be concerted, but, presumably due to the nonplanarity of cyclohexyne, it was asynchronous with incipient bond lengths of 2.490 Å and 2.739 Å.

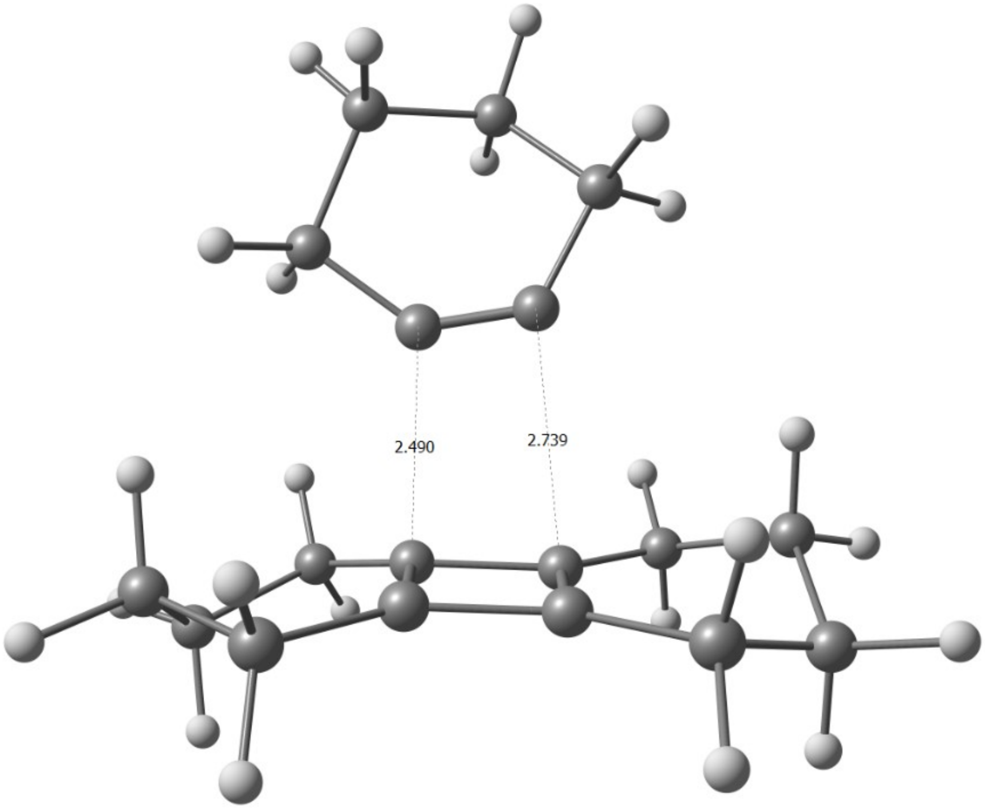


Figure 6.8: The geometry of the transition state of the second step of Pathway II; [4+2]-cycloaddition of cyclohexyne to the cyclobutadiene intermediate (cyclohexyne dimer) to form the Dewar benzene trimer. The energy barrier was 6.4 kcal/mol.

The pathway of the Dewar benzene opening to give the benzene derivative was found to have a relatively high energy barrier of 43.1 kcal/mol, as expected for a symmetry disallowed process; the geometry of the transition state for this reaction is shown below in Figure 6.9.

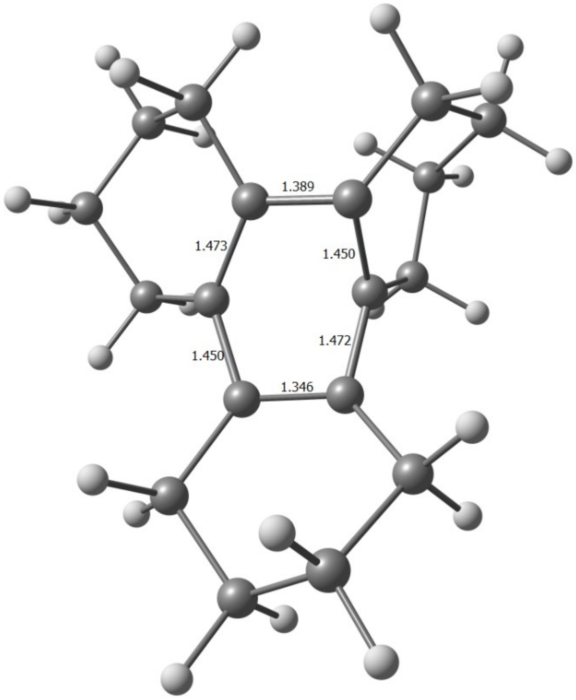
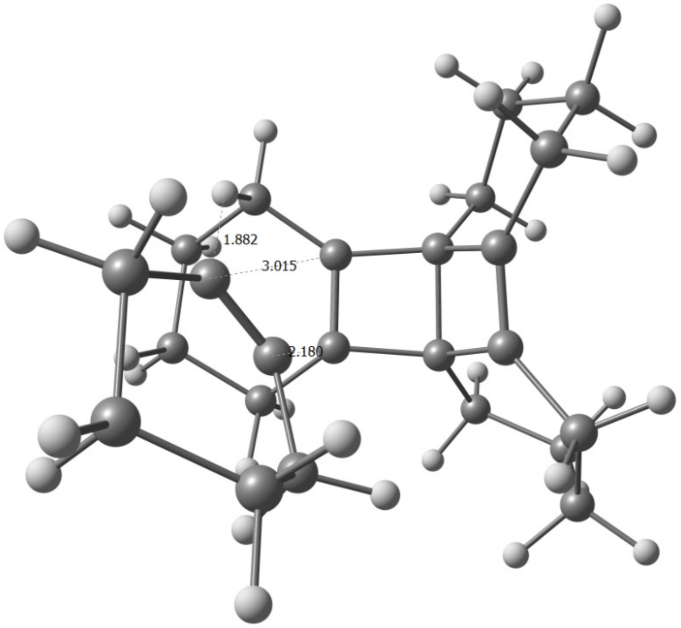


Figure 6.9: The geometry of the transition state corresponding to the side reaction in Pathway II; the Dewar benzene trimer opening to give the benzene derivative. The energy barrier was 43.1 kcal/mol.

The last step in Pathway II is the cycloaddition of cyclohexyne with the Dewar benzene trimer, a (2+2)-cycloaddition. The four possible modes of attack were investigated and each was found to be a stepwise process. The first transition states, TS_1, for the four possible sites of addition are shown below in Figures 6.10 and 6.11. The energy of the first transition state corresponding to an addition at the front of B, $TSBf_1$, was 20.1 kcal/mol above the reactants, while the first transition state for the addition at the back of B, $TSBb_1$, was found to lie 17.6 kcal/mol above the reactants. Both $TSBf_1$ and $TSBb_1$, have similar geometries; the incipient bond lengths for the carbons are unequal and there seems to be an intramolecular hydrogen transfer occurring. The imaginary frequency mode corresponds to one of the carbons in the triple bond bonding to a carbon in the double bond, while the other carbon in the triple bond picks up the hydrogen located on the alpha carbon relative to the double bond. To aid the reader, the distances between relevant atoms are shown in Figure 6.10.

TSBf$_1$



TSBb$_1$

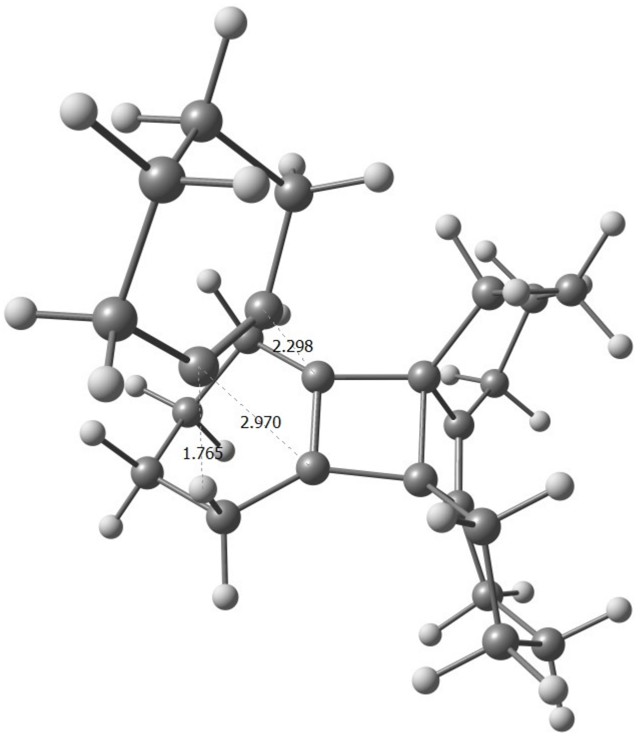
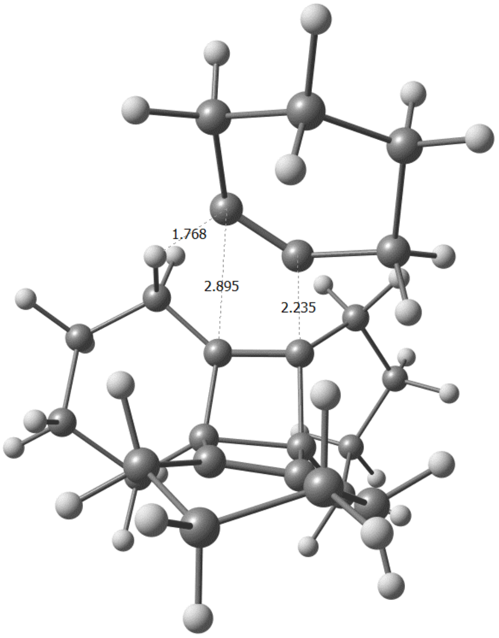


Figure 6.10: The geometries of the two first transition states, TSBf$_1$ and TSBb$_1$, for step three of Pathway II; the addition of cyclohexyne to site B of the Dewar benzene trimer. The energy barriers for this step were 20.1 kcal/mol and 17.6 kcal/mol for TSBf$_1$ and TSBb$_1$, respectively.

The first step in the addition of cyclohexyne to the front of position A, $TSAf_1$, was found to have a TS similar to $TSBf_1$ and $TSBb_1$ with unequal incipient bond lengths and the beginning of a hydrogen transfer occurring. However, the addition of cyclohexyne to the back of A, $TSAb_1$, was found to have a TS unlike the previous three. The triple bond in cyclohexyne was found to be perpendicular to the double bond in the trimer with only one carbon-carbon bond beginning to form. The transition states for cyclohexyne addition to the A site can be seen in Figure 6.11. The energy barriers for this step were determined to be 18.2 kcal/mol and 24.5 kcal/mol for TSAf1 and $TSAb_1$, respectively.

TSAf$_1$



TSAb$_1$

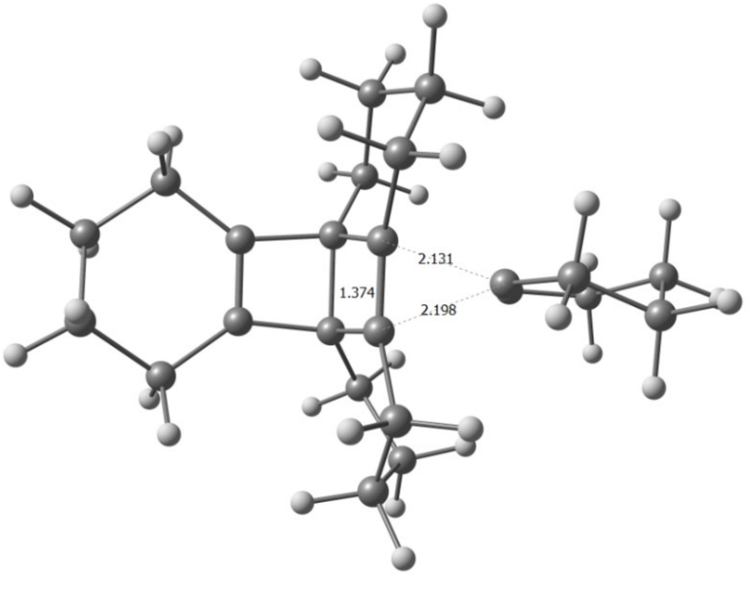


Figure 6.11: The geometries of the two first transition states, TSAf$_1$ and TSAb$_1$, for step three of Pathway II; the addition of cyclohexyne to site A of the Dewar benzene trimer. The energy barriers for this step were 18.2 kcal/mol and 24.5 kcal/mol for TSAf1 and TSAb$_1$, respectively.

In the second step of the addition of cyclohexyne, Af, Bf, and Bb were found to have similar TS$_2$ geometries, with the IRC showing transfer of the hydrogen back to the alpha carbon and the final carbon-carbon bond being formed to yield the associated tetramer. As an example of the geometry of these transition states, $TSBf_2$ is shown below in Figure 6.12 with scaled displacement vectors showing the hydrogen transfer. The energy barriers for this step were 86.7 kcal/mol, 94.4 kcal/mol, and 98.0 kcal/mol for $TSBb_2$, $TSBf_2$, and $TSAf_2$, respectively.

$TSBf_2$

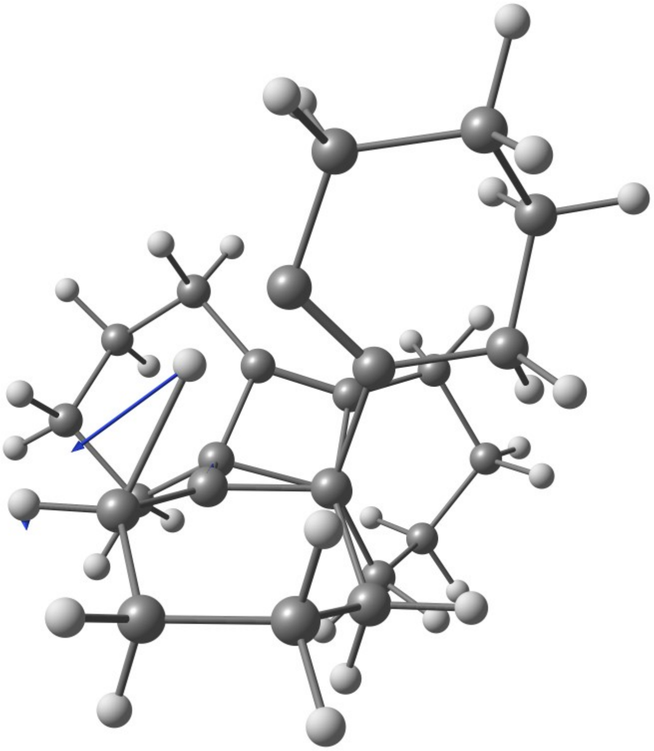


Figure 6.12: The geometry of the second transition state, $TSBf_2$, associated with step three of Pathway II; the addition of cyclohexyne to site B of the Dewar benzene trimer. Similar geometries were found for $TSAf_2$ and $TSBb_2$.

The second step transition state associated with the addition of cyclohexyne to the back of A, $TSAb_2$ was found to have a different geometry than the rest. The imaginary vibrational mode corresponded to the closing of the four-membered ring, forming a C_{32}-C_3 bond, which completed the formation of the tetramer. This transition state along with the scaled vibrational vectors can be seen in Figure 6.13. The energy barrier was 7.4 kcal/mol for this step.

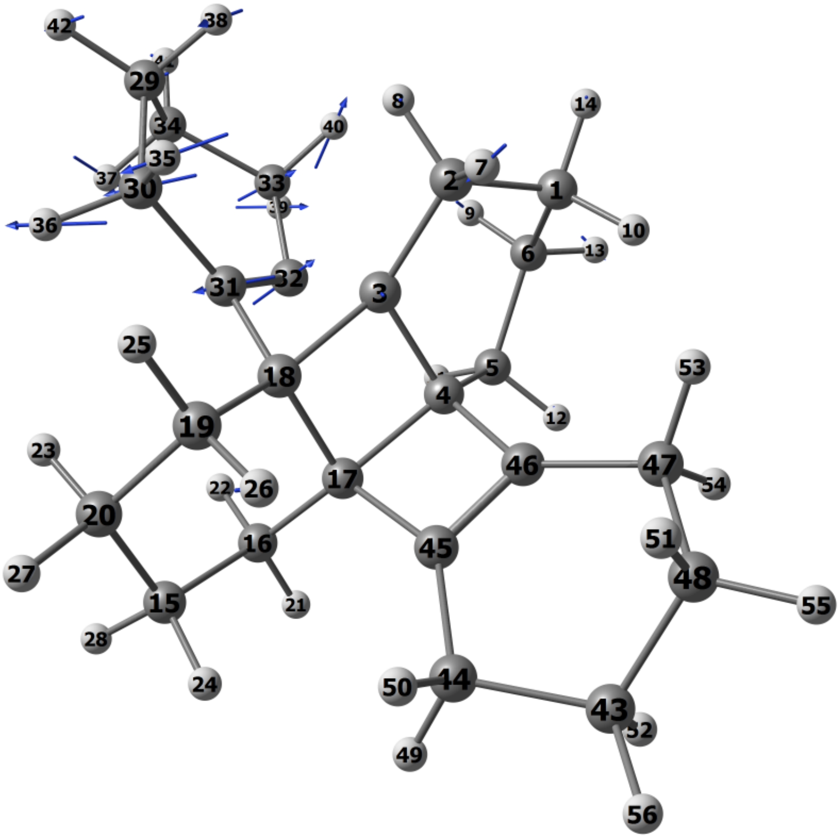


Figure 6.13: The geometry of the second transition state, TSAb$_2$, for step three of Pathway II; the addition of cyclohexyne to site A of the Dewar benzene trimer. The energy barrier was 7.4 kcal/mol.

To clearly compare the energy profiles of the four stepwise additions of cyclohexyne to the Dewar benzene trimer, Figure 6.14 is presented below. The path highlighted in green is associated with the formation of the cyclohexyne tetramer under study and was found not be viable due to a limiting barrier of 94.4 kcal/mol in the second step.

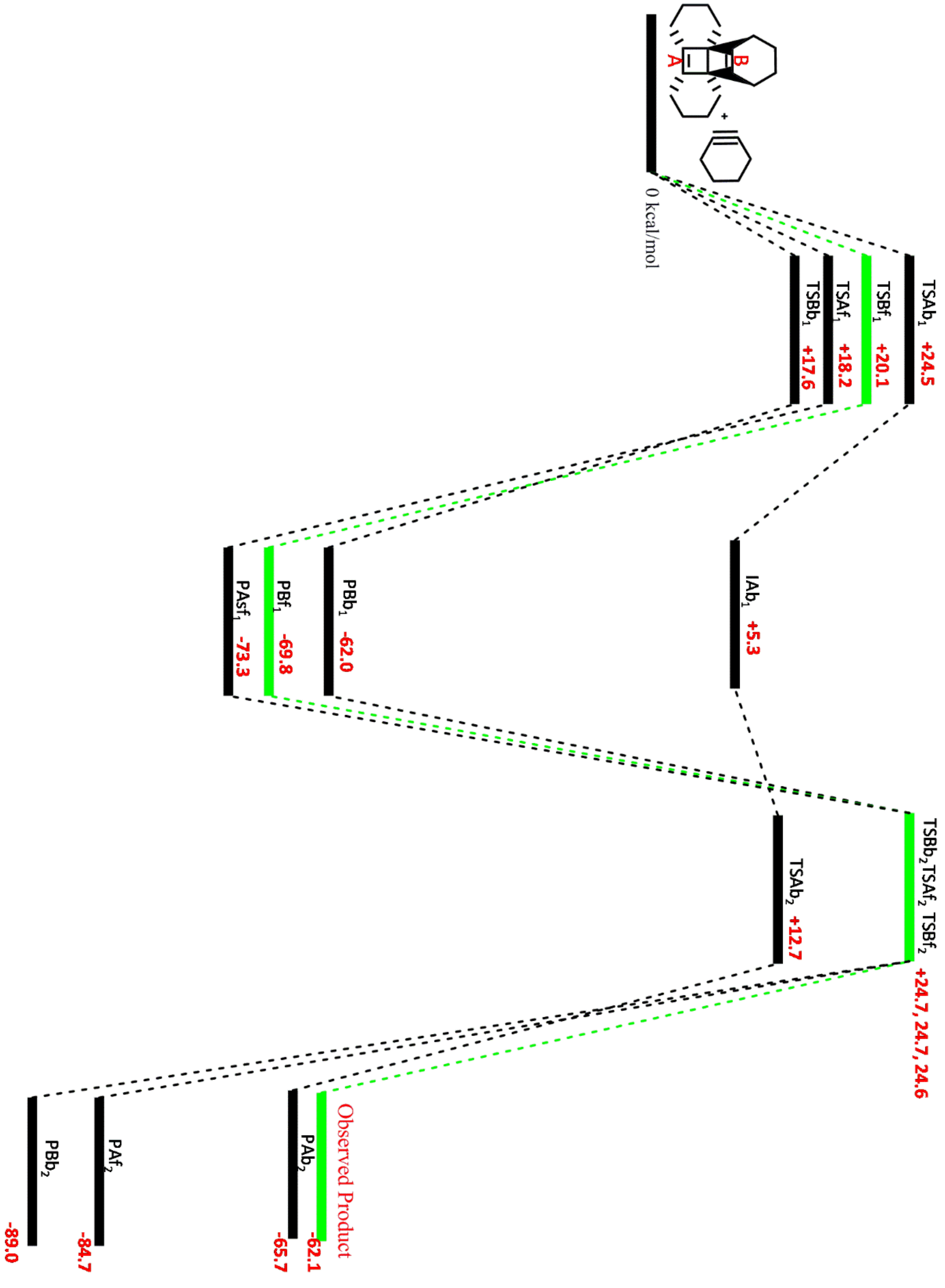


Figure 6.14: The energy profile for step three of Pathway II, the addition of cyclohexyne to the Dewar benzene trimer. All reactions were found to go through two transition states to reach their associated tetramers. However, the pathway that yielded the experimentally observed tetramer, highlighted in green, was found to have a 94.4 kcal/mol limiting energy barrier

6.3.3 Comparison of Pathway I to Pathway II

The results show that Pathway I is more energetically favorable. Both Pathway I and Pathway II begin with the dimerization of cyclohexyne, which was determined to be a two-step mechanism with an 8.1 kcal/mol limiting energy barrier. The second step of Pathway I, the Diels-Alder addition of two cyclohexyne dimers, had an extremely low energy barrier of 0.8 kcal/mol. The second step of Pathway II was found to have a reasonable barrier of 6.4 kcal/mol. However, after analyzing step three of Pathway II, the addition of cyclohexyne to the Dewar benzene trimer, the path that led to the desired tetramer was found to have a limiting energy barrier of 94.4 kcal/mol. In addition to having a large limiting energy barrier, this pathway was found not to be the most energetically favorable route relative to the other three possible additions.

6.3.4 Proposition and Exploration of a Third Pathway to the Cyclohexyne Tetramer

As mentioned above, the tetramer product was obtained in 50% yield. However, it was found that replacing the tetramethylsilane (TMS) with bromine on the starting material and using *n*-butyllithium instead tetra-*n*-butylammonium fluoride (TBAF) gave an 80% yield of the tetramer. These two methods of generating cyclohexyne are shown below in Figure 6.15.

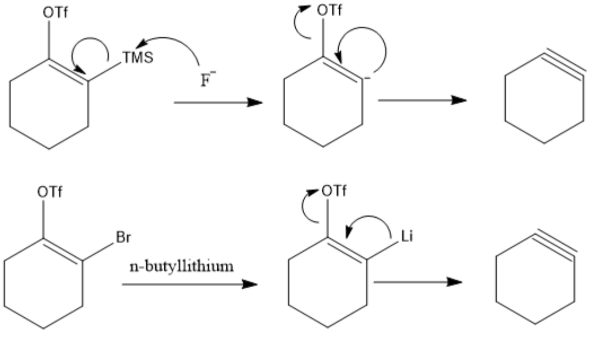


Figure 6.15: Two methods for generating cyclohexyne. The first method resulted in 50% yield of the cyclohexyne tetramer, while the second method resulted in an 80% yield.

If the two methods generated cyclohexyne in full without any side reactions then their yields should be the same. Furthermore, when cyclohexyne was generated by the first method in the presence of a diene such as furan, a Diels-Alder adduct could be isolated. However, when the experiment was repeated but the cyclohexyne was produced by the second method, which based on the yield of the tetramer appeared to produce cyclohexyne more efficiently, no Diels-Alder adduct was detected. Thus, the method of cyclohexyne generation affected the subsequent reactivity.

As shown above, the computational findings indicated that the Diels-Alder reaction between two cyclobutadiene molecules is essentially barrierless, so if at any point there are two dimers generated in solution, the tetramer formation should follow this pathway. A computational search for alternative mechanisms for the generation of the cyclohexyne dimer was performed. Only the carbon-carbon bond forming steps were probed as the elimination steps are unlikely to be rate determining.

6.3.4.1 Starting Material Anion Attacking Cyclohexyne

An alternative route that is not strictly a dimerization reaction that could potentially provide the "cyclohexyne dimer" (cyclobutadiene derivative) is shown in Figure 6.16. The anion that was thought to eliminate exclusively to cyclohexyne might instead react with a molecule cyclohexyne, and the intermediate could proceed via a 4π-electrocyclization to the product shown below, which in turn could eliminate triflate to provide the cyclobutadiene. (As computations on these molecules would be lengthy, the triflate group was replaced with formate for computational efficiency.)

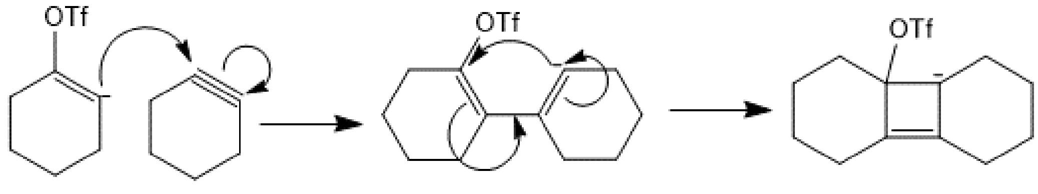
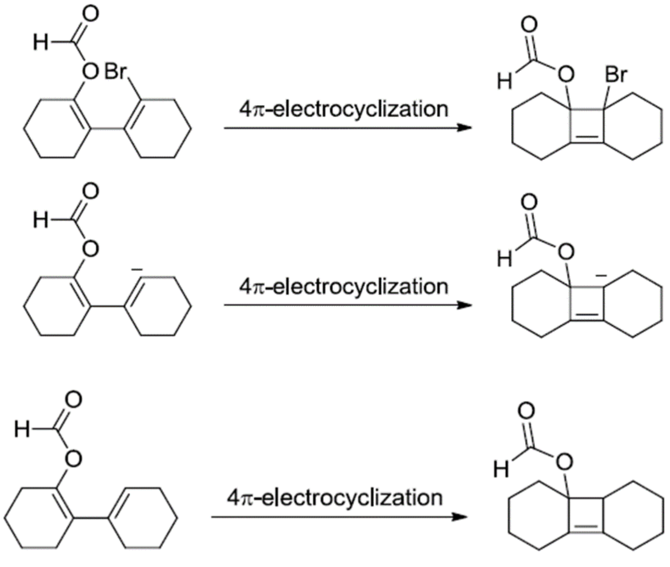


Figure 6.16: A possible mechanism that was investigated computationally for the generation of the cyclohexyne dimer: attack of an anionic compound on cyclohexyne to form a complex that could undergo 4π-electrocyclization to yield an anionic cyclobutene possessing an excellent leaving group.

A TS for the first step was found to lie 2.4 kcal/mol above the reactants. The second step, 4π-electrocyclization, was found to have a barrier of 32.9 kcal/mol. Two other 4π-electrocyclizations, neutral and brominated, were investigated to compare the energy the associated energy barriers. The brominated species could be generated from the same anion attacking the starting material (with subsequent elimination of triflate). The brominated and neutral species were found to undergo 4π-electrocyclizations with barriers of 84.7 and 66.5 kcal/mol, respectively. Figure 6.17 summarizes the results found for the 4π-electrocyclizations reactions.



$\Delta G_A^{\ddagger}$=84.7 kcal/mol

$\Delta G_A^{\ddagger}$=32.9 kcal/mol

$\Delta G_A^{\ddagger}$=66.5 kcal/mol

Figure 6.17: Comparison of the energy barriers associated with three different 4π-electrocyclizations. The anion has the lowest barrier, followed by the neutral species and the brominated species.

The results support a third pathway, showing that the 4π-electrocyclization involving the anionic species generated from an anionic starting material attacking cyclohexyne has the lowest energy barrier compared to the neutral and brominated species. The final step of this pathway would be the same as Pathway I, with two cyclohexyne dimers undergoing [4+2]-cycloaddition to form the tetramer observed from experiment.

6.4 Conclusions

Three pathways for the formation of a tetramer of cyclohexyne have been modelled. Pathway I was found to be limited by the first step in the formation of the cyclohexyne dimer, with a calculated energy barrier of 8.1 kcal/mol. Pathway II was found to be too energetically unfavorable due to the addition of cyclohexyne to the cyclohexyne trimer having a calculated barrier of 94.4 kcal/mol. Furthermore, out of the four possible pathways in step three of Pathway II, the pathway leading to the desired tetramer was found to be the least favorable kinetically.

The calculations suggest that the formation of the tetramer is most likely to occur from a Diels-Alder reaction between two cyclohexyne dimers with an energy barrier of 0.8 kcal/mol. An alternative pathway was explored and the calculated and experimental results support the notion that the cyclohexyne dimer is generated from a multistep reaction of a starting material anion and cyclohexyne which then undergoes an almost barrierless Diels-Alder cyclization to give the tetramer observed in experiment.

Chapter 7

Conclusions and Future Work

7.1 Investigation of the Five- to Twelve-Membered Cyclic Alkynes

In chapter 4, the results of a systematic study of the singlet and triplet states of cyclopentyne through cyclododecyne were presented. The singlet state cycloalkyne series was found to have a smooth trend in geometric and electronic structure properties as a function of ring size. The data we report reveal two regimes that have a transition point at a ring size of eight. The data suggest that as the ring size decreases, the occupancy of the π orbitals contributing to the triple bond decreases while the occupancy of the σ bond increases. Furthermore, likely due to the decrease in triple bond length, it was found that as the ring size decreases, the electron density at the triple bond critical point increases. The calculations for the triplet state cycloalkynes show an anomaly in the electronic and geometric structure at a ring size of eight at all levels of theory.

It was found that for cyclopentyne and cyclohexyne the triplet state is higher in energy relative to the singlet state. The results obtained using the coupled cluster method suggest that, relative to the triplet state, the singlet state of cyclohexyne lies 43 kcal/mol lower in energy, while singlet state cyclopentyne lies 15 kcal/mol lower in energy. These data reinforce the previous calculations done by Olivella and coworkers.[17] The limited structural data available for the cycloalkyne series, cyclononyne[5] and cyclooctyne[4], matches quite well with the calculated data.

7.2 Regioselectivity Search

In Chapter Five, while in most instances the selectivity of [4+2]-cycloadditions involving cyclohexyne was calculated to be negligible, the reaction of 3,3-dimethylcyclohexyne and 2-*tert*-butylfuran was predicted to be slightly selective with a $\Delta\Delta G_{A,B}^{\ddagger}$ of 0.6 kcal/mol. To determine how the selectivity changes as a function ring size, the seven- through nine-membered cycloalkyne analogues were also modeled undergoing [4+2]-cycloadditions with 2-*tert*-butylfuran.

As expected due to steric hindrance, it was found that the *syn*-TS for all ring sizes was higher in energy than the *anti*-TS. The calculations revealed that as the size of the cycloalkyne ring increased, there was an almost linear increase in $\Delta\Delta G_{A,B}^{\ddagger}$ up until the cyclooctyne analogue with $\Delta\Delta G_{A,B}^{\ddagger}$ calculated to be 0.6 kcal/mol, 2.4 kcal/mol, and 4.0 kcal/mol for the six- through eight-membered analogues, respectively. When the ring size was increased again to the nine-membered analogue, $\Delta\Delta G_{A,B}^{\ddagger}$ was found to decrease relative to the to the eight-membered analogue but by only 0.3 kcal/mol, which suggested that the maximum $\Delta\Delta G_{A,B}^{\ddagger}$ for the cycloalkyne analogues in this particular reaction is around 4.0 kcal/mol.

The geometries of the transition states were similar with differences mostly arising from the lengths of the incipient bonds. All *anti*-transition states showed longer incipient bond lengths between the *tert*-butyl substituted carbon on the 2-*tert*-butylfuran and the carbon of the triple bond further away from the dimethyl group, where all *syn*-transition states showed a longer incipient bond length associated with the substituted carbons, shorter incipient bond lengths associated with the unsubstituted carbons. In general, the incipient bond lengths were longer for the smaller rings, indicative of earlier transition states for lower energy barriers.

The distance between the two bulky substituents, dimethyl and *tert*-butyl, were found to become slightly shorter as ring size increased, but the large jump in $\Delta\Delta G_{A,B}^{\ddagger}$ and $\Delta G^{\ddagger}$ as ring size increased can likely be attributed to the reactivity of the cycloalkyne.

7.3 Tetramerization of Cyclohexyne

In Chapter Six, three pathways for the formation of a tetramer of cyclohexyne were modelled. Pathway I was found to be limited by the first step in the formation of the cyclohexyne dimer, with a calculated energy barrier of 8.1 kcal/mol. Pathway II was found to be too energetically unfavorable due to the addition of cyclohexyne to the cyclohexyne trimer having a calculated barrier of 94.4 kcal/mol. Furthermore, out of the four possible pathways in step three of Pathway II, the pathway leading to the desired tetramer was found to be the least favorable kinetically.

The calculations suggest that the formation of the tetramer is most likely to occur from a Diels-Alder reaction between two cyclohexyne dimers with an energy barrier of 0.8 kcal/mol. Although determined to be high in energy, an alternative pathway was explored and the calculated and experimental results support the notion that the cyclohexyne dimer is generated from a multistep side reaction of a starting material and cyclohexyne which then undergoes an almost barrierless Diels-Alder cyclization to give the tetramer observed in experiment.

7.4 Future Work

The work presented in this thesis is a good starting point for an understanding of the small-ring cycloalkyne series and their reactions. However, there are numerous other areas that can be examined to better understand these strained systems. A couple of future directions the studies in this thesis can take are presented below.

7.4.1 Electronically Biased Diels-Alder

It would be useful to study the consequence of electronically biasing the dienophile or diene in the selectivity study of Chapter Five. The results show that the cyclohexyne ring is only slightly selective in [4+2]-cycloadditions when the substituents on the diene and dienophile are bulky. Houk and coworkers recently published computational results on the cycloadditions of 3-methoxycyclohexyne with imidazole and methyl azide.[82] The results show selective additions with $\Delta\Delta G^{\ddagger}$ on the order of 2.9 kcal/mol and 2.8 kcal/mol for the addition of imidazole and methyl azide, respectively. Although in their case the diene is an azide, a systematic investigation on whether substituting a cycloalkyne with an electron donating or withdrawing group effects the selectivity of [4+2]-cycloadditions with other dienes could provide more information on how these small cycloalkynes undergo cyclization reactions.

7.4.2 Tetramerization of Larger Cycloalkynes

With an understanding of how cyclohexyne tetramerizes, the next step would be to model the tetramerization of larger cycloalkynes. From the studies contained in this document, it is evident that the properties of cycloalkynes change as a function of ring size in the regime below the nine-membered ring. It would be of great interest to see if the symmetrical transition state shown in Figure 6.7 is predicted for all cycloalkynes, or if it is unique to the six-membered ring. Although the calculations show that Pathway III seems to be the most reasonable mechanism for the generation of the cyclohexyne tetramer, as the ring size is increased and the ring strain decreases there may be different efficient pathways for the larger cycloalkynes to reach a tetrameric product that were unavailable to the six-membered ring analogue. Calculations on the seven-membered analogue, cycloheptyne, and its tetramerization are currently underway.

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Appendix

Cartesian Coordinates and Energies for all Compounds in Chapter 4, 5, and 6

Chapter 4

Singlet States

B3LYP/6-311G(d,p)

Cyclopentyne

```
6      -0.000001    1.118258   -0.115558
6       1.271902    0.189665    0.103711
6       0.609220   -1.153764   -0.076616
6      -0.609218   -1.153765   -0.076616
6      -1.271902    0.189664    0.103710
1      -0.000001    1.458888   -1.154315
1       1.688991    0.281885    1.110317
1       2.070883    0.411278   -0.605949
1      -1.688991    0.281883    1.110317
1      -2.070883    0.411276   -0.605949
1      -0.000001    2.014440    0.513797
(Hartree/Particle)
 Thermal correction to Energy=
0.096184
 Thermal correction to Enthalpy=
0.097128
 Thermal correction to Gibbs Free Energy=
0.063109
 Sum of electronic and zero-point Energies=
-193.926065
 Sum of electronic and thermal Energies=
-193.920835
 Sum of electronic and thermal Enthalpies=
-193.919891
 Sum of electronic and thermal Free Energies=
-193.953910
```

Cyclohexyne

```
6      -1.589024   -0.199880    0.115070
6      -0.606196   -1.299215    0.025250
6       0.606198   -1.299215   -0.025250
6       1.589024   -0.199878   -0.115070
6       0.720533    1.055354    0.280398
6      -0.720535    1.055353   -0.280399
1      -0.678685    1.101717   -1.373557
1      -1.984805   -0.108111    1.131617
1       2.445596   -0.292004    0.557689
1       1.984805   -0.108110   -1.131616
1       1.234906    1.960843   -0.059393
1       0.678683    1.101716    1.373556
1      -1.234907    1.960842    0.059394
1      -2.445596   -0.292007   -0.557689
(Hartree/Particle)
 Thermal correction to Energy=
0.126703
 Thermal correction to Enthalpy=
0.127647
 Thermal correction to Gibbs Free Energy=
0.092549
 Sum of electronic and zero-point Energies=
-233.275429
 Sum of electronic and thermal Energies=
-233.269812
 Sum of electronic and thermal Enthalpies=
-233.268868
 Sum of electronic and thermal Free Energies=
-233.303965
```

Cycloheptyne

```
6       1.750955   -0.542697    0.298688
6       0.590304   -1.428806    0.127062
6      -0.590304   -1.428806   -0.127062
6       1.314162    0.756140   -0.437738
6      -1.750955   -0.542698   -0.298688
6       0.000000    1.483219    0.000000
6      -1.314162    0.756140    0.437737
1       1.949962   -0.364499    1.361494
1      -1.949962   -0.364499   -1.361494
1       1.226654    0.486205   -1.493744
1      -0.246078    2.149962   -0.834228
1       2.677807   -0.926062   -0.138237
1       2.120440    1.496919   -0.374493
1      -2.677807   -0.926062    0.138237
1       0.246078    2.149961    0.834229
1      -2.120440    1.496918    0.374492
1      -1.226655    0.486205    1.493744
(Hartree/Particle)
 Thermal correction to Energy=
0.157231
 Thermal correction to Enthalpy=
0.158175
 Thermal correction to Gibbs Free Energy=
0.120254
 Sum of electronic and zero-point Energies=
-272.583192
 Sum of electronic and thermal Energies=
-272.576481
 Sum of electronic and thermal Enthalpies=
-272.575537
 Sum of electronic and thermal Free Energies=
-272.613458
```

Cyclooctyne

```
6       1.852952    0.570410    0.287978
6       1.944421   -0.922900   -0.132648
6      -1.852952    0.570411   -0.287978
6       0.600755   -1.480979   -0.037113
6      -1.944421   -0.922900    0.132648
6      -0.600755   -1.480979    0.037113
1       2.805891    1.049274    0.036455
1       2.669080   -1.446987    0.498648
1      -1.759935    0.618906   -1.378169
1      -2.669080   -1.446986   -0.498648
1       1.759935    0.618906    1.378169
1       2.312581   -1.000656   -1.162506
1      -2.805891    1.049275   -0.036455
1      -2.312581   -1.000655    1.162506
6       0.697293    1.380571   -0.353451
1       0.578128    1.075732   -1.399507
1       1.035263    2.421113   -0.389087
6      -0.697293    1.380571    0.353451
1      -0.578128    1.075732    1.399507
1      -1.035263    2.421113    0.389087
(Hartree/Particle)
 Thermal correction to Energy=
0.187132
 Thermal correction to Enthalpy=
0.188077
 Thermal correction to Gibbs Free Energy=
0.147498
 Sum of electronic and zero-point Energies=
-311.905109
 Sum of electronic and thermal Energies=
-311.897282
 Sum of electronic and thermal Enthalpies=
-311.896338
 Sum of electronic and thermal Free Energies=
-311.936916
```

Cyclononyne

6	0.000000	1.387670	0.784019
1	0.000000	0.576718	1.514128
1	0.000000	2.310119	1.378063
6	1.343296	1.412108	0.012816
1	2.106801	1.708025	0.743686
1	1.306277	2.232177	-0.715972
6	1.883846	0.167467	-0.724730
1	1.285078	-0.042657	-1.615733
1	2.891059	0.415270	-1.080276
6	1.967212	-1.140929	0.106822
1	2.575398	-1.879126	-0.426376
1	2.470464	-0.956879	1.063751
6	0.602008	-1.619185	0.310554
6	-0.602007	-1.619185	0.310554
6	-1.967211	-1.140930	0.106821
1	-2.575396	-1.879128	-0.426376
1	-2.470464	-0.956880	1.063750
6	-1.883846	0.167467	-0.724730
1	-2.891060	0.415269	-1.080275
1	-1.285079	-0.042656	-1.615734
6	-1.343297	1.412107	0.012816
1	-2.106801	1.708023	0.743687
1	-1.306279	2.232178	-0.715970

(Hartree/Particle)

Thermal correction to Energy=
0.217204

Thermal correction to Enthalpy=
0.218148

Thermal correction to Gibbs Free Energy=
0.175313

Sum of electronic and zero-point Energies=
-351.201001

Sum of electronic and thermal Energies=
-351.192176

Sum of electronic and thermal Enthalpies=
-351.191232

Sum of electronic and thermal Free Energies=
-351.234068

Cyclodecyne

6	0.503496	1.316193	0.959282
1	0.199885	0.418947	1.498510
1	0.658956	2.083159	1.728209
6	1.893684	1.102712	0.310981
1	2.610871	0.970571	1.131559
1	2.182093	2.041294	-0.179888
6	2.142910	-0.032619	-0.704981
1	1.529069	0.107040	-1.598823
1	3.184318	0.054578	-1.036257
6	1.939725	-1.480558	-0.189980
1	2.311089	-2.184960	-0.942505
1	2.547110	-1.643522	0.709002
6	0.530288	-1.727252	0.101402
6	-0.649597	-1.652916	0.328469
6	-1.996364	-1.161942	0.602071
1	-2.738574	-1.966556	0.601184
1	-2.002640	-0.747919	1.617718
6	-2.429039	-0.066261	-0.414900
1	-3.240355	0.512903	0.041133
1	-2.862360	-0.567223	-1.286819
6	-0.642629	1.836834	0.062312
1	-1.413605	2.261043	0.718818
1	-0.249906	2.688503	-0.508051
6	-1.339971	0.889857	-0.940573
1	-1.832130	1.521954	-1.689103
1	-0.598854	0.305899	-1.489188

(Hartree/Particle)

Thermal correction to Energy=
0.247135

Thermal correction to Enthalpy=
0.248079

Thermal correction to Gibbs Free Energy=
0.202441

Sum of electronic and zero-point Energies=
-390.500156

Sum of electronic and thermal Energies=
-390.490110

Sum of electronic and thermal Enthalpies=
-390.489166

Sum of electronic and thermal Free Energies=
-390.534803

Cycloundecyne

6	1.760939	-1.763619	-0.139126
1	2.108633	-2.742816	0.207705
1	2.268241	-1.585262	-1.094207
6	2.158045	-0.689666	0.910890
1	3.070571	-1.028618	1.412303
1	1.380495	-0.691789	1.678348
6	2.423568	0.763484	0.434655
1	2.277689	1.409027	1.307865
1	3.490340	0.845976	0.196060
6	1.689226	1.396212	-0.772878
1	2.030422	2.438392	-0.796800
1	2.076296	0.949940	-1.696361
6	0.146967	1.376927	-0.867136
1	-0.150331	2.170884	-1.563889
1	-0.159585	0.442967	-1.332499
6	-0.642281	1.559664	0.437295
1	-0.500817	2.584256	0.801233
1	-0.242988	0.904578	1.217227
6	-2.158844	1.287604	0.287180
1	-2.482793	1.576731	-0.721150
1	-2.698350	1.952792	0.970249
6	-2.661231	-0.139282	0.594348
1	-2.325758	-0.431647	1.595519
1	-3.755679	-0.100213	0.636903
6	-0.882140	-1.645655	-0.370042
6	0.311550	-1.798765	-0.327591
6	-2.295485	-1.275022	-0.395632
1	-2.577661	-0.976293	-1.413264
1	-2.910603	-2.150199	-0.157022

(Hartree/Particle)

Thermal correction to Energy=
0.277086

Thermal correction to Enthalpy=
0.278030

Thermal correction to Gibbs Free Energy=
0.228581

Sum of electronic and zero-point Energies=
-429.792304

Sum of electronic and thermal Energies=
-429.780744

Sum of electronic and thermal Enthalpies=
-429.779800

Sum of electronic and thermal Free Energies=
-429.829249

Cyclododecyne

6	-2.915242	-0.804251	-0.16544
1	-3.842678	-0.863440	0.41425
1	-3.177230	-1.074493	-1.19572
6	-1.881300	-1.811075	0.39957
1	-2.326639	-2.811344	0.40937
1	-1.695509	-1.542289	1.44456
6	-0.548813	-1.811581	-0.37640
1	-0.588796	-2.545210	-1.19048
1	-0.433006	-0.835833	-0.85292
6	0.683778	-2.079090	0.498979
1	0.656785	-3.112324	0.866322
1	0.629489	-1.447924	1.393007
6	2.030382	-1.849205	-0.210089
1	2.098460	-2.537580	-1.062075
1	2.835761	-2.142072	0.474868
6	2.331662	-0.425946	-0.728029
1	1.587089	-0.135006	-1.476572
1	3.278372	-0.487229	-1.275913
6	2.468066	0.684539	0.338970
1	3.171024	1.440938	-0.030992
1	2.939338	0.257153	1.232402
6	1.167948	1.400679	0.755091
1	0.408642	0.663747	1.023832
1	1.360777	1.981934	1.664935
6	-1.770301	1.596558	-0.081757
6	-2.376829	0.556582	-0.134248

```
6       0.589900    2.342626   -0.312665
1       0.626650    1.867788   -1.297962
1       1.204286    3.247773   -0.378970
6      -0.877831    2.755295   -0.038205
1      -0.948945    3.244641    0.940951
1      -1.192399    3.499984   -0.777547
(Hartree/Particle)
 Thermal correction to Energy=
0.306751
 Thermal correction to Enthalpy=
0.307695
 Thermal correction to Gibbs Free Energy=
0.256343
 Sum of electronic and zero-point Energies=
-469.100797
 Sum of electronic and thermal Energies=
-469.088273
 Sum of electronic and thermal Enthalpies=
-469.087329
 Sum of electronic and thermal Free Energies=
-469.138682
```

HF/3-21G

Cyclopentyne

```
6       0.000001    1.138077   -0.072291
6       1.300116    0.184120    0.066040
6       0.600899   -1.159694   -0.048130
6      -0.600901   -1.159693   -0.048130
6      -1.300116    0.184121    0.066040
1       0.000001    1.583946   -1.058333
1       1.780333    0.301679    1.026270
1       2.014933    0.378569   -0.718345
1      -1.780332    0.301681    1.026270
1      -2.014933    0.378572   -0.718345
1       0.000001    1.933966    0.661307
(Hartree/Particle)
 Thermal correction to Energy=
0.101966
 Thermal correction to Enthalpy=
0.102911
 Thermal correction to Gibbs Free Energy=
0.069640
 Sum of electronic and zero-point Energies=
-191.465694
 Sum of electronic and thermal Energies=
-191.461058
 Sum of electronic and thermal Enthalpies=
-191.460113
 Sum of electronic and thermal Free Energies=
-191.493384
```

Cyclohexyne

```
6       1.601132   -0.203199   -0.120730
6       0.597489   -1.293037   -0.026508
6      -0.597490   -1.293037    0.026507
6      -1.601132   -0.203198    0.120730
6      -0.724994    1.057499   -0.291564
6       0.724994    1.057499    0.291564
1       0.667921    1.078593    1.373814
1       1.972967   -0.101308   -1.132234
1      -2.441099   -0.304832   -0.551878
1      -1.972967   -0.101308    1.132235
1      -1.230198    1.959968    0.036059
1      -0.667920    1.078593   -1.373814
1       1.230198    1.959968   -0.036059
1       2.441098   -0.304833    0.551878
(Hartree/Particle)
 Thermal correction to Energy=
0.136061
 Thermal correction to Enthalpy=
0.137005
 Thermal correction to Gibbs Free Energy=
0.102484
 Sum of electronic and zero-point Energies=
-230.319553
 Sum of electronic and thermal Energies=
-230.314285
 Sum of electronic and thermal Enthalpies=
-230.313341
 Sum of electronic and thermal Free Energies=
-230.347862
```

Cycloheptyne

```
6       1.758482   -0.546276    0.309820
6       0.582858   -1.414231    0.120925
6      -0.582858   -1.414231   -0.120925
6       1.323892    0.751742   -0.448310
6      -1.758482   -0.546276   -0.309820
6       0.000000    1.480956    0.000000
6      -1.323892    0.751741    0.448310
1       1.932048   -0.352927    1.361890
1      -1.932048   -0.352927   -1.361890
1       1.226923    0.473388   -1.490163
1      -0.254032    2.134953   -0.828803
1       2.670112   -0.937133   -0.123133
1       2.116880    1.491444   -0.385176
1      -2.670112   -0.937133    0.123133
1       0.254032    2.134953    0.828803
1      -2.116880    1.491444    0.385176
1      -1.226923    0.473388    1.490163
(Hartree/Particle)
 Thermal correction to Energy=
0.168959
 Thermal correction to Enthalpy=
0.169903
 Thermal correction to Gibbs Free Energy=
0.132686
 Sum of electronic and zero-point Energies=
-269.125015
 Sum of electronic and thermal Energies=
-269.118747
 Sum of electronic and thermal Enthalpies=
-269.117803
 Sum of electronic and thermal Free Energies=
-269.155021
```

Cyclooctyne

```
6       1.868587    0.586479    0.279370
6       1.957161   -0.921425   -0.117681
6      -1.868587    0.586479   -0.279370
6       0.593118   -1.443207   -0.030996
6      -1.957161   -0.921425    0.117681
6      -0.593118   -1.443207    0.030996
1       2.801693    1.066724    0.002734
1       2.644283   -1.442472    0.538264
1      -1.774668    0.656208   -1.356763
1      -2.644283   -1.442472   -0.538264
1       1.774668    0.656208    1.356763
1       2.327496   -1.013086   -1.133251
1      -2.801693    1.066724   -0.002734
1      -2.327496   -1.013086    1.133251
6       0.682058    1.344630   -0.391151
1       0.532208    0.955053   -1.391351
1       0.990160    2.378714   -0.504837
6      -0.682058    1.344630    0.391151
1      -0.532208    0.955053    1.391351
1      -0.990160    2.378714    0.504837
(Hartree/Particle)
 Thermal correction to Energy=
0.201348
 Thermal correction to Enthalpy=
0.202292
 Thermal correction to Gibbs Free Energy=
0.163002
 Sum of electronic and zero-point Energies=
-307.946730
 Sum of electronic and thermal Energies=
-307.939588
 Sum of electronic and thermal Enthalpies=
-307.938644
```

```
 Sum of electronic and thermal Free Energies=
-307.977934
```

Cyclononyne

```
6       0.000000    1.355073   -0.803504
1       0.000000    0.526875   -1.493403
1       0.000000    2.256637   -1.412645
6      -1.340405    1.409534   -0.013808
1      -2.105703    1.693606   -0.732199
1      -1.276781    2.225601    0.701737
6      -1.876056    0.164671    0.741496
1      -1.262517   -0.050085    1.606931
1      -2.869120    0.415354    1.104208
6      -1.971145   -1.133734   -0.114739
1      -2.567889   -1.874675    0.405251
1      -2.450836   -0.926372   -1.065537
6      -0.594035   -1.597205   -0.305759
6       0.594035   -1.597205   -0.305759
6       1.971145   -1.133734   -0.114739
1       2.567889   -1.874675    0.405251
1       2.450836   -0.926372   -1.065537
6       1.876056    0.164671    0.741496
1       2.869120    0.415354    1.104208
1       1.262517   -0.050085    1.606931
6       1.340405    1.409534   -0.013808
1       2.105703    1.693606   -0.732199
1       1.276780    2.225601    0.701738
(Hartree/Particle)
 Thermal correction to Energy=
0.233490
 Thermal correction to Enthalpy=
0.234434
 Thermal correction to Gibbs Free Energy=
0.192787
 Sum of electronic and zero-point Energies=
-346.734390
 Sum of electronic and thermal Energies=
-346.726252
 Sum of electronic and thermal Enthalpies=
-346.725308
 Sum of electronic and thermal Free Energies=
-346.766955
```

Cyclodecyne

```
6      -0.497560    1.286905   -0.973348
1      -0.199285    0.383129   -1.475618
1      -0.648114    2.036499   -1.747347
6      -1.892099    1.103090   -0.307793
1      -2.612356    0.964743   -1.110734
1      -2.151413    2.041229    0.176944
6      -2.133343   -0.031050    0.722259
1      -1.502691    0.097449    1.590639
1      -3.161442    0.063213    1.061597
6      -1.945480   -1.475168    0.177314
1      -2.309018   -2.186880    0.911091
1      -2.531457   -1.606316   -0.726991
6      -0.524681   -1.702542   -0.102418
6       0.640127   -1.620564   -0.322690
6       1.999473   -1.156262   -0.605400
1       2.716141   -1.969141   -0.584900
1       2.010453   -0.741299   -1.608481
6       2.432998   -0.062355    0.421377
1       3.222027    0.532214   -0.028419
1       2.862368   -0.565978    1.281055
6       0.644828    1.827388   -0.071378
1       1.421482    2.226037   -0.719822
1       0.246312    2.675405    0.480121
6       1.320045    0.874961    0.951048
1       1.792182    1.500826    1.704300
1       0.578949    0.282449    1.462752
(Hartree/Particle)
 Thermal correction to Energy=
0.265755
 Thermal correction to Enthalpy=
0.266700
 Thermal correction to Gibbs Free Energy=
0.222371
 Sum of electronic and zero-point Energies=
-385.526993
 Sum of electronic and thermal Energies=
-385.517715
 Sum of electronic and thermal Enthalpies=
-385.516771
 Sum of electronic and thermal Free Energies=
-385.561099
```

Cycloundecyne

```
6      -1.762840    1.742227   -0.156718
1      -2.092582    2.725134    0.163783
1      -2.249374    1.528696   -1.101641
6      -2.163530    0.696998    0.924771
1      -3.085539    1.028987    1.391247
1      -1.404386    0.721974    1.694787
6      -2.396818   -0.774008    0.458964
1      -2.180029   -1.418213    1.304781
1      -3.459701   -0.887434    0.264154
6      -1.689769   -1.355007   -0.796947
1      -2.048572   -2.378114   -0.871818
1      -2.063640   -0.843345   -1.678265
6      -0.137334   -1.376727   -0.882092
1       0.145287   -2.211399   -1.518422
1       0.194940   -0.481727   -1.376407
6       0.620961   -1.512358    0.453175
1       0.453272   -2.507393    0.854666
1       0.234007   -0.806622    1.174465
6       2.151713   -1.280690    0.291215
1       2.458096   -1.550561   -0.715655
1       2.674566   -1.954309    0.963475
6       2.659846    0.147999    0.613946
1       2.299292    0.446512    1.591957
1       3.744077    0.105716    0.671930
6       0.874538    1.604309   -0.376303
6      -0.304218    1.749614   -0.321731
6       2.300373    1.259098   -0.410774
1       2.571227    0.931441   -1.410115
1       2.891529    2.141943   -0.187954
(Hartree/Particle)
 Thermal correction to Energy=
0.298047
 Thermal correction to Enthalpy=
0.298992
 Thermal correction to Gibbs Free Energy=
0.250963
 Sum of electronic and zero-point Energies=
-424.311802
 Sum of electronic and thermal Energies=
-424.301141
 Sum of electronic and thermal Enthalpies=
-424.300196
 Sum of electronic and thermal Free Energies=
-424.348225
```

Cyclododecyne

```
6      -2.913226   -0.764680   -0.180603
1      -3.839444   -0.785521    0.383735
1      -3.143175   -1.036006   -1.206229
6      -1.901630   -1.779315    0.423353
1      -2.353672   -2.765005    0.452209
1      -1.707342   -1.479431    1.446672
6      -0.572917   -1.815367   -0.373836
1      -0.629558   -2.572557   -1.149864
1      -0.448326   -0.862209   -0.865101
6       0.660243   -2.079640    0.514349
1       0.622665   -3.099476    0.887731
1       0.624342   -1.429198    1.380002
6       1.999552   -1.875533   -0.228712
1       2.029156   -2.554811   -1.076961
1       2.812153   -2.163795    0.432514
6       2.284289   -0.442992   -0.748249
1       1.512190   -0.141844   -1.444718
1       3.205084   -0.496201   -1.321955
6       2.461880    0.639392    0.351573
1       3.174193    1.381759    0.002261
1       2.902423    0.176295    1.229810
6       1.163520    1.373370    0.764784
```

```
1       0.395062    0.652016    0.995560
1       1.352288    1.941937    1.671285
6      -1.720465    1.606728   -0.094390
6      -2.326795    0.583612   -0.143614
6       0.632543    2.341575   -0.313255
1       0.661352    1.874549   -1.289671
1       1.265170    3.222990   -0.352617
6      -0.832571    2.777044   -0.031773
1      -0.897917    3.235096    0.950297
1      -1.143183    3.516252   -0.762738
(Hartree/Particle)
 Thermal correction to Energy=
0.329767
 Thermal correction to Enthalpy=
0.330711
 Thermal correction to Gibbs Free Energy=
0.281285
 Sum of electronic and zero-point Energies=
-463.117392
 Sum of electronic and thermal Energies=
-463.105891
 Sum of electronic and thermal Enthalpies=
-463.104947
 Sum of electronic and thermal Free Energies=
-463.154373
```

CCSD/cc-PVDZ

Cyclopentyne

```
6      -1.266762   -0.199727    0.125284
6      -0.624606    1.161665   -0.090465
6       0.624607    1.161665   -0.090464
6       1.266763   -0.199728    0.125284
6      -0.000001   -1.109834   -0.143546
1      -1.633721   -0.286326    1.164332
1      -2.104675   -0.437659   -0.551190
1       2.104674   -0.437659   -0.551192
1       1.633722   -0.286327    1.164332
1      -0.000001   -1.381370   -1.215816
1      -0.000001   -2.054909    0.432980
(Hartree/Particle)
 Thermal correction to Energy=
0.097441
 Thermal correction to Enthalpy=
0.098385
 Thermal correction to Gibbs Free Energy=
0.065387
 Sum of electronic and zero-point Energies=
-193.292345
 Sum of electronic and thermal Energies=
-193.287571
 Sum of electronic and thermal Enthalpies=
-193.286626
 Sum of electronic and thermal Free Energies=
-193.319625
```

Cyclohexyne

```
6      -1.595709   -0.184250    0.120350
6      -0.618470   -1.311015    0.023950
6       0.618473   -1.311014   -0.023949
6       1.595709   -0.184248   -0.120351
6       0.716585    1.048359    0.296615
6      -0.716587    1.048359   -0.296614
1      -0.645929    1.059548   -1.402138
1      -1.969240   -0.080743    1.155959
1       2.472902   -0.277879    0.543185
1       1.969239   -0.080742   -1.155960
1       1.231625    1.980501   -0.005457
1       0.645928    1.059547    1.402138
1      -1.231628    1.980500    0.005458
1      -2.472901   -0.277882   -0.543187
(Hartree/Particle)
 Thermal correction to Energy=
0.128114
 Thermal correction to Enthalpy=
0.129058
 Thermal correction to Gibbs Free Energy=
0.094083
 Sum of electronic and zero-point Energies=
-232.508701
 Sum of electronic and thermal Energies=
-232.503166
 Sum of electronic and thermal Enthalpies=
-232.502222
 Sum of electronic and thermal Free Energies=
-232.537197
```

Cycloheptyne

```
6      -1.759196   -0.524444   -0.307543
6      -0.599252   -1.440875   -0.140257
6       0.599253   -1.440873    0.140261
6      -1.303947    0.748159    0.459955
6       1.759198   -0.524442    0.307541
6       0.000000    1.479138    0.000002
6       1.303944    0.748159   -0.459958
1      -1.939689   -0.319833   -1.379841
1       1.939695   -0.319828    1.379839
1      -1.185670    0.441241    1.516042
1       0.264976    2.152710    0.839451
1      -2.701410   -0.912403    0.118244
1      -2.114460    1.503809    0.441653
1       2.701410   -0.912402   -0.118248
1      -0.264973    2.152719   -0.839441
1       2.114457    1.503809   -0.441662
1       1.185662    0.441239   -1.516043
(Hartree/Particle)
 Thermal correction to Energy=
0.158789
 Thermal correction to Enthalpy=
0.159733
 Thermal correction to Gibbs Free Energy=
0.121883
 Sum of electronic and zero-point Energies=
-271.685943
 Sum of electronic and thermal Energies=
-271.679268
 Sum of electronic and thermal Enthalpies=
-271.678324
 Sum of electronic and thermal Free Energies=
-271.716174
```

Cyclooctyne

```
6       1.863748    0.580142    0.288716
6       1.971548   -0.910939   -0.129372
6      -1.863749    0.580141   -0.288715
6       0.611669   -1.478488   -0.030108
6      -1.971547   -0.910941    0.129373
6      -0.611668   -1.478489    0.030106
1       2.819243    1.077897    0.033660
1       2.701446   -1.441451    0.507922
1      -1.763487    0.634619   -1.390318
1      -2.701446   -1.441452   -0.507920
1       1.763483    0.634620    1.390320
1       2.332607   -0.988823   -1.172551
1      -2.819245    1.077895   -0.033656
1      -2.332603   -0.988825    1.172553
6       0.691010    1.358824   -0.367966
1       0.560231    1.007460   -1.410914
1       1.017554    2.413071   -0.447501
6      -0.691011    1.358825    0.367964
1      -0.560232    1.007465    1.410914
1      -1.017554    2.413073    0.447495
(Hartree/Particle)
 Thermal correction to Energy=
0.188908
 Thermal correction to Enthalpy=
0.189852
 Thermal correction to Gibbs Free Energy=
0.149168
 Sum of electronic and zero-point Energies=
-310.877006
 Sum of electronic and thermal Energies=
-310.869153
```

```
 Sum of electronic and thermal Enthalpies=
-310.868209
 Sum of electronic and thermal Free Energies=
-310.908894
```

Triplet States

B3LYP/6-311G(d,p)

Cyclohexyne

```
6       0.610835    1.397080   -0.159632
6       0.258604    0.613406   -1.381610
6      -0.258604   -0.613406   -1.381610
6      -0.610835   -1.397080   -0.159632
6      -0.610835   -0.464996    1.081192
6       0.610835    0.464996    1.081192
1       1.525524   -0.136897    1.066300
1      -0.103136    2.218903   -0.022474
1      -1.601022   -1.852215   -0.277618
1       0.103136   -2.218903   -0.022474
1      -0.636933   -1.067814    1.994094
1      -1.525524    0.136897    1.066300
1       0.636933    1.067814    1.994094
1       1.601022    1.852215   -0.277618
(Hartree/Particle)
 Thermal correction to Energy=
0.125883
 Thermal correction to Enthalpy=
0.126827
 Thermal correction to Gibbs Free Energy=
0.091605
 Sum of electronic and zero-point Energies=
-233.207008
 Sum of electronic and thermal Energies=
-233.201584
 Sum of electronic and thermal Enthalpies=
-233.200640
 Sum of electronic and thermal Free Energies=
-233.235861
```

Cycloheptyne

```
6       1.596455   -0.467669    0.333405
6       0.644199   -1.602897    0.169119
6      -0.644200   -1.602897   -0.169119
6       1.205468    0.768637   -0.516853
6      -1.596455   -0.467668   -0.333405
6       0.000000    1.576421    0.000000
6      -1.205468    0.768637    0.516853
1       1.707845   -0.198887    1.391938
1      -1.707845   -0.198886   -1.391938
1       1.007411    0.418403   -1.534591
1      -0.330534    2.236484   -0.810113
1       2.584379   -0.810815   -0.000261
1       2.070130    1.437122   -0.583212
1      -2.584379   -0.810814    0.000261
1       0.330535    2.236484    0.810113
1      -2.070129    1.437123    0.583212
1      -1.007411    0.418404    1.534591
(Hartree/Particle)
 Thermal correction to Energy=
0.155583
 Thermal correction to Enthalpy=
0.156527
 Thermal correction to Gibbs Free Energy=
0.117696
 Sum of electronic and zero-point Energies=
-272.498909
 Sum of electronic and thermal Energies=
-272.492276
 Sum of electronic and thermal Enthalpies=
-272.491332
 Sum of electronic and thermal Free Energies=
-272.530162
```

Cyclooctyne

```
6    1.679477   0.534289   0.423439
6    1.769794  -0.852362  -0.259361
6   -1.679488   0.534268  -0.423435
6    0.667656  -1.821882  -0.095421
6   -1.769778  -0.852384   0.259368
6   -0.667630  -1.821891   0.095411
1    2.694792   0.946413   0.414290
1    2.715144  -1.329824   0.027239
1   -1.424970   0.396961  -1.481004
1   -2.715125  -1.329859  -0.027221
1    1.424952   0.396981   1.481006
1    1.862951  -0.716455  -1.352408
1   -2.694809   0.946375  -0.414279
1   -1.862925  -0.716480   1.352416
6    0.741040   1.577053  -0.207539
1    0.810085   1.517594  -1.301824
1    1.138370   2.562938   0.057553
6   -0.741062   1.577047   0.207534
1   -0.810107   1.517597   1.301819
1   -1.138404   2.562926  -0.057567
(Hartree/Particle)
 Thermal correction to Energy=
0.184060
 Thermal correction to Enthalpy=
0.185004
 Thermal correction to Gibbs Free Energy=
0.141257
 Sum of electronic and zero-point Energies=
-311.766145
 Sum of electronic and thermal Energies=
-311.757881
 Sum of electronic and thermal Enthalpies=
-311.756936
 Sum of electronic and thermal Free Energies=
-311.800683
```

Cyclononyne

```
6    0.000000   1.397629  -0.874962
1    0.000000   0.505252  -1.509296
1    0.000000   2.249119  -1.565168
6   -1.305147   1.465850  -0.066666
1   -2.127222   1.649961  -0.769436
1   -1.270255   2.345856   0.588384
6   -1.687511   0.245322   0.784168
1   -0.988312   0.092357   1.608129
1   -2.656259   0.456935   1.250422
6   -1.852436  -1.080216  -0.009620
1   -2.471002  -1.752908   0.600259
1   -2.444323  -0.871254  -0.911667
6   -0.667847  -1.879459  -0.408545
6    0.667847  -1.879459  -0.408545
6    1.852436  -1.080216  -0.009620
1    2.471002  -1.752908   0.600259
1    2.444324  -0.871254  -0.911667
6    1.687511   0.245322   0.784168
1    2.656259   0.456935   1.250422
1    0.988312   0.092357   1.608129
6    1.305147   1.465850  -0.066666
1    2.127222   1.649961  -0.769436
1    1.270255   2.345856   0.588384
(Hartree/Particle)
 Thermal correction to Energy=
0.214929
 Thermal correction to Enthalpy=
0.215873
 Thermal correction to Gibbs Free Energy=
0.171209
 Sum of electronic and zero-point Energies=
-351.081158
 Sum of electronic and thermal Energies=
-351.072119
 Sum of electronic and thermal Enthalpies=
-351.071174
```

```
 Sum of electronic and thermal Free Energies=
-351.115838
```

Cyclodecyne

6	-0.794214	1.463382	-0.827761
1	-0.367640	0.714653	-1.501128
1	-1.120605	2.277655	-1.485109
6	-2.069212	0.908629	-0.162285
1	-2.817659	0.770958	-0.952865
1	-2.478258	1.680157	0.502070
6	-1.974998	-0.407640	0.630974
1	-1.359926	-0.273329	1.522965
1	-2.978790	-0.644643	0.996950
6	-1.432832	-1.618392	-0.183771
1	-2.181523	-2.420417	-0.202336
1	-1.299685	-1.342240	-1.240517
6	-0.167251	-2.202081	0.341210
6	1.120004	-1.928278	0.128083
6	1.804849	-0.912327	-0.712287
1	2.671518	-1.383677	-1.194441
1	1.144047	-0.618519	-1.540161
6	2.288339	0.330617	0.073227
1	2.783856	1.011851	-0.629023
1	3.062930	-0.006203	0.770079
6	0.295964	2.047506	0.094326
1	0.931085	2.703328	-0.514790
1	-0.198763	2.709672	0.816334
6	1.227465	1.102046	0.879942
1	1.768520	1.725807	1.600561
1	0.652213	0.394177	1.481467

```
(Hartree/Particle)
 Thermal correction to Energy=
0.244596
 Thermal correction to Enthalpy=
0.245540
 Thermal correction to Gibbs Free Energy=
0.198806
 Sum of electronic and zero-point Energies=
-390.375051
 Sum of electronic and thermal Energies=
-390.364950
 Sum of electronic and thermal Enthalpies=
-390.364005
 Sum of electronic and thermal Free Energies=
-390.410739
```

Cycloundecyne

6	-1.464602	1.878254	0.141570
1	-1.255701	2.785058	0.727918
1	-2.454055	2.051369	-0.305776
6	-1.535700	0.667799	1.101639
1	-2.094612	0.990504	1.988117
1	-0.527157	0.452573	1.454469
6	-2.204050	-0.626895	0.601192
1	-2.125862	-1.350443	1.421382
1	-3.278894	-0.436835	0.489857
6	-1.738367	-1.308580	-0.705864
1	-2.264656	-2.270058	-0.744228
1	-2.118894	-0.735839	-1.559303
6	-0.230673	-1.540463	-0.957766
1	-0.141503	-2.313243	-1.729372
1	0.172220	-0.636643	-1.408509
6	0.667308	-1.927885	0.238229
1	0.813140	-3.013181	0.247760
1	0.178653	-1.697019	1.189974
6	2.058308	-1.252086	0.229558
1	2.472282	-1.273674	-0.786092
1	2.729893	-1.869851	0.835423
6	2.138166	0.184939	0.803536
1	1.419378	0.284083	1.621802
1	3.121807	0.302738	1.271891
6	0.838152	1.569063	-1.059524
6	-0.477729	1.784130	-0.969259
6	2.007135	1.405919	-0.150448
1	2.890855	1.406510	-0.806615
1	2.115416	2.318773	0.454134

```
(Hartree/Particle)
 Thermal correction to Energy=
0.274306
 Thermal correction to Enthalpy=
0.275250
 Thermal correction to Gibbs Free Energy=
0.224133
 Sum of electronic and zero-point Energies=
-429.655487
 Sum of electronic and thermal Energies=
-429.643761
 Sum of electronic and thermal Enthalpies=
-429.642817
 Sum of electronic and thermal Free Energies=
-429.693935
```

Cyclododecyne

6	-3.003654	-0.800419	-0.236786
1	-3.924406	-0.899379	0.351522
1	-3.164991	-1.394372	-1.147928
6	-1.832264	-1.442559	0.556696
1	-2.155874	-2.437015	0.884560
1	-1.668212	-0.863903	1.471144
6	-0.522420	-1.554534	-0.237273
1	-0.612489	-2.357992	-0.978929
1	-0.383219	-0.637126	-0.810260
6	0.706643	-1.802181	0.649385
1	0.618438	-2.790183	1.117918
1	0.695115	-1.087328	1.477549
6	2.066610	-1.739870	-0.075413
1	2.113682	-2.580705	-0.778703
1	2.857405	-1.926675	0.661833
6	2.421743	-0.463725	-0.869172
1	1.643832	-0.263620	-1.612687
1	3.315003	-0.701793	-1.458040
6	2.746485	0.825518	-0.084072
1	3.179159	1.541481	-0.794033
1	3.543252	0.604301	0.636990
6	1.594917	1.522139	0.668221
1	1.232008	0.859272	1.457880
1	2.002650	2.396034	1.188428
6	-2.116563	1.685256	-0.385594
6	-2.874574	0.621283	-0.663029
6	0.409172	1.951852	-0.219897
1	0.338143	1.292031	-1.085914
1	0.582181	2.952293	-0.628092
6	-0.955578	1.918531	0.512561
1	-0.939047	1.122453	1.273350
1	-1.115738	2.844486	1.079644

```
(Hartree/Particle)
 Thermal correction to Energy=
0.304393
 Thermal correction to Enthalpy=
0.305337
 Thermal correction to Gibbs Free Energy=
0.252396
 Sum of electronic and zero-point Energies=
-468.963453
 Sum of electronic and thermal Energies=
-468.950827
 Sum of electronic and thermal Enthalpies=
-468.949882
 Sum of electronic and thermal Free Energies=
-469.002824
```

HF/3-21G

Cyclohexyne

6	1.521270	-0.154228	-0.126315
6	0.657249	-1.384692	-0.060380
6	-0.657249	-1.384692	0.060380
6	-1.521270	-0.154228	0.126315
6	-0.697140	1.080637	-0.331973
6	0.697140	1.080637	0.331973
1	0.580308	1.046832	1.409632

```
1       1.877966   -0.007380   -1.140982
1      -2.388020   -0.278158   -0.513529
1      -1.877966   -0.007380    1.140982
1      -1.233644    1.988403   -0.081757
1      -0.580308    1.046832   -1.409632
1       1.233644    1.988403    0.081757
1       2.388020   -0.278158    0.513529
(Hartree/Particle)
 Thermal correction to Energy=
0.135514
 Thermal correction to Enthalpy=
0.136458
 Thermal correction to Gibbs Free Energy=
0.101100
 Sum of electronic and zero-point Energies=
-230.295619
 Sum of electronic and thermal Energies=
-230.290530
 Sum of electronic and thermal Enthalpies=
-230.289586
 Sum of electronic and thermal Free Energies=
-230.324943
```

Cycloheptyne

```
 6       1.586614   -0.452145    0.347286
 6       0.638515   -1.603804    0.167623
 6      -0.638515   -1.603804   -0.167623
 6       1.190411    0.754668   -0.543026
 6      -1.586614   -0.452145   -0.347286
 6       0.000000    1.577657    0.000000
 6      -1.190411    0.754668    0.543026
 1       1.641787   -0.155112    1.390316
 1      -1.641787   -0.155112   -1.390316
 1       0.960060    0.379626   -1.533324
 1      -0.354506    2.223979   -0.797160
 1       2.576974   -0.790419    0.057967
 1       2.044310    1.416643   -0.641872
 1      -2.576974   -0.790419   -0.057967
 1       0.354506    2.223979    0.797160
 1      -2.044310    1.416643    0.641873
 1      -0.960060    0.379626    1.533324
(Hartree/Particle)
 Thermal correction to Energy=
0.167481
 Thermal correction to Enthalpy=
0.168425
 Thermal correction to Gibbs Free Energy=
0.130404
 Sum of electronic and zero-point Energies=
-269.078572
 Sum of electronic and thermal Energies=
-269.072398
 Sum of electronic and thermal Enthalpies=
-269.071454
 Sum of electronic and thermal Free Energies=
-269.109476
```

Cyclooctyne

```
  6      -1.665731    0.518868   -0.455578
  6      -1.785333   -0.837958    0.282813
  6       1.665704    0.518917    0.455590
  6      -0.660292   -1.801506    0.106298
  6       1.785370   -0.837906   -0.282795
  6       0.660351   -1.801488   -0.106324
  1      -2.666026    0.938414   -0.501734
  1      -2.707106   -1.324987   -0.017390
  1       1.353359    0.349169    1.480936
 1       2.707148   -1.324909    0.017436
 1      -1.353402    0.349126   -1.480931
 1      -1.879786   -0.659444    1.354462
 1       2.665983    0.938499    0.501765
 1       1.879851   -0.659390   -1.354441
 6      -0.743450    1.566103    0.211566
 1      -0.810777    1.477452    1.292100
 1      -1.138566    2.545860   -0.040198
 6       0.743399    1.566116   -0.211580
 1       0.810728    1.477441   -1.292111
 1       1.138491    2.545888    0.040161
(Hartree/Particle)
```

```
 Thermal correction to Energy=
0.195902
 Thermal correction to Enthalpy=
0.196846
 Thermal correction to Gibbs Free Energy=
0.157256
 Sum of electronic and zero-point Energies=
-307.819572
 Sum of electronic and thermal Energies=
-307.812958
 Sum of electronic and thermal Enthalpies=
-307.812014
 Sum of electronic and thermal Free Energies=
-307.851604
```

Cyclononyne

```
6       0.000000   -1.355668   -0.892476
1       0.000000   -0.438097   -1.466047
1       0.000000   -2.171494   -1.610141
6       1.298347   -1.467329   -0.068084
1       2.122005   -1.644271   -0.754783
1       1.231570   -2.343102    0.571917
6       1.674304   -0.245749    0.794912
1       0.965171   -0.084293    1.591144
1       2.626812   -0.464816    1.268796
6       1.861443    1.060614   -0.020623
1       2.506445    1.723802    0.551025
1       2.401772    0.826517   -0.934730
6       0.662628    1.878791   -0.385846
6      -0.662628    1.878791   -0.385846
6      -1.861443    1.060614   -0.020623
1      -2.506446    1.723802    0.551025
1      -2.401772    0.826517   -0.934730
6      -1.674304   -0.245749    0.794912
1      -2.626812   -0.464816    1.268796
1      -0.965171   -0.084293    1.591144
6      -1.298347   -1.467330   -0.068084
1      -2.122005   -1.644271   -0.754783
1      -1.231570   -2.343102    0.571917
(Hartree/Particle)
 Thermal correction to Energy=
0.231400
 Thermal correction to Enthalpy=
0.232344
 Thermal correction to Gibbs Free Energy=
0.188449
 Sum of electronic and zero-point Energies=
-346.641002
 Sum of electronic and thermal Energies=
-346.632504
 Sum of electronic and thermal Enthalpies=
-346.631560
 Sum of electronic and thermal Free Energies=
-346.675455
```

Cyclodecyne

```
6      -0.841521   -1.426894    0.834206
1      -0.372655   -0.696332    1.475796
1      -1.184537   -2.222819    1.490333
6      -2.107799   -0.827849    0.176967
1      -2.832507   -0.640562    0.965504
1      -2.544315   -1.580391   -0.474082
6      -1.939000    0.479456   -0.630303
1      -1.322458    0.304687   -1.498722
1      -2.918035    0.766646   -0.998371
6      -1.345354    1.662754    0.202663
1      -2.059996    2.478593    0.228026
1      -1.195206    1.358137    1.234063
6      -0.062326    2.196726   -0.364322
6       1.201443    1.871434   -0.152898
6       1.823628    0.838264    0.733707
1       2.704285    1.269499    1.201191
1       1.143183    0.579000    1.535526
6       2.260620   -0.431806   -0.047456
1       2.677295   -1.147200    0.655296
1       3.063798   -0.137282   -0.715092
6       0.197726   -2.054055   -0.127615
1       0.807933   -2.748208    0.444601
```

```
1      -0.343383   -2.652137   -0.856505
6       1.161476   -1.115119   -0.893716
1       1.666163   -1.728606   -1.635318
1       0.617074   -0.360485   -1.439645
(Hartree/Particle)
 Thermal correction to Energy=
0.263570
 Thermal correction to Enthalpy=
0.264514
 Thermal correction to Gibbs Free Energy=
0.219188
 Sum of electronic and zero-point Energies=
-385.429103
 Sum of electronic and thermal Energies=
-385.419751
 Sum of electronic and thermal Enthalpies=
-385.418807
 Sum of electronic and thermal Free Energies=
-385.464133
```

Cycloundecyne

```
6       1.714313    1.482858    0.435925
1       2.388623    2.253461    0.796982
1       1.270267    1.029160    1.315871
6       2.544748    0.421737   -0.371968
1       3.571614    0.765680   -0.416463
1       2.183680    0.387242   -1.393287
6       2.537123   -1.016013    0.215484
1       3.429300   -1.529658   -0.129674
1       2.601691   -0.966077    1.298772
6       1.302710   -1.854180   -0.193380
1       1.288694   -1.950766   -1.275623
1       1.390738   -2.853911    0.222041
6       0.000409   -1.192852    0.274424
1       0.000194   -1.132182    1.360311
1       0.000312   -0.191215   -0.107483
6      -1.301509   -1.854631   -0.193853
1      -1.389138   -2.854616    0.221084
1      -1.287119   -1.950691   -1.276127
6      -2.536376   -1.017169    0.215141
1      -2.601124   -0.967738    1.298449
1      -3.428199   -1.531223   -0.130332
6      -2.545431    0.420976   -0.371422
1      -2.185531    0.387380   -1.393170
1      -3.572650    0.764092   -0.414580
6      -0.662752    2.151552   -0.397398
6       0.661687    2.151941   -0.397337
6      -1.715072    1.482315    0.436070
1      -1.270959    1.028933    1.316151
1      -2.389488    2.252921    0.796970
(Hartree/Particle)
 Thermal correction to Energy=
0.295531
 Thermal correction to Enthalpy=
0.296475
 Thermal correction to Gibbs Free Energy=
0.247652
 Sum of electronic and zero-point Energies=
-424.214014
 Sum of electronic and thermal Energies=
-424.203348
 Sum of electronic and thermal Enthalpies=
-424.202404
 Sum of electronic and thermal Free Energies=
-424.251227
```

Cyclododecyne

```
 6      -2.618538   -0.056553   -0.397960
 1      -3.695153    0.057123   -0.497081
 1      -2.176595    0.301572   -1.326155
 6      -2.307367   -1.569659   -0.232016
 1      -2.919246   -2.103197   -0.952678
 1      -2.621735   -1.893494    0.754573
 6      -0.827320   -1.951897   -0.467345
 1      -0.770922   -3.014853   -0.685501
 1      -0.472461   -1.432618   -1.350466
 6       0.085401   -1.653634    0.739886
 1      -0.223206   -2.299201    1.558237
 1      -0.071369   -0.641238    1.066540
 6       1.585590   -1.907796    0.462335
 1       1.691822   -2.931967    0.113719
 1       2.133193   -1.839960    1.398464
 6       2.260525   -0.970493   -0.571422
 1       1.615832   -0.834008   -1.430090
 1       3.147590   -1.477589   -0.941478
 6       2.731029    0.403463   -0.032619
 1       3.318430    0.883596   -0.811564
 1       3.403250    0.229006    0.802924
 6       1.630701    1.389216    0.420184
 1       1.088896    0.979761    1.260468
 1       2.111091    2.298643    0.771380
 6      -1.384159    1.855946    0.830855
 6      -2.175546    0.798914    0.748637
 6       0.643375    1.759721   -0.701472
 1       0.260796    0.863588   -1.169232
 1       1.165790    2.326164   -1.466979
 6      -0.559025    2.591661   -0.189040
 1      -0.191981    3.503696    0.272492
 1      -1.182012    2.891643   -1.027706
(Hartree/Particle)
 Thermal correction to Energy=
0.327195
 Thermal correction to Enthalpy=
0.328140
 Thermal correction to Gibbs Free Energy=
0.277450
 Sum of electronic and zero-point Energies=
-463.010929
 Sum of electronic and thermal Energies=
-462.999237
 Sum of electronic and thermal Enthalpies=
-462.998293
 Sum of electronic and thermal Free Energies=
-463.048982
```

CCSD/cc-PVDZ

Cyclohexyne

```
6       0.623015    1.401417   -0.148180
6       0.268630    0.620269   -1.391272
6      -0.268630   -0.620269   -1.391272
6      -0.623015   -1.401417   -0.148180
6      -0.623015   -0.451705    1.076311
6       0.623015    0.451705    1.076311
1       1.531331   -0.181061    1.039759
1      -0.106674    2.222046   -0.001416
1      -1.618801   -1.868274   -0.267176
1       0.106674   -2.222046   -0.001416
1      -0.674888   -1.045437    2.007680
1      -1.531331    0.181061    1.039759
1       0.674888    1.045437    2.007680
1       1.618801    1.868274   -0.267176
(Hartree/Particle)
 Thermal correction to Energy=
0.127518
 Thermal correction to Enthalpy=
0.128462
 Thermal correction to Gibbs Free Energy=
0.093306
 Sum of electronic and zero-point Energies=
-232.446291
 Sum of electronic and thermal Energies=
-232.440920
 Sum of electronic and thermal Enthalpies=
-232.439975
 Sum of electronic and thermal Free Energies=
-232.475132
```

Cycloheptyne

```
6       1.602203   -0.451175    0.338716
6       0.653471   -1.613146    0.175063
6      -0.653471   -1.613145   -0.175064
6       1.193147    0.759237   -0.536273
6      -1.602204   -0.451175   -0.338715
6       0.000000    1.576204    0.000000
```

```
6      -1.193147    0.759237    0.536273
1       1.689023   -0.160700    1.405067
1      -1.689023   -0.160700   -1.405067
1       0.963899    0.378989   -1.550165
1      -0.350907    2.241662   -0.813187
1       2.606572   -0.794882    0.023402
1       2.061254    1.436819   -0.644640
1      -2.606572   -0.794882   -0.023401
1       0.350907    2.241662    0.813187
1      -2.061254    1.436819    0.644640
1      -0.963899    0.378989    1.550165
```

Cyclohexyne Closer Look

ωB97XD/6-311G(d,p)

```
 6      -0.232264    0.735087    1.047328
 6       0.232264    1.573030   -0.194851
 6       0.068699    0.600810   -1.294107
 6      -0.068699   -0.600810   -1.294107
 6      -0.232264   -1.573030   -0.194851
 6       0.232264   -0.735087    1.047328
 1      -0.370523    2.478909   -0.288813
 1       1.277777    1.880727   -0.100406
 1       1.326570   -0.762137    1.080427
 1      -1.326570    0.762137    1.080427
 1       0.370523   -2.478909   -0.288813
 1      -1.277777   -1.880727   -0.100406
 1      -0.129364   -1.222307    1.958573
 1       0.129364    1.222307    1.958573
(Hartree/Particle)
 Thermal correction to Energy=
0.127899
 Thermal correction to Enthalpy=
0.128843
 Thermal correction to Gibbs Free Energy=
0.094485
 Sum of electronic and zero-point Energies=
-233.189338
 Sum of electronic and thermal Energies=
-233.183766
 Sum of electronic and thermal Enthalpies=
-233.182822
 Sum of electronic and thermal Free Energies=
-233.217179
```

M062X/6-311G(d,p)

```
 6      -0.237696    0.733267    1.043964
 6       0.237696    1.573910   -0.191508
 6       0.074422    0.599987   -1.291946
 6      -0.074422   -0.599987   -1.291946
 6      -0.237696   -1.573910   -0.191508
 6       0.237696   -0.733267    1.043964
 1      -0.361019    2.480723   -0.288453
 1       1.283791    1.873857   -0.092270
 1       1.331599   -0.750842    1.058013
 1      -1.331599    0.750842    1.058013
 1       0.361019   -2.480723   -0.288453
 1      -1.283791   -1.873857   -0.092270
 1      -0.108440   -1.221265    1.959653
 1       0.108440    1.221265    1.959653
(Hartree/Particle)
 Thermal correction to Energy=
0.128155
 Thermal correction to Enthalpy=
0.129099
 Thermal correction to Gibbs Free Energy=
0.094834
 Sum of electronic and zero-point Energies=
-233.158866
 Sum of electronic and thermal Energies=
-233.153337
 Sum of electronic and thermal Enthalpies=
-233.152392
 Sum of electronic and thermal Free Energies=
-233.186658
```

MP2/6-311G(d,p)

```
6       1.587308   -0.182841   -0.118512
6       0.618661   -1.299228   -0.043382
6      -0.618661   -1.299228    0.043382
6      -1.587308   -0.182841    0.118512
6      -0.707867    1.040327   -0.305043
6       0.707867    1.040327    0.305043
1       0.619844    1.028702    1.398294
1       1.965429   -0.064035   -1.140464
1      -2.449617   -0.280908   -0.548215
1      -1.965428   -0.064034    1.140464
1      -1.222375    1.966689   -0.021276
1      -0.619844    1.028702   -1.398294
1       1.222375    1.966689    0.021276
1       2.449616   -0.280908    0.548215
(Hartree/Particle)
 Thermal correction to Energy=
0.128948
 Thermal correction to Enthalpy=
0.129892
 Thermal correction to Gibbs Free Energy=
0.095474
 Sum of electronic and zero-point Energies=
-232.538040
 Sum of electronic and thermal Energies=
-232.532809
 Sum of electronic and thermal Enthalpies=
-232.531865
 Sum of electronic and thermal Free Energies=
-232.566283
```

Chapter 5

ωB97XD/6-311G(d,p)

Six-Membered Ring

3,3-DimethylCyclohexyne

```
6       1.208898   -1.280318    0.347993
6       0.001828   -1.199773    0.318770
6      -0.933897   -0.083204    0.015571
6       0.060991    0.907988   -0.711379
6       1.470706    1.024683   -0.101857
6       2.265732   -0.325113   -0.038603
1       3.095599   -0.246866    0.667032
1       0.152717    0.579652   -1.752754
1      -0.403861    1.900826   -0.728323
1       1.394526    1.420111    0.916116
1       2.048198    1.751783   -0.682091
1       2.686069   -0.586041   -1.014416
6      -2.076849   -0.457030   -0.928644
6      -1.491450    0.537285    1.301463
1      -1.697457   -0.951891   -1.825620
1      -2.779056   -1.133711   -0.435394
1      -2.624148    0.440699   -1.233193
1      -2.111147    1.406591    1.060033
1      -0.687459    0.856165    1.968198
1      -2.109730   -0.184430    1.840534
(Hartree/Particle)
 Thermal correction to Energy=
0.186562
 Thermal correction to Enthalpy=
0.187506
 Thermal correction to Gibbs Free Energy=
0.146590
 Sum of electronic and zero-point Energies=
-311.763660
 Sum of electronic and thermal Energies=
-311.755411
 Sum of electronic and thermal Enthalpies=
-311.754467
 Sum of electronic and thermal Free Energies=
-311.795384
```

2-*tert*-butylfuran

```
6      -2.503489    0.626477   -0.000001
```

```
6      -2.340988   -0.714928    0.000001
6      -1.182336    1.181899   -0.000002
6      -0.321506    0.132202    0.000000
8      -1.023556   -1.031649    0.000002
1      -3.440716    1.159682   -0.000003
1      -0.914774    2.226110   -0.000004
1      -3.025075   -1.546661    0.000003
6       1.175905    0.009945    0.000000
6       1.624490   -0.755340    1.256849
6       1.797549    1.409768   -0.000002
6       1.624489   -0.755344   -1.256846
1       1.181204   -1.753092    1.284327
1       1.324205   -0.222983    2.163428
1       2.713409   -0.862298    1.264850
1       2.887982    1.331187   -0.000002
1       1.499355    1.975787    0.886842
1       1.499355    1.975784   -0.886849
1       1.324204   -0.222990   -2.163427
1       2.713408   -0.862302   -1.264848
1       1.181203   -1.753096   -1.284321
(Hartree/Particle)
 Thermal correction to Energy=
0.192546
 Thermal correction to Enthalpy=
0.193490
 Thermal correction to Gibbs Free Energy=
0.150016
 Sum of electronic and zero-point Energies=
-387.078471
 Sum of electronic and thermal Energies=
-387.069437
 Sum of electronic and thermal Enthalpies=
-387.068493
 Sum of electronic and thermal Free Energies=
-387.111967
```

Anti-TS

```
6       0.368272   -2.038453    1.150379
6       0.131197   -1.968455   -0.217931
6       1.356728   -1.097375    1.413423
6       1.703285   -0.534434    0.189580
8       1.114709   -1.235447   -0.798449
1      -0.206505   -2.611839    1.860666
1       1.720538   -0.779420    2.377031
1      -0.402807   -2.635936   -0.875252
6       2.830623    0.385357   -0.197326
6       4.099871   -0.463275   -0.406512
6       3.062999    1.395997    0.930724
6       2.491902    1.127361   -1.495951
1       3.946307   -1.200728   -1.198318
1       4.367995   -0.996497    0.509439
1       4.939997    0.177022   -0.692223
1       3.869709    2.080858    0.654977
1       3.352337    0.900901    1.861886
1       2.158401    1.979832    1.116928
1       1.598756    1.741957   -1.365354
1       3.326856    1.774067   -1.781278
1       2.302773    0.427365   -2.311819
6      -1.194491   -0.168462   -0.121501
6      -0.462494    0.792323    0.141459
6      -2.666782   -0.324538   -0.253034
6      -2.418431    2.156218    0.558370
6      -0.883172    2.205838    0.318941
6      -3.145600    1.165832   -0.364752
1      -3.002040    1.485501   -1.403624
1      -2.847372    3.154762    0.422844
1      -2.594761    1.876729    1.602823
1      -0.385970    2.711080    1.153065
1      -0.650944    2.785815   -0.582089
1      -4.223244    1.202070   -0.165948
6      -3.086590   -1.093395   -1.508064
6      -3.253634   -1.003853    0.990300
1      -4.172933   -1.052025   -1.637867
1      -2.798472   -2.146209   -1.434402
1      -2.615257   -0.671486   -2.399185
1      -2.847814   -2.013314    1.103288
1      -4.342378   -1.083140    0.906502
1      -3.012944   -0.443907    1.896868
(Hartree/Particle)
 Thermal correction to Energy=
0.380823
 Thermal correction to Enthalpy=
0.381767
 Thermal correction to Gibbs Free Energy=
0.318311
 Sum of electronic and zero-point Energies=
-698.839772
 Sum of electronic and thermal Energies=
-698.821966
 Sum of electronic and thermal Enthalpies=
-698.821022
 Sum of electronic and thermal Free Energies=
-698.884478
```

Syn-*TS*

```
6      -0.723084    2.357356    1.023714
6      -0.536758    2.312669   -0.355514
6      -1.417017    1.197375    1.352033
6      -1.680837    0.542959    0.156906
8      -1.327823    1.334167   -0.871549
1      -0.281795    3.077877    1.694530
1      -1.638947    0.821005    2.337199
1      -0.253006    3.091123   -1.046546
6      -2.547784   -0.644752   -0.157612
6      -1.956008   -1.445185   -1.323853
6      -3.947215   -0.127538   -0.545446
6      -2.652222   -1.537054    1.082911
1      -0.984722   -1.855397   -1.042747
1      -1.812087   -0.812860   -2.201936
1      -2.626957   -2.267020   -1.591419
1      -4.610540   -0.968848   -0.767223
1      -3.893280    0.509857   -1.431145
1      -4.387775    0.453932    0.268908
1      -3.143986   -1.018647    1.910831
1      -3.243294   -2.426829    0.850001
1      -1.661418   -1.856853    1.414862
6       1.224367    1.094626   -0.302770
6       0.922070   -0.079594   -0.047159
6       1.876336   -1.218649    0.160447
6       3.227864   -0.513109    0.517556
6       3.583445    0.686404   -0.374064
6       2.513054    1.813888   -0.344585
1       2.628731    2.469190   -1.213666
1       3.164705   -0.173284    1.558334
1       4.037505   -1.251742    0.473031
1       3.700536    0.347962   -1.408660
1       4.551457    1.093885   -0.065719
1       2.627923    2.441269    0.548368
6       1.455301   -2.133623    1.313106
6       2.027592   -2.048993   -1.121048
1       1.272449   -1.554257    2.221986
1       0.535540   -2.668845    1.060025
1       2.233202   -2.875075    1.525553
1       2.769200   -2.841201   -0.972767
1       2.343663   -1.428366   -1.962124
1       1.080862   -2.520894   -1.395010
(Hartree/Particle)
 Thermal correction to Energy=
0.380810
 Thermal correction to Enthalpy=
0.381754
 Thermal correction to Gibbs Free Energy=
0.318478
 Sum of electronic and zero-point Energies=
-698.838866
 Sum of electronic and thermal Energies=
-698.821091
 Sum of electronic and thermal Enthalpies=
-698.820147
 Sum of electronic and thermal Free Energies=
-698.883424
```

***Anti*-P**

```
6      -0.156355   -2.042859   -1.185951
6       0.320091   -1.732673    0.250823
6      -1.114529   -1.158434   -1.419513
6      -1.226865   -0.316042   -0.117364
```

```
8      -0.908682   -1.334028    0.844151
1       0.269926   -2.783539   -1.847069
1      -1.677204   -0.991198   -2.326546
1       0.787235   -2.541526    0.808202
6      -2.579682    0.322901    0.218747
6      -3.650158   -0.778702    0.229328
6      -2.964914    1.383190   -0.820639
6      -2.501929    0.965025    1.609881
1      -3.382126   -1.570922    0.929647
1      -3.766056   -1.229438   -0.760681
1      -4.616438   -0.359254    0.524887
1      -3.985874    1.726199   -0.629583
1      -2.937732    0.985652   -1.839460
1      -2.313727    2.257771   -0.776268
1      -1.760951    1.768478    1.637856
1      -3.471905    1.390922    1.883644
1      -2.222410    0.222879    2.359460
6       1.046149   -0.377164    0.198243
6       0.092329    0.512653   -0.056087
6       2.522709   -0.123056    0.261326
6       1.841195    2.152960   -0.705979
6       0.348491    1.941291   -0.415024
6       2.730551    1.406690    0.289347
1       2.508501    1.767590    1.300876
1       2.077028    3.220634   -0.688769
1       2.055860    1.802294   -1.721162
1      -0.235868    2.217353   -1.298538
1       0.015175    2.608448    0.390265
1       3.785704    1.630068    0.097446
6       3.118489   -0.737724    1.536145
6       3.204609   -0.753828   -0.965131
1       4.179725   -0.482894    1.621379
1       3.037788   -1.828655    1.528381
1       2.602306   -0.365372    2.424960
1       3.023850   -1.832914   -0.999433
1       4.287368   -0.598659   -0.923790
1       2.828195   -0.327063   -1.897835
(Hartree/Particle)
 Thermal correction to Energy=
0.384171
 Thermal correction to Enthalpy=
0.385115
 Thermal correction to Gibbs Free Energy=
0.325715
 Sum of electronic and zero-point Energies=
-698.922889
 Sum of electronic and thermal Energies=
-698.906275
 Sum of electronic and thermal Enthalpies=
-698.905330
 Sum of electronic and thermal Free Energies=
-698.964730
```

Syn-P

```
6       0.456098   -2.310226    1.236173
6       0.005988   -2.258570   -0.242137
6       1.059131   -1.148389    1.442332
6       0.990125   -0.392782    0.086028
8       1.067199   -1.513952   -0.807344
1       0.245327   -3.106533    1.935316
1       1.470904   -0.748930    2.358145
1      -0.140297   -3.206354   -0.756730
6       2.165581    0.541755   -0.271614
6       2.052820    0.956822   -1.745170
6       3.469595   -0.258109   -0.088682
6       2.258914    1.783910    0.618873
1       1.110152    1.466061   -1.952315
1       2.105398    0.081262   -2.393313
1       2.871989    1.633770   -2.006482
1       4.318860    0.340656   -0.430859
1       3.441529   -1.186088   -0.659351
1       3.638500   -0.510349    0.962280
1       2.226858    1.527282    1.681919
1       3.213189    2.284849    0.432534
1       1.470974    2.507922    0.413844
6      -1.114473   -1.221179   -0.330062
6      -1.355994    1.197886    0.278254
6      -2.560442   -1.502562   -0.537739
6      -2.857640    0.803049    0.339103
6      -3.299165   -0.181193   -0.738131
6      -0.548264   -0.039046   -0.083850
1      -2.694321   -2.166960   -1.398921
1      -3.055018    0.343114    1.315293
1      -3.457131    1.718214    0.298528
1      -3.069719    0.215905   -1.732859
1      -4.381230   -0.331577   -0.693500
1      -2.968309   -2.038986    0.331461
6      -0.987689    1.680110    1.693047
1      -1.693925    2.453549    2.011704
1      -1.048555    0.853072    2.406361
1       0.013123    2.102668    1.749703
6      -1.185907    2.342618   -0.731434
1      -1.804738    3.196834   -0.438523
1      -1.489033    2.028082   -1.733781
1      -0.154188    2.689582   -0.791655
(Hartree/Particle)
 Thermal correction to Energy=
0.384513
 Thermal correction to Enthalpy=
0.385457
 Thermal correction to Gibbs Free Energy=
0.327550
 Sum of electronic and zero-point Energies=
-698.913185
 Sum of electronic and thermal Energies=
-698.896951
 Sum of electronic and thermal Enthalpies=
-698.896007
 Sum of electronic and thermal Free Energies=
-698.953915
```

Seven-Membered Ring

3,3-DimethylCycloheptyne

```
6      -2.262721   -0.912360   -0.109933
6      -0.930972   -1.504462    0.078341
6       0.236510   -1.221356    0.166185
6      -2.055632    0.554787    0.340688
6       1.212669   -0.115900    0.038465
6      -0.971901    1.417868   -0.370219
6       0.404168    0.874242   -0.854447
1      -2.563058   -0.976596   -1.161012
1      -1.823233    0.510852    1.408595
1      -0.786674    2.261272    0.303723
1      -3.051723   -1.381575    0.483078
1      -3.002934    1.098795    0.252836
1      -1.427378    1.861427   -1.262496
1       1.033297    1.751342   -1.055766
1       0.263152    0.369736   -1.815011
6       1.530579    0.497319    1.407845
1       2.063801   -0.217849    2.038903
1       2.162478    1.382267    1.282156
1       0.618460    0.794732    1.929690
6       2.506315   -0.521451   -0.672770
1       3.059775   -1.252338   -0.077722
1       2.292956   -0.966922   -1.647400
1       3.146987    0.352736   -0.824506
(Hartree/Particle)
 Thermal correction to Energy=
0.217349
 Thermal correction to Enthalpy=
0.218293
 Thermal correction to Gibbs Free Energy=
0.174695
 Sum of electronic and zero-point Energies=
-351.061355
 Sum of electronic and thermal Energies=
-351.051985
 Sum of electronic and thermal Enthalpies=
-351.051041
 Sum of electronic and thermal Free Energies=
-351.094638
```

Anti-TS

```
6       0.508220    2.102049    0.075537
6       0.315459    0.639298   -0.043081
6       1.033786   -0.362824   -0.152651
```

6	1.851023	2.319462	0.797819
6	2.477383	-0.703799	-0.318516
6	3.129677	1.858220	0.060295
6	3.125056	0.604795	-0.841907
1	0.518866	2.566576	-0.918598
1	1.775914	1.794674	1.755144
1	3.910714	1.742265	0.819863
1	-0.290935	2.593872	0.638927
1	1.971800	3.382155	1.037493
1	3.469990	2.679370	-0.580809
1	4.171958	0.396774	-1.099160
1	2.620611	0.845454	-1.783603
6	3.083265	-1.133623	1.023605
1	2.611204	-2.052521	1.382774
1	4.156159	-1.323723	0.914626
1	2.943314	-0.364855	1.786737
6	2.702595	-1.808046	-1.358978
1	2.298425	-2.763685	-1.015334
1	2.221647	-1.554144	-2.307210
1	3.772725	-1.947799	-1.541103
6	-0.570318	-1.873311	1.459899
6	-0.337603	-2.042021	0.089964
6	-1.477785	-0.835621	1.558354
6	-1.790626	-0.452597	0.246044
8	-1.308523	-1.390868	-0.599196
1	-0.021906	-2.353032	2.255556
1	-1.803866	-0.329556	2.453085
1	0.122039	-2.866346	-0.432209
6	-2.928250	0.390700	-0.275455
6	-3.269321	1.480397	0.745452
6	-4.150667	-0.527700	-0.469688
6	-2.555710	1.028028	-1.620166
1	-2.403431	2.112068	0.955625
1	-4.067824	2.116618	0.354124
1	-3.618774	1.051158	1.688478
1	-4.429418	-1.008511	0.471863
1	-3.935281	-1.309616	-1.201319
1	-5.005761	0.053721	-0.827826
1	-3.422116	1.549144	-2.038373
1	-2.230898	0.268379	-2.333643
1	-1.744095	1.748065	-1.500712

```
(Hartree/Particle)
 Thermal correction to Energy=
0.411408
 Thermal correction to Enthalpy=
0.412352
 Thermal correction to Gibbs Free Energy=
0.347078
 Sum of electronic and zero-point Energies=
-738.128417
 Sum of electronic and thermal Energies=
-738.109575
 Sum of electronic and thermal Enthalpies=
-738.108631
 Sum of electronic and thermal Free Energies=
-738.173905
```

***Syn*-TS**

6	1.373340	-1.245052	1.329096
6	0.537681	-2.273022	-0.451840
6	0.652794	-2.361050	0.945036
6	1.745994	-0.586217	0.154277
8	1.452180	-1.368751	-0.898866
1	-2.901016	-1.260723	1.319531
1	-4.235989	0.621105	0.973862
1	-2.698064	-1.773916	-1.684157
6	2.765034	0.498672	-0.071067
6	4.165196	-0.146779	-0.020336
6	-1.523162	1.695824	1.544209
6	-0.779813	2.615387	-0.661162
1	-4.686644	0.170029	-0.648008
1	-3.381444	2.226612	-0.535782
1	-2.724897	1.029271	-1.636236
1	-2.173283	-2.873885	-0.417044
1	-0.520813	1.822607	1.961553
1	-2.095733	2.608735	1.740220
1	-2.001160	0.868376	2.073423
1	-4.242499	-1.864271	0.364334
1	0.218165	2.801114	-0.260095
6	-3.832759	0.220815	0.037174
6	-1.078642	-1.025824	-0.513187
6	-0.739542	0.130133	-0.208941
6	-2.329564	-1.814490	-0.651717
6	-1.449880	1.424781	0.035093
6	-3.356752	-1.220264	0.325198
6	-2.867906	1.256651	-0.574375
1	0.125846	-3.059709	1.576395
1	1.554441	-0.890083	2.331075
1	0.280943	-3.047520	-1.160029
1	-0.688195	2.437731	-1.736230
1	-1.375001	3.522514	-0.514840
1	4.934936	0.610000	-0.200088
1	3.379405	2.345142	0.876319
1	4.261535	-0.922157	-0.784261
6	2.651281	1.546152	1.041016
1	4.350852	-0.603214	0.955492
1	2.854361	1.110044	2.023126
1	1.652866	1.985774	1.065389
6	2.559789	1.145338	-1.445541
1	3.281201	1.955473	-1.586699
1	1.551845	1.549540	-1.539667
1	2.702367	0.415079	-2.244271

```
(Hartree/Particle)
 Thermal correction to Energy=
0.411654
 Thermal correction to Enthalpy=
0.412598
 Thermal correction to Gibbs Free Energy=
0.348636
 Sum of electronic and zero-point Energies=
-738.125685
 Sum of electronic and thermal Energies=
-738.107119
 Sum of electronic and thermal Enthalpies=
-738.106175
 Sum of electronic and thermal Free Energies=
-738.170138
```

***Anti*-P**

6	-0.238710	1.904269	-0.008811
6	0.015167	0.426755	0.100651
6	-0.876223	-0.560182	0.189603
6	-1.452162	2.219130	-0.892693
6	-2.376974	-0.550770	0.341433
6	-2.808525	1.988424	-0.211915
6	-2.874354	0.835820	0.794542
1	-0.364720	2.352881	0.984496
1	-1.372273	1.602000	-1.793099
1	-3.573370	1.849977	-0.983258
1	0.637236	2.389693	-0.438606
1	-1.401780	3.260332	-1.227206
1	-3.092354	2.897832	0.329286
1	-3.918548	0.733041	1.112041
1	-2.312382	1.106490	1.695645
6	-3.032215	-0.974666	-0.984373
1	-2.730644	-1.989559	-1.261614
1	-4.123064	-0.966125	-0.890970
1	-2.751473	-0.309896	-1.804326
6	-2.778202	-1.558840	1.435373
1	-2.496897	-2.580926	1.170728
1	-2.298583	-1.310609	2.386138
1	-3.862286	-1.544327	1.582965
6	0.395307	-1.846452	-1.512441
6	-0.053082	-1.847105	-0.036602
6	1.291216	-0.873919	-1.586995
6	1.388307	-0.293591	-0.148567
8	1.161219	-1.492019	0.603623
1	-0.007765	-2.471329	-2.296317
1	1.810708	-0.496554	-2.455453
1	-0.449302	-2.778527	0.359552
6	2.720363	0.344779	0.283866
6	3.199468	1.415748	-0.706655
6	3.786204	-0.762495	0.330890
6	2.565742	0.952479	1.684212
1	2.497170	2.242793	-0.818876
1	4.142858	1.838751	-0.349302
1	3.387139	0.993212	-1.697085
1	3.883005	-1.256616	-0.640394
1	3.527819	-1.523793	1.066839
1	4.756894	-0.331159	0.593623

```
1       3.539761    1.269620    2.068568
1       2.145532    0.216120    2.372640
1       1.909612    1.826531    1.675898
(Hartree/Particle)
 Thermal correction to Energy=
0.414627
 Thermal correction to Enthalpy=
0.415572
 Thermal correction to Gibbs Free Energy=
0.353766
 Sum of electronic and zero-point Energies=
-738.198282
 Sum of electronic and thermal Energies=
-738.180592
 Sum of electronic and thermal Enthalpies=
-738.179648
 Sum of electronic and thermal Free Energies=
-738.241453
```

***Syn*-P**

```
6       2.395025    1.491060   -0.789866
6       0.951217    1.096859   -0.659055
6       0.345777   -0.048206   -0.324768
6       3.228344    0.969875    0.384853
6       1.031697   -1.372888   -0.012297
6       3.540588   -0.526442    0.264427
6       2.505694   -1.363247   -0.492334
1       2.821741    1.155361   -1.741320
1       2.669306    1.169380    1.304808
1       3.704690   -0.948621    1.260787
1       2.445486    2.584579   -0.812912
1       4.164540    1.531679    0.461523
1       4.488854   -0.648310   -0.270820
1       2.856378   -2.400747   -0.462883
1       2.509040   -1.084362   -1.551571
6       0.988859   -1.616435    1.507121
1      -0.032540   -1.727062    1.872890
1       1.534698   -2.531862    1.758042
1       1.444737   -0.786078    2.051883
6       0.395550   -2.563184   -0.752211
1      -0.648593   -2.719589   -0.499229
1       0.461248   -2.418321   -1.834388
1       0.933440   -3.482582   -0.501474
6      -0.348373    2.358207    0.998909
6      -0.109287    2.192106   -0.519472
6      -0.971367    1.244578    1.350615
6      -1.143515    0.422957    0.038404
8      -1.272159    1.495530   -0.899763
1      -0.002964    3.177914    1.612052
1      -1.273875    0.916213    2.334351
1       0.033845    3.095820   -1.109390
6      -2.442836   -0.412384   -0.052005
6      -3.623712    0.544887    0.215914
6      -2.533480   -1.522447    1.002878
6      -2.613617   -0.969649   -1.471944
1      -3.612210    1.384799   -0.477639
1      -4.565873    0.001716    0.096949
1      -3.593029    0.945542    1.232953
1      -2.406263   -1.123764    2.013726
1      -1.809501   -2.322508    0.865373
1      -3.528022   -1.975400    0.957505
1      -3.541850   -1.545470   -1.537992
1      -1.790318   -1.616853   -1.770274
1      -2.665076   -0.149597   -2.189854
(Hartree/Particle)
 Thermal correction to Energy=
0.414954
 Thermal correction to Enthalpy=
0.415898
 Thermal correction to Gibbs Free Energy=
0.355465
 Sum of electronic and zero-point Energies=
-738.186627
 Sum of electronic and thermal Energies=
-738.169223
 Sum of electronic and thermal Enthalpies=
-738.168278
 Sum of electronic and thermal Free Energies=
-738.228711
```

Eight-Membered Ring

3,3-DimethylCyclooctyne

6	2.602951	0.046869	0.289567
6	2.205473	-1.415690	-0.052155
6	-0.887906	1.208064	-0.442841
6	0.750011	-1.493652	-0.003990
6	-1.516411	-0.160430	-0.005585
6	-0.386947	-1.096646	-0.002371
1	3.664658	0.172987	0.049720
1	2.691721	-2.110177	0.640360
1	-0.746153	1.182423	-1.528849
1	2.510960	0.189039	1.371670
1	2.561147	-1.675636	-1.056223
1	-1.638476	1.984087	-0.248746
6	1.785476	1.146665	-0.434372
1	1.598391	0.836790	-1.468890
1	2.439485	2.021670	-0.504395
6	0.449386	1.626150	0.219971
1	0.442471	1.347157	1.278791
1	0.464168	2.720772	0.210724
6	-2.609958	-0.569863	-1.012125
1	-3.074870	-1.514071	-0.717546
1	-3.390791	0.195623	-1.057271
1	-2.192070	-0.694998	-2.013658
6	-2.134060	-0.053364	1.405764
1	-2.957775	0.667119	1.402980
1	-2.525636	-1.021127	1.728219
1	-1.395327	0.269723	2.141934

```
(Hartree/Particle)
 Thermal correction to Energy=
0.245406
 Thermal correction to Enthalpy=
0.246350
 Thermal correction to Gibbs Free Energy=
0.199817
 Sum of electronic and zero-point Energies=
-390.498671
 Sum of electronic and thermal Energies=
-390.488042
 Sum of electronic and thermal Enthalpies=
-390.487098
 Sum of electronic and thermal Free Energies=
-390.533631
```

***Anti*-TS**

```
6       1.566481   -0.561241    1.679484
6       0.431100   -1.957955    0.368056
6       0.685362   -1.615365    1.728079
6       1.892815   -0.358217    0.311858
8       1.472801   -1.457206   -0.381949
1      -2.958442    0.531277   -1.570415
1      -1.155736    3.794968    0.425536
1       0.648605    2.482103   -0.244930
6       3.089855    0.362371   -0.281738
6      -2.722977   -1.981403    0.810124
6       3.419535    1.619784    0.542191
6      -2.232989   -2.012348   -1.654034
1      -1.141431    2.440025    1.540265
1      -3.041649    2.766762   -0.844694
1      -3.392230    3.208929    0.809242
1      -0.572337    2.212167   -1.462161
1      -3.020743    0.717765    1.421584
1      -4.498087    1.223958    0.648331
1      -4.227897   -0.429494   -0.847406
1      -1.559102   -2.865014   -1.543915
1      -3.234453   -2.404491   -1.858089
6      -0.321508    2.007599   -0.411886
6      -2.836019    2.489100    0.197562
6      -1.347129    2.717607    0.500044
```

```
6      -0.252384    0.542705   -0.199745
6      -2.251373   -1.127398   -0.386270
6      -0.885146   -0.540650   -0.153027
1      -1.904951   -1.437044   -2.522918
1      -3.744425   -2.334725    0.638892
1      -2.091042   -2.861616    0.949217
1      -2.712549   -1.415112    1.743729
1       0.136074   -1.980366    2.582197
1       1.879923    0.069079    2.497066
6      -3.255081    0.032495   -0.641707
1       0.050070   -2.901300    0.004884
1       5.189514   -0.119901   -0.637307
6      -3.425459    1.090479    0.475389
1       4.269077    2.142428    0.094254
1       4.101642   -1.510316   -0.799724
6       4.300126   -0.604795   -0.223198
1       4.517348   -0.898735    0.806949
1       3.694185    1.365542    1.569261
1       2.579370    2.315993    0.579451
6       2.828510    0.738649   -1.753183
1       3.732777    1.166763   -2.195797
1       2.025510    1.471480   -1.843292
1       2.546255   -0.141977   -2.332610
(Hartree/Particle)
 Thermal correction to Energy=
0.437596
 Thermal correction to Enthalpy=
0.438540
 Thermal correction to Gibbs Free Energy=
0.371006
 Sum of electronic and zero-point Energies=
-777.655505
 Sum of electronic and thermal Energies=
-777.635368
 Sum of electronic and thermal Enthalpies=
-777.634424
 Sum of electronic and thermal Free Energies=
-777.701959
```

***Syn*-TS**

```
6       3.327614   -1.716670    0.062070
6       2.164269   -1.737919   -0.949862
6       2.644312    1.654895   -0.293976
6       0.942873   -0.964115   -0.529919
6       1.097075    1.616403   -0.077782
6       0.612105    0.214616   -0.219310
1       3.998064   -2.545939   -0.194133
1       1.900744   -2.785227   -1.133398
1       2.848160    1.342661   -1.323681
1       2.934773   -1.938489    1.061474
1       2.517982   -1.349763   -1.913049
1       2.939846    2.709368   -0.236223
6       4.178964   -0.439887    0.119711
1       4.581780   -0.229955   -0.880014
1       5.048706   -0.668476    0.746778
6       3.524805    0.837078    0.680738
1       2.960029    0.577325    1.581382
1       4.335933    1.487603    1.023182
6       0.462366    2.521085   -1.156173
1      -0.617732    2.592537   -1.022333
1       0.877375    3.532028   -1.093424
1       0.655973    2.131263   -2.158543
6       0.754290    2.190374    1.314306
1       1.153745    3.204919    1.415573
1      -0.325267    2.230105    1.459425
1       1.169354    1.579596    2.118222
6      -0.640492   -2.237814    1.088183
6      -0.467212   -2.155352   -0.335337
6      -1.438211   -1.168161    1.417262
6      -1.863077   -0.571204    0.203697
8      -1.523632   -1.398794   -0.817437
1      -0.070115   -2.867568    1.753835
1      -1.669690   -0.801678    2.405440
1      -0.232100   -2.994526   -0.978299
6      -3.081398    0.298603   -0.049056
6      -3.131132    1.484601    0.927838
6      -4.332261   -0.592750    0.180247
6      -3.102109    0.807116   -1.501989
1      -2.316047    2.185767    0.744952
1      -4.074266    2.024388    0.804648
1      -3.072367    1.157315    1.969256
1      -4.389048   -0.934636    1.216574
1      -4.304786   -1.472213   -0.466914
1      -5.242027   -0.028061   -0.045375
1      -3.127535   -0.024172   -2.208068
1      -2.219046    1.406213   -1.726299
(Hartree/Particle)
 Thermal correction to Energy=
0.437576
 Thermal correction to Enthalpy=
0.438520
 Thermal correction to Gibbs Free Energy=
0.370233
 Sum of electronic and zero-point Energies=
-777.650417
 Sum of electronic and thermal Energies=
-777.630199
 Sum of electronic and thermal Enthalpies=
-777.629255
 Sum of electronic and thermal Free Energies=
-777.697542
```

***Anti*-P**

```
6      -0.649357    2.623494    0.306454
6      -0.143906    1.668115   -0.805927
6      -3.038759    0.427342   -0.488830
6       0.080678    0.248221   -0.355697
6      -2.273177   -0.920749   -0.445181
6      -0.783935   -0.762960   -0.198800
1      -0.293572    3.636375    0.086299
1       0.787250    2.067924   -1.204884
1      -2.757035    0.969604   -1.394649
1      -0.188856    2.339725    1.259283
1      -0.842120    1.688692   -1.646079
1      -4.096752    0.177800   -0.624816
6      -2.173821    2.687891    0.476165
1      -2.614159    3.150559   -0.416857
1      -2.388342    3.372792    1.304589
6      -2.890393    1.353821    0.745272
1      -2.370758    0.829876    1.553851
1      -3.887425    1.584066    1.133138
6      -2.471344   -1.638928   -1.802173
1      -1.963208   -2.606988   -1.816242
1      -3.535154   -1.814477   -1.993942
1      -2.067510   -1.039228   -2.621450
6      -2.900380   -1.800852    0.664255
1      -3.976301   -1.899422    0.493689
1      -2.478358   -2.808376    0.671755
1      -2.758785   -1.370572    1.658586
6       0.410310   -1.504921    1.861881
6       0.064657   -1.915314    0.412892
6       1.268941   -0.500442    1.727891
6       1.464829   -0.315912    0.191777
8       1.321711   -1.692308   -0.228193
1      -0.029821   -1.917320    2.758589
1       1.710415    0.117992    2.495540
1      -0.279645   -2.932959    0.248234
6       2.832347    0.228369   -0.284195
6       3.935026   -0.726147    0.227816
6       3.118072    1.632485    0.285700
6       2.890585    0.244476   -1.825176
1       3.785268   -1.735752   -0.154693
1       4.915944   -0.368214   -0.098736
1       3.942113   -0.780370    1.319751
1       3.146708    1.623862    1.378558
1       2.386420    2.379994   -0.022831
1       4.098441    1.972374   -0.060876
1       3.895594    0.519013   -2.159238
1       2.189572    0.957575   -2.263236
1       2.654148   -0.744015   -2.222535
(Hartree/Particle)
 Thermal correction to Energy=
0.440537
 Thermal correction to Enthalpy=
0.441481
 Thermal correction to Gibbs Free Energy=
0.376924
 Sum of electronic and zero-point Energies=
-777.699296
```

Sum of electronic and thermal Energies= -777.680133

Sum of electronic and thermal Enthalpies= -777.679188

Sum of electronic and thermal Free Energies= -777.743746

Syn-P

6	-3.353541	1.437347	-0.199090
6	-2.204119	1.234154	-1.214452
6	-2.192928	-1.661539	-0.196518
6	-0.841589	0.952663	-0.631227
6	-0.641280	-1.571234	-0.098326
6	-0.129943	-0.140965	-0.305065
1	-4.121702	2.066047	-0.662438
1	-2.102537	2.157386	-1.795992
1	-2.506485	-1.383792	-1.204324
1	-2.977555	2.000191	0.663574
1	-2.490105	0.469598	-1.938514
1	-2.433093	-2.726373	-0.111819
6	-4.007749	0.139172	0.285914
1	-4.565909	-0.317772	-0.541360
1	-4.751530	0.392275	1.049760
6	-3.023663	-0.888602	0.861844
1	-2.362971	-0.371648	1.563665
1	-3.586878	-1.609645	1.461669
6	-0.079680	-2.545407	-1.158852
1	1.005864	-2.623898	-1.116176
1	-0.487921	-3.549103	-1.003389
1	-0.352873	-2.220291	-2.166410
6	-0.265052	-2.081419	1.315878
1	-0.734548	-3.055620	1.485759
1	0.804124	-2.207316	1.445736
1	-0.614737	-1.404546	2.097643
6	0.259182	2.197663	1.243289
6	0.063230	2.161323	-0.289648
6	1.028281	1.146333	1.509577
6	1.315830	0.474004	0.136798
8	1.321380	1.650684	-0.704007
1	-0.206206	2.895308	1.925261
1	1.349294	0.769007	2.469827
1	-0.171533	3.100236	-0.788605
6	2.725255	-0.172799	-0.072907
6	3.006846	-1.443092	0.747461
6	3.776696	0.879781	0.363901
6	2.942461	-0.464231	-1.572249
1	2.463426	-2.315239	0.385746
1	4.072309	-1.678836	0.671984
1	2.782258	-1.307525	1.809141
1	3.728374	1.073045	1.439061
1	3.627766	1.824559	-0.156264
1	4.779910	0.507180	0.137355
1	2.854608	0.451282	-2.156998
1	2.215918	-1.177986	-1.961956
1	3.942266	-0.880921	-1.727855

(Hartree/Particle)

Thermal correction to Energy= 0.440919

Thermal correction to Enthalpy= 0.441863

Thermal correction to Gibbs Free Energy= 0.378177

Sum of electronic and zero-point Energies= -777.682225

Sum of electronic and thermal Energies= -777.663307

Sum of electronic and thermal Enthalpies= -777.662363

Sum of electronic and thermal Free Energies= -777.726050

Nine-Membered Ring

3,3-DimethylCyclononyne

6	1.139760	1.437480	0.588605
1	0.811755	0.782187	1.397431
1	1.474838	2.359159	1.079317
6	2.399960	0.860908	-0.086554
1	3.205972	0.928522	0.654962
1	2.691997	1.536285	-0.900640
6	2.421272	-0.571683	-0.644781
1	1.787105	-0.648080	-1.533014
1	3.446078	-0.776613	-0.974109
6	1.989576	-1.679372	0.342263
1	2.287529	-2.660183	-0.039213
1	2.489412	-1.549111	1.308735
6	0.538829	-1.585058	0.485811
6	-0.568375	-1.133485	0.372845
6	-1.666967	-0.235297	-0.010174
6	-0.997251	0.826909	-0.931137
1	-1.802194	1.391075	-1.420010
1	-0.474694	0.284592	-1.725493
6	-0.058291	1.860495	-0.285102
1	-0.673884	2.525857	0.331111
1	0.322806	2.492672	-1.097120
6	-2.729122	-0.997054	-0.817841
1	-3.165282	-1.801470	-0.220534
1	-3.531911	-0.318182	-1.121609
1	-2.290478	-1.438758	-1.716006
6	-2.320441	0.411732	1.219069
1	-3.059043	1.155188	0.902812
1	-2.830544	-0.343640	1.821759
1	-1.583162	0.907054	1.853611

(Hartree/Particle)

Thermal correction to Energy= 0.278050

Thermal correction to Enthalpy= 0.278994

Thermal correction to Gibbs Free Energy= 0.230857

Sum of electronic and zero-point Energies= -429.658042

Sum of electronic and thermal Energies= -429.646652

Sum of electronic and thermal Enthalpies= -429.645708

Sum of electronic and thermal Free Energies= -429.693845

Anti-TS

6	1.217117	-2.274650	-1.092443
6	0.717427	-2.102584	0.221753
6	2.017457	-1.184245	-1.318827
6	2.021718	-0.431331	-0.117917
8	1.527089	-1.221583	0.867027
1	-3.090105	3.332441	-0.385444
1	-1.623601	1.305768	1.376729
1	-2.033987	1.666091	-1.893005
6	3.046295	0.581975	0.350623
6	-2.205701	-2.572273	-0.860305
6	-2.272480	-1.781646	1.518778
6	4.302077	-0.201620	0.785907
1	-2.925530	2.362981	1.869829
1	-1.236527	3.220110	-1.942275
1	0.513069	1.649188	-1.954566
1	0.511521	2.356538	-0.359284
1	-4.133736	-0.972830	-0.455201
1	-3.003983	0.021786	-1.338777
1	-2.093072	-2.284418	-1.909266
1	-3.973581	0.318508	1.545278
1	-4.441740	1.305797	0.187330
6	-0.058725	1.694014	-1.019698
1	-1.447195	-3.324456	-0.633211
1	-3.185623	-3.042349	-0.735187
6	-3.589189	0.769891	0.624160
1	-1.603254	-2.603553	1.780239
1	-3.298344	-2.129914	1.676805
6	-2.167447	2.835558	-0.059765
1	-2.078032	-0.960573	2.211531
1	-1.556804	3.615722	0.412530
6	-1.417958	2.348160	-1.303041
1	0.873982	-3.007538	-1.806031
1	2.468560	-0.878079	-2.250211
6	-0.744719	-0.697200	-0.143408
6	-0.105859	0.326781	-0.462339
6	-2.087030	-1.341524	0.056490

```
6      -2.526297    1.803880    1.015642
1       0.286484   -2.860592    0.858795
1       4.207292    2.222229   -0.438531
6      -3.226093   -0.366323   -0.342278
1       5.069404    0.489087    1.149286
1       2.586584    2.125613   -1.132921
6       3.433279    1.532600   -0.786899
1       3.841425    0.986090   -1.641639
1       4.716538   -0.768747   -0.051864
1       4.062229   -0.903899    1.586999
6       2.515059    1.366973    1.557122
1       3.279874    2.062558    1.914845
1       2.256584    0.689962    2.373205
1       1.621274    1.940526    1.306464
(Hartree/Particle)
 Thermal correction to Energy=
0.472520
 Thermal correction to Enthalpy=
0.473464
 Thermal correction to Gibbs Free Energy=
0.405591
 Sum of electronic and zero-point Energies=
-816.703236
 Sum of electronic and thermal Energies=
-816.682743
 Sum of electronic and thermal Enthalpies=
-816.681799
 Sum of electronic and thermal Free Energies=
-816.749672
```

Syn-TS

```
6       1.241673   -2.239181    1.304629
6       0.734945   -2.274548   -0.028508
6       1.963871   -1.078358    1.377446
6       1.980775   -0.521268    0.074723
8       1.524507   -1.457003   -0.786085
1      -4.972731   -0.558609   -0.661422
1      -2.188600    0.223944   -1.656619
1      -3.370558   -1.001893    1.186009
6       3.017286    0.411648   -0.518147
6      -0.144188    1.761030    1.999746
6      -0.361451    2.461172   -0.398927
6       3.298934    1.598698    0.407009
1      -3.719237    0.793637   -2.281421
1      -3.988955   -2.458253    0.450515
1      -1.726310   -2.915100    0.788131
1      -1.890495   -2.635112   -0.928435
1      -2.500545    2.512472    1.404272
1      -2.661489    0.780922    1.547869
1      -0.528654    1.102710    2.783832
1      -3.004180    2.540411   -0.928463
1      -4.276146    1.757535   -0.028997
6      -1.924645   -2.129149    0.046749
1       0.935937    1.623170    1.948452
1      -0.350707    2.797144    2.286653
6      -3.243697    1.624710   -0.377248
1       0.722770    2.551706   -0.423342
1      -0.773292    3.445905   -0.155166
6      -3.935625   -0.817322   -0.909765
1      -0.699659    2.188363   -1.401057
1      -3.992984   -1.502051   -1.765451
6      -3.340671   -1.593255    0.268771
1       0.928826   -2.880314    2.114416
1       2.387124   -0.617968    2.256969
6      -0.438492    0.036845    0.277901
6      -0.794802   -1.155414    0.118723
6      -0.809904    1.434951    0.649912
6      -3.216636    0.455225   -1.368049
1       0.400518   -3.160388   -0.553839
1       5.093842    0.201621   -1.140391
6      -2.343633    1.570079    0.863683
1       4.124239    2.189933    0.000563
1       4.151148   -1.294404   -1.278801
6       4.319408   -0.407565   -0.664052
1       4.688269   -0.733498    0.312034
1       3.594123    1.266548    1.406429
1       2.436500    2.256599    0.510665
6       2.586059    0.888688   -1.910290
1       3.335451    1.574476   -2.316444
1       1.625202    1.401437   -1.880548
1       2.489297    0.043160   -2.593563
(Hartree/Particle)
 Thermal correction to Energy=
0.472466
 Thermal correction to Enthalpy=
0.473410
 Thermal correction to Gibbs Free Energy=
0.405833
 Sum of electronic and zero-point Energies=
-816.697689
 Sum of electronic and thermal Energies=
-816.677251
 Sum of electronic and thermal Enthalpies=
-816.676306
 Sum of electronic and thermal Free Energies=
-816.743883
```

Anti-P

```
6      -2.327416    1.867743    1.012565
1      -1.500684    1.262592    1.393325
1      -2.713720    2.430707    1.869367
6      -1.811152    2.876897   -0.012392
1      -1.065342    3.520795    0.470708
1      -2.639506    3.534991   -0.302640
6      -1.189752    2.293426   -1.281782
1      -1.920569    1.725221   -1.854650
1      -0.911560    3.134358   -1.927453
6       0.098082    1.502465   -1.056222
1       0.561368    1.320642   -2.037631
1       0.778118    2.195701   -0.556110
6       0.195208    0.186049   -0.333683
6      -0.599470   -0.835921    0.008307
6      -2.069888   -1.228609    0.002700
6      -3.086072   -0.170452   -0.469532
1      -4.019146   -0.713755   -0.663153
1      -2.770827    0.205038   -1.442182
6      -3.450731    0.966678    0.494703
1      -3.963269    0.525511    1.355650
1      -4.201765    1.594724   -0.001285
6      -2.203805   -2.427115   -0.962960
1      -1.556214   -3.259773   -0.676825
1      -3.232494   -2.798954   -0.961149
1      -1.944778   -2.133670   -1.984274
6      -2.473885   -1.696543    1.417429
1      -3.546156   -1.914754    1.443540
1      -1.950999   -2.607887    1.712619
1      -2.262626   -0.932309    2.168459
6       1.111992   -2.419820   -0.872597
6       0.399853   -1.962354    0.413297
6       1.904786   -1.406436   -1.186021
6       1.671355   -0.355160   -0.073989
8       1.418603   -1.215083    1.036048
1       0.923303   -3.337675   -1.410347
1       2.539274   -1.281104   -2.051260
1       0.028197   -2.741955    1.072119
6       2.858646    0.566550    0.281064
6       3.360004    1.393032   -0.913384
6       4.022143   -0.338467    0.729433
6       2.482282    1.477869    1.458430
1       2.645047    2.137355   -1.261232
1       4.268442    1.926806   -0.619335
1       3.621379    0.753522   -1.761066
1       4.330114   -1.014357   -0.073530
1       3.737187   -0.946560    1.587588
1       4.883735    0.277653    1.003348
1       3.355150    2.054443    1.778929
1       2.136025    0.877650    2.301711
1       1.690406    2.186720    1.206180
(Hartree/Particle)
 Thermal correction to Energy=
0.475281
 Thermal correction to Enthalpy=
0.476226
 Thermal correction to Gibbs Free Energy=
0.409069
 Sum of electronic and zero-point Energies=
-816.751070
 Sum of electronic and thermal Energies=
-816.731210
```

```
 Sum of electronic and thermal Enthalpies=
-816.730265
 Sum of electronic and thermal Free Energies=
-816.797422
```

Syn-P

```
6       2.566495   -0.641317   -1.575379
1       1.485086   -0.584371   -1.702651
1       2.953551   -1.093766   -2.494461
6       3.151575    0.781371   -1.473176
1       2.536425    1.463362   -2.070861
1       4.143280    0.780397   -1.939353
6       3.332475    1.352161   -0.064860
1       3.936774    0.653379    0.518699
1       3.942510    2.256930   -0.144625
6       2.050003    1.724399    0.719456
1       2.198296    1.493839    1.780343
1       1.953750    2.814362    0.683817
6       0.709585    1.186555    0.278114
6       0.070068    0.008538    0.299191
6       0.586380   -1.322759    0.849599
6       2.134025   -1.385195    0.913380
1       2.376420   -2.246785    1.547354
1       2.510501   -0.522892    1.458970
6       2.891548   -1.588193   -0.412871
1       2.707593   -2.611294   -0.754925
1       3.966123   -1.548497   -0.196638
6       0.064196   -1.418972    2.298663
1      -1.024419   -1.338186    2.344087
1       0.348666   -2.376322    2.746557
1       0.480644   -0.613098    2.909520
6       0.151285   -2.579637    0.077265
1       0.652661   -3.449345    0.514078
1      -0.916385   -2.768483    0.125078
1       0.437903   -2.530138   -0.973902
6      -1.223340    2.375292    1.216772
6      -0.357815    2.237822   -0.051905
6      -1.889589    1.233642    1.271372
6      -1.461271    0.431308    0.007863
8      -1.218059    1.511311   -0.895005
1      -1.198899    3.194528    1.920489
1      -2.563723    0.876157    2.035775
1      -0.004372    3.151943   -0.526256
6      -2.586151   -0.434706   -0.608426
6      -3.744969    0.516535   -0.978353
6      -3.165104   -1.453779    0.384306
6      -2.116509   -1.094703   -1.911512
1      -3.440701    1.227163   -1.745903
1      -4.587777   -0.071320   -1.354478
1      -4.088514    1.086852   -0.111241
1      -3.711954   -0.949396    1.185771
1      -2.421023   -2.094858    0.851359
1      -3.878223   -2.100317   -0.135097
1      -2.969699   -1.548919   -2.424470
1      -1.373111   -1.871135   -1.751763
1      -1.684237   -0.340443   -2.572229
(Hartree/Particle)
 Thermal correction to Energy=
0.475813
 Thermal correction to Enthalpy=
0.476757
 Thermal correction to Gibbs Free Energy=
0.411531
 Sum of electronic and zero-point Energies=
-816.737573
 Sum of electronic and thermal Energies=
-816.718017
 Sum of electronic and thermal Enthalpies=
-816.717073
 Sum of electronic and thermal Free Energies=
-816.782300
```

Chapter 6

ωB97XD/6-311G(d,p)

Pathway I

Cyclohexyne Dimerization

Cyclohexyne

```
6      -0.232264    0.735087    1.047328
6       0.232264    1.573030   -0.194851
6       0.068699    0.600810   -1.294107
6      -0.068699   -0.600810   -1.294107
6      -0.232264   -1.573030   -0.194851
6       0.232264   -0.735087    1.047328
1      -0.370523    2.478909   -0.288813
1       1.277777    1.880727   -0.100406
1       1.326570   -0.762137    1.080427
1      -1.326570    0.762137    1.080427
1       0.370523   -2.478909   -0.288813
1      -1.277777   -1.880727   -0.100406
1      -0.129364   -1.222307    1.958573
1       0.129364    1.222307    1.958573
(Hartree/Particle)
 Thermal correction to Energy=
0.127899
 Thermal correction to Enthalpy=
0.128843
 Thermal correction to Gibbs Free Energy=
0.094485
 Sum of electronic and zero-point Energies=
-233.189338
 Sum of electronic and thermal Energies=
-233.183766
 Sum of electronic and thermal Enthalpies=
-233.182822
 Sum of electronic and thermal Free Energies=
-233.217179
```

TS1

```
6      -3.794868   -0.037520    0.364238
6      -3.159704   -1.382237   -0.118980
6      -1.706344   -1.103353   -0.105621
6      -1.108455   -0.039125   -0.050990
6      -1.609729    1.345916    0.090707
6      -3.127731    1.216367   -0.231235
1      -3.466593   -2.203196    0.533771
1      -3.489786   -1.632961   -1.131957
1      -3.245620    1.197682   -1.320236
1      -3.714772    0.001019    1.456077
1      -1.109781    2.042753   -0.586886
1      -1.436952    1.703695    1.110672
1      -3.649552    2.107451    0.132125
1      -4.862414   -0.035472    0.119807
6       3.794733    0.037795    0.364524
6       3.159463    1.382335   -0.119036
6       1.706161    1.103153   -0.106059
6       1.108446    0.038868   -0.051341
6       1.609940   -1.346090    0.090368
6       3.128027   -1.216251   -0.231094
1       3.466015    2.203422    0.533706
1       3.489786    1.632991   -1.131954
1       3.246272   -1.197617   -1.320059
1       3.714252   -0.000661    1.456338
1       1.110356   -2.042935   -0.587480
1       1.436869   -1.704037    1.110227
1       3.649916   -2.107197    0.132500
1       4.862365    0.035914    0.120469
(Hartree/Particle)
 Thermal correction to Energy=
0.257253
 Thermal correction to Enthalpy=
0.258197
 Thermal correction to Gibbs Free Energy=
0.204904
 Sum of electronic and zero-point Energies=
-466.381369
 Sum of electronic and thermal Energies=
-466.369183
 Sum of electronic and thermal Enthalpies=
-466.368239
 Sum of electronic and thermal Free Energies=
-466.421531
```

TS2

```
 6      -3.381036   -0.339246   -0.432532
 6      -2.875460   -0.854091    0.929635
 6      -1.444745   -0.515154    1.197505
 6      -0.735832    0.111770    0.280307
 6      -1.273910    1.005186   -0.810205
 6      -2.806673    1.050944   -0.725699
 1      -3.006285   -1.938749    1.017194
 1      -3.469632   -0.439670    1.754585
 1      -3.217475    1.451485   -1.656311
 1      -3.062599   -1.030647   -1.222225
 1      -0.846079    2.008775   -0.732125
 1      -0.955701    0.600929   -1.781377
 1      -3.104208    1.736080    0.076932
 1      -4.475001   -0.314685   -0.449622
 6       3.342365    0.440620   -0.362434
 6       2.696541    1.067652    0.900160
 6       1.311364    0.538767    0.999535
 6       0.751233   -0.298553    0.216598
 6       1.425076   -1.222799   -0.747940
 6       2.945689   -1.033374   -0.557386
 1       2.710800    2.159972    0.841644
 1       3.246779    0.804454    1.810211
 1       3.479906   -1.449723   -1.415602
 1       3.018718    1.014641   -1.238340
 1       1.138901   -2.264788   -0.576449
 1       1.119058   -0.971715   -1.771383
 1       3.263266   -1.604812    0.322206
 1       4.431869    0.528124   -0.304592
(Hartree/Particle)
 Thermal correction to Energy=
0.256662
 Thermal correction to Enthalpy=
0.257606
 Thermal correction to Gibbs Free Energy=
0.208111
 Sum of electronic and zero-point Energies=
-466.389799
 Sum of electronic and thermal Energies=
-466.378650
 Sum of electronic and thermal Enthalpies=
-466.377706
 Sum of electronic and thermal Free Energies=
-466.427201
```

Product

```
6       3.196120    0.672430    0.374016
6       1.977704    1.551809    0.028904
6       0.786758    0.664874    0.002595
6       0.786758   -0.664874   -0.002595
6       1.977704   -1.551809   -0.028904
6       3.196120   -0.672430   -0.374016
1       1.867852    2.354042    0.767404
1       2.117559    2.046824   -0.942145
1       3.189542   -0.476517   -1.452359
1       3.189542    0.476517    1.452359
1       1.867852   -2.354042   -0.767404
1       2.117559   -2.046824    0.942145
1       4.121368   -1.212971   -0.154560
1       4.121368    1.212971    0.154560
6      -3.196120   -0.672430    0.374016
6      -1.977704   -1.551809    0.028904
6      -0.786758   -0.664874    0.002595
6      -0.786758    0.664874   -0.002595
6      -1.977704    1.551809   -0.028904
6      -3.196120    0.672430   -0.374016
1      -1.867852   -2.354042    0.767404
1      -2.117559   -2.046824   -0.942145
1      -3.189542    0.476517   -1.452359
1      -3.189542   -0.476517    1.452359
1      -1.867852    2.354042   -0.767404
1      -2.117559    2.046824    0.942145
1      -4.121368    1.212971   -0.154560
1      -4.121368   -1.212971    0.154560
(Hartree/Particle)
 Thermal correction to Energy=
0.261681
 Thermal correction to Enthalpy=
0.262625
 Thermal correction to Gibbs Free Energy=
0.216313
 Sum of electronic and zero-point Energies=
-466.517813
 Sum of electronic and thermal Energies=
-466.507199
 Sum of electronic and thermal Enthalpies=
-466.506255
 Sum of electronic and thermal Free Energies=
-466.552568
```

Cyclohexyne Dimer Dimerization

TS

```
6       2.034084   -2.512538    1.462717
6       0.516651   -2.390222    1.684261
6       0.155273   -0.980094    1.391227
6       1.017158    0.061191    1.386810
6       2.461191    0.022022    1.727674
6       2.815571   -1.406921    2.195495
1      -0.027583   -3.112205    1.066936
1       0.268952   -2.637241    2.726808
1       2.592517   -1.487958    3.265637
1       2.237284   -2.454248    0.386840
1       2.676066    0.740049    2.527619
1       3.091346    0.331265    0.884478
1       3.890017   -1.580293    2.085518
1       2.386272   -3.490164    1.804308
6      -2.034294    2.578357    1.350988
6      -0.516107    2.465425    1.572114
6      -0.155154    1.043967    1.339146
6      -1.016791    0.003022    1.387063
6      -2.460201    0.058292    1.728794
6      -2.813027    1.506312    2.134662
1       0.025766    3.160497    0.922667
1      -0.264781    2.756713    2.602327
1      -2.585859    1.634328    3.199349
1      -2.241681    2.473045    0.279482
1      -2.673988   -0.624336    2.559394
1      -3.092272   -0.286487    0.900959
1      -3.887905    1.674782    2.021281
1      -2.384904    3.570219    1.650582
6       2.814879    1.405940   -2.196783
6       2.459890   -0.022976   -1.729421
6       0.155225    0.980593   -1.385959
6      -0.156063   -1.043522   -1.345488
6       0.517312    2.389914   -1.682195
6       2.035009    2.511725   -1.462677
1       2.672712   -0.740592   -2.530274
1       3.091448   -0.333471   -0.887700
1       2.239735    2.453394   -0.387084
1       2.590646    1.487747   -3.266623
1      -0.025676    3.113864   -1.066119
1       0.268727    2.634598   -2.725127
1       2.387025    3.489246   -1.804739
1       3.889585    1.578457   -2.087988
6      -2.815466   -1.505538   -2.132235
6      -2.461400   -0.057215   -1.728282
6      -1.017534   -0.002887   -1.388796
6       1.016313   -0.061765   -1.386206
6      -0.517682   -2.465487   -1.574075
6      -2.035480   -2.577316   -1.349354
1      -2.675893    0.624462   -2.559519
1      -3.092165    0.289189   -0.900124
1      -2.240250   -2.470725   -0.277491
1      -2.590616   -1.634449   -3.197300
1       0.025483   -3.158544   -0.923526
1      -0.268553   -2.760003   -2.603861
1      -2.387455   -3.569235   -1.647161
1      -3.890145   -1.673581   -2.016434
(Hartree/Particle)
 Thermal correction to Energy=
0.525285
 Thermal correction to Enthalpy=
0.526230
```

```
 Thermal correction to Gibbs Free Energy=
0.454738
 Sum of electronic and zero-point Energies=
-933.054842
 Sum of electronic and thermal Energies=
-933.033340
 Sum of electronic and thermal Enthalpies=
-933.032396
 Sum of electronic and thermal Free Energies=
-933.103887
```

Product

```
6       2.159238    2.416004    1.956038
6       1.574229    2.569378    0.530177
6       1.159568    1.218109    0.066037
6       0.765087    0.056731    0.967452
6       1.687258   -0.062689    2.182400
6       2.774258    1.025829    2.174653
1       0.731716    3.270796    0.540598
1       2.322747    2.982426   -0.154257
1       3.505886    0.822440    1.383721
1       1.360159    2.556636    2.693767
1       2.139284   -1.059072    2.246209
1       1.096621    0.067511    3.096359
1       3.318592    1.004535    3.123475
1       2.898896    3.198481    2.143539
6       2.095699   -2.008332   -2.103571
6       1.811286   -1.937414   -0.594154
6       0.839866   -0.805234   -0.334259
6       1.254546    0.464749   -1.034999
6       1.743053    0.508478   -2.436443
6       2.684990   -0.696474   -2.645744
1       1.445738   -2.898700   -0.219967
1       2.750134   -1.727802   -0.064961
1       3.631652   -0.497530   -2.128971
1       1.161205   -2.232024   -2.635190
1       2.246444    1.450737   -2.671711
1       0.892610    0.413125   -3.124803
1       2.919462   -0.804228   -3.708752
1       2.783764   -2.831430   -2.318597
6      -2.474014    2.683652   -0.782637
6      -2.279178    2.024426    0.595035
6      -1.688830    0.673366    0.369712
6      -1.605327    0.035159   -0.798395
6      -2.150591    0.514179   -2.099331
6      -3.074417    1.713282   -1.814522
1      -1.619716    2.633533    1.224302
1      -3.235607    1.952873    1.128417
1      -4.032013    1.339695   -1.432792
1      -1.495766    3.021093   -1.146139
1      -2.696120   -0.275558   -2.628358
1      -1.326647    0.816387   -2.758712
1      -3.291422    2.248330   -2.743424
1      -3.108184    3.570639   -0.695318
6      -1.399648   -3.161492    1.015908
6      -1.248350   -2.511500   -0.364080
6      -0.721790   -1.080984   -0.272996
6      -0.784253   -0.293043    1.095169
6      -1.252037   -1.028535    2.342830
6      -2.132202   -2.231002    1.986799
1      -0.612591   -3.126651   -1.009777
1      -2.235278   -2.491232   -0.838874
1      -3.069267   -1.892502    1.527984
1      -0.410968   -3.398537    1.431679
1      -1.777653   -0.342781    3.016493
1      -0.390384   -1.410187    2.900990
1      -2.399938   -2.769860    2.900539
1      -1.934005   -4.111004    0.916044
(Hartree/Particle)
 Thermal correction to Energy=
0.529342
 Thermal correction to Enthalpy=
0.530287
 Thermal correction to Gibbs Free Energy=
0.461837
 Sum of electronic and zero-point Energies=
-933.182622
 Sum of electronic and thermal Energies=
-933.162407
 Sum of electronic and thermal Enthalpies=
-933.161463
 Sum of electronic and thermal Free Energies=
-933.229912
```

Pathway II

Cyclohexyne addition to Cyclohexyne Dimer

TS

```
6       2.695035   -2.041817    0.571220
6       1.955154   -1.090171    1.530597
6       1.747573    0.341925   -0.540606
6       1.388245    0.003403    0.702532
6       2.729455   -0.377730   -1.391572
6       3.553190   -1.297275   -0.467727
1       1.173069   -1.625400    2.076852
1       2.647910   -0.684942    2.281891
1       4.294623   -0.686004    0.060312
1       1.944893   -2.643415    0.046659
1       3.390914    0.310610   -1.928836
1       2.202189   -0.965033   -2.155087
1       4.110794   -2.022555   -1.067351
1       3.328189   -2.729439    1.139807
6      -0.958709    3.241010   -0.607747
6       0.221144    2.603657   -1.367048
6       0.722368    1.469725   -0.552988
6       0.328822    1.160832    0.695636
6      -0.476739    2.022032    1.604038
6      -0.685885    3.378845    0.900185
1      -0.095417    2.274203   -2.363115
1       1.022933    3.337899   -1.525666
1       0.217327    3.985059    1.036124
1      -1.848593    2.620054   -0.753843
1       0.047207    2.168407    2.555593
1      -1.437108    1.556331    1.853630
1      -1.507409    3.923914    1.373722
1      -1.184080    4.223971   -1.030611
6      -2.801189   -2.698180    0.152363
6      -1.298620   -2.852314   -0.226035
6      -0.739376   -1.473604   -0.187227
6      -1.381679   -0.428699   -0.170379
6      -2.820507   -0.114342   -0.154873
6      -3.484484   -1.485784   -0.505623
1      -0.804089   -3.549276    0.457562
1      -1.189899   -3.271374   -1.232407
1      -3.451685   -1.608491   -1.593873
1      -2.871271   -2.595702    1.241413
1      -3.126518    0.645647   -0.879634
1      -3.140625    0.235122    0.833317
1      -4.540005   -1.459722   -0.216381
1      -3.346131   -3.608942   -0.118545
(Hartree/Particle)
 Thermal correction to Energy=
0.391393
 Thermal correction to Enthalpy=
0.392337
 Thermal correction to Gibbs Free Energy=
0.329447
 Sum of electronic and zero-point Energies=
-699.714473
 Sum of electronic and thermal Energies=
-699.697536
 Sum of electronic and thermal Enthalpies=
-699.696592
 Sum of electronic and thermal Free Energies=
-699.759483
```

P

```
6      -2.187905   -2.784619   -0.342631
6      -1.895190   -1.729666   -1.437612
6      -1.064766   -0.651708   -0.831659
6      -0.201388   -0.816041    0.430212
6      -0.862687   -1.669741    1.509396
6      -2.248510   -2.164109    1.061224
1      -1.390505   -2.203865   -2.286756
1      -2.829061   -1.305115   -1.821794
```

```
1      -2.959879   -1.329373    1.058888
1      -1.394405   -3.541693   -0.347918
1      -0.929799   -1.120460    2.454857
1      -0.230925   -2.544960    1.702350
1      -2.626348   -2.899732    1.777375
1      -3.119623   -3.308289   -0.571486
6      -1.085835    3.018328    0.743554
6      -0.706841    1.699417    1.438361
6      -0.110290    0.755783    0.413144
6      -0.972345    0.678909   -0.848070
6      -1.562002    1.874364   -1.501279
6      -2.096677    2.808287   -0.394059
1      -0.017167    1.878916    2.268364
1      -1.614385    1.247534    1.860463
1      -3.010163    2.369129    0.024947
1      -0.178125    3.486263    0.340134
1      -2.354056    1.611103   -2.208560
1      -0.783326    2.404400   -2.066158
1      -2.377000    3.773143   -0.826676
1      -1.501402    3.719593    1.473421
6       3.568151   -0.920194   -0.704497
6       2.417311   -1.724772   -0.069260
6       1.307603   -0.775747    0.235184
6       1.385616    0.556167    0.227122
6       2.606164    1.361873   -0.057666
6       3.821517    0.417789    0.010884
1       2.081501   -2.515064   -0.750250
1       2.758662   -2.228580    0.844240
1       4.052225    0.218276    1.063983
1       3.312761   -0.714907   -1.750874
1       2.722852    2.187937    0.652631
1       2.528917    1.819010   -1.053645
1       4.701135    0.905137   -0.419395
1       4.486565   -1.514326   -0.712233
(Hartree/Particle)
 Thermal correction to Energy=
0.395703
 Thermal correction to Enthalpy=
0.396647
 Thermal correction to Gibbs Free Energy=
0.338376
 Sum of electronic and zero-point Energies=
-699.872352
 Sum of electronic and thermal Energies=
-699.857001
 Sum of electronic and thermal Enthalpies=
-699.856057
 Sum of electronic and thermal Free Energies=
-699.914328
```

Cyclohexyne addition to Cyclohexyne Trimer (Dewar Benzene Derivative). Four Sites of Addition

Bf

TS1

```
6      -1.687593    3.159315   -1.066873
6      -1.302135    2.697781    0.353995
6      -1.137047    1.213096    0.326047
6      -1.021682    0.350057   -0.937652
6      -1.840540    0.854787   -2.120528
6      -2.602924    2.142988   -1.766268
1      -0.405154    3.224232    0.697554
1      -2.099393    2.954360    1.060563
1      -3.447924    1.907839   -1.107570
1      -0.778315    3.279608   -1.669596
1      -2.527886    0.081819   -2.481960
1      -1.159356    1.076889   -2.951209
1      -3.024147    2.581248   -2.675591
1      -2.165713    4.141179   -1.021858
6      -2.972278   -2.133105    1.430693
6      -2.701018   -1.618706    0.006927
6      -1.396364   -0.844959    0.013322
6      -1.379015    0.180639    1.137995
6      -1.802378   -0.127790    2.524360
6      -3.080987   -0.991388    2.452964
1      -2.674544   -2.445151   -0.709540
1      -3.515367   -0.946916   -0.294206
1      -3.923163   -0.348087    2.170729
1      -2.161105   -2.810627    1.727272
1      -1.972464    0.776696    3.115684
1      -1.007586   -0.699468    3.020961
1      -3.309346   -1.398331    3.442240
1      -3.893930   -2.722441    1.445547
6       2.971861    2.190071    1.027519
6       2.085079    1.672041   -0.133259
6       1.816288    0.255924    0.207120
6       2.388779   -0.537361    0.975406
6       3.527438   -0.177957    1.873868
6       4.077667    1.197341    1.414836
1       1.190533    2.284942   -0.243014
1       2.630214    1.732715   -1.082548
1       4.727243    1.040325    0.545360
1       2.329566    2.373350    1.896641
1       4.325819   -0.925744    1.866656
1       3.167656   -0.123397    2.907622
1       4.701863    1.629792    2.203886
1       3.416766    3.149418    0.744309
6       1.535974   -3.002601   -1.415820
6       0.740354   -2.626390   -0.147843
6      -0.103885   -1.497655   -0.422890
6       0.295601   -0.439667   -1.190815
6       1.206104   -0.607054   -2.377880
6       2.165650   -1.790897   -2.131979
1       0.258944   -3.480555    0.331905
1       1.489986   -2.149204    0.604278
1       2.999955   -1.431509   -1.526914
1       0.860807   -3.526194   -2.102338
1       1.778629    0.295285   -2.612126
1       0.574052   -0.803403   -3.254172
1       2.582950   -2.122147   -3.087903
1       2.332711   -3.707592   -1.160128
(Hartree/Particle)
 Thermal correction to Energy=
0.523991
 Thermal correction to Enthalpy=
0.524936
 Thermal correction to Gibbs Free Energy=
0.454283
 Sum of electronic and zero-point Energies=
-933.051293
 Sum of electronic and thermal Energies=
-933.030289
 Sum of electronic and thermal Enthalpies=
-933.029344
 Sum of electronic and thermal Free Energies=
-933.099997
```

TS2

```
6       0.998263   -3.210827   -1.481361
6       0.802611   -2.868217    0.013810
6       0.910551   -1.390760    0.155919
6       0.738637   -0.395861   -0.965899
6       1.334348   -0.826671   -2.300603
6       1.955320   -2.230395   -2.177941
1      -0.159931   -3.244843    0.373000
1       1.578573   -3.346672    0.620310
1       2.892169   -2.174800   -1.610488
1       0.029284   -3.171427   -1.993276
1       2.073919   -0.106942   -2.666319
1       0.538151   -0.865855   -3.051997
1       2.210818   -2.601830   -3.174171
1       1.363105   -4.235603   -1.582796
6       3.113576    1.675384    1.520066
6       2.729918    1.356673    0.065976
6       1.375208    0.675412    0.055344
6       1.325023   -0.484807    1.040080
6       1.812952   -0.331833    2.429508
6       3.158725    0.420761    2.403078
1       2.732646    2.262995   -0.547315
1       3.463362    0.666507   -0.366997
1       3.934748   -0.252871    2.020459
1       2.384707    2.383308    1.934924
1       1.911246   -1.299814    2.927471
1       1.069453    0.254724    2.984073
1       3.448937    0.696372    3.420401
```

```
1       4.085567    2.176144    1.542653
6      -2.955089   -2.015287    0.929185
6      -2.362769   -1.329061   -0.299593
6      -1.673527   -0.034315    0.090463
6      -1.819528    0.678081    1.230172
6      -2.803436    0.129886    2.245235
6      -3.732020   -0.996296    1.761763
1      -1.665601   -2.000873   -0.818256
1      -3.164862   -1.127255   -1.025751
1      -4.527684   -0.569416    1.137059
1      -2.138805   -2.424647    1.539472
1      -3.405444    0.948852    2.657305
1      -2.211407   -0.234790    3.099149
1      -4.225257   -1.485859    2.609338
1      -3.592930   -2.855628    0.635136
6      -1.011872    3.391733   -1.280397
6      -0.164506    2.854838   -0.117957
6       0.158826    1.472018   -0.171829
6      -0.625053    0.458693   -0.896975
6      -1.181703    1.034444   -2.205922
6      -1.934463    2.330033   -1.891470
1       0.619275    3.516928    0.249058
1      -0.872930    2.516631    0.751502
1      -2.738525    2.101028   -1.187425
1      -0.328165    3.769397   -2.050322
1      -1.842949    0.301385   -2.676436
1      -0.373763    1.243115   -2.919845
1      -2.389754    2.733885   -2.799880
1      -1.597915    4.246082   -0.933956
(Hartree/Particle)
 Thermal correction to Energy=
0.521987
 Thermal correction to Enthalpy=
0.522932
 Thermal correction to Gibbs Free Energy=
0.453352
 Sum of electronic and zero-point Energies=
-933.043881
 Sum of electronic and thermal Energies=
-933.023103
 Sum of electronic and thermal Enthalpies=
-933.022159
 Sum of electronic and thermal Free Energies=
-933.091739
```

Intermediate

```
6       0.424696   -3.257707   -1.344232
6       0.355522   -2.828204    0.145199
6       0.745942   -1.394539    0.233148
6       0.614944   -0.383536   -0.889264
6       0.937054   -0.944592   -2.269125
6       1.407161   -2.405644   -2.162801
1      -0.652189   -2.999748    0.538428
1       1.038164   -3.431240    0.752420
1       2.397486   -2.441253   -1.693215
1      -0.568474   -3.165131   -1.799281
1       1.688142   -0.334340   -2.781786
1       0.034121   -0.913009   -2.890975
1       1.516692   -2.831290   -3.164634
1       0.694851   -4.314558   -1.411869
6       3.732006    1.113997    1.054200
6       2.996066    0.915436   -0.281659
6       1.556546    0.533664   -0.001856
6       1.481579   -0.595526    1.010039
6       2.273854   -0.609793    2.264550
6       3.708191   -0.149286    1.927803
1       3.055230    1.817271   -0.898452
1       3.478794    0.101290   -0.838335
1       4.219216   -0.957625    1.390856
1       3.262568    1.941437    1.601632
1       2.276956   -1.595885    2.737765
1       1.830165    0.095367    2.979780
1       4.269400    0.024811    2.850487
1       4.769480    1.408266    0.869325
6      -3.423067   -1.662182    0.491060
6      -2.582378   -0.874891   -0.511993
6      -1.700004    0.158180    0.151917
6      -1.922799    0.564184    1.401072
6      -3.043624    0.064561    2.270962
6      -4.095694   -0.711706    1.478738
1      -1.961142   -1.553294   -1.106947
1      -3.247149   -0.376378   -1.229825
1      -4.723427   -0.006412    0.920779
1      -2.777669   -2.354398    1.045438
1      -3.508674    0.908423    2.792028
1      -2.623028   -0.575565    3.058764
1      -4.756151   -1.258513    2.157716
1      -4.166521   -2.269131   -0.033715
6      -0.680047    3.660998   -0.665123
6       0.459894    2.900765   -0.036715
6       0.466388    1.575457   -0.005582
6      -0.553694    0.679280   -0.682407
6      -1.064965    1.443625   -1.913073
6      -1.682489    2.761851   -1.425669
1       1.338183    3.465902    0.268081
1      -1.246984    1.294873    1.837417
1      -2.522437    2.517366   -0.769113
1      -0.239196    4.386348   -1.360379
1      -1.804518    0.867782   -2.477725
1      -0.226868    1.643616   -2.589800
1      -2.096117    3.319081   -2.270635
1      -1.215397    4.259608    0.080639
(Hartree/Particle)
 Thermal correction to Energy=
0.528987
 Thermal correction to Enthalpy=
0.529931
 Thermal correction to Gibbs Free Energy=
0.460263
 Sum of electronic and zero-point Energies=
-933.194201
 Sum of electronic and thermal Energies=
-933.173461
 Sum of electronic and thermal Enthalpies=
-933.172517
 Sum of electronic and thermal Free Energies=
-933.242185
```

Product

```
6       2.159238    2.416004    1.956038
6       1.574229    2.569378    0.530177
6       1.159568    1.218109    0.066037
6       0.765087    0.056731    0.967452
6       1.687258   -0.062689    2.182400
6       2.774258    1.025829    2.174653
1       0.731716    3.270796    0.540598
1       2.322747    2.982426   -0.154257
1       3.505886    0.822440    1.383721
1       1.360159    2.556636    2.693767
1       2.139284   -1.059072    2.246209
1       1.096621    0.067511    3.096359
1       3.318592    1.004535    3.123475
1       2.898896    3.198481    2.143539
6       2.095699   -2.008332   -2.103571
6       1.811286   -1.937414   -0.594154
6       0.839866   -0.805234   -0.334259
6       1.254546    0.464749   -1.034999
6       1.743053    0.508478   -2.436443
6       2.684990   -0.696474   -2.645744
1       1.445738   -2.898700   -0.219967
1       2.750134   -1.727802   -0.064961
1       3.631652   -0.497530   -2.128971
1       1.161205   -2.232024   -2.635190
1       2.246444    1.450737   -2.671711
1       0.892610    0.413125   -3.124803
1       2.919462   -0.804228   -3.708752
1       2.783764   -2.831430   -2.318597
6      -2.474014    2.683652   -0.782637
6      -2.279178    2.024426    0.595035
6      -1.688830    0.673366    0.369712
6      -1.605327    0.035159   -0.798395
6      -2.150591    0.514179   -2.099331
6      -3.074417    1.713282   -1.814522
1      -1.619716    2.633533    1.224302
1      -3.235607    1.952873    1.128417
1      -4.032013    1.339695   -1.432792
1      -1.495766    3.021093   -1.146139
1      -2.696120   -0.275558   -2.628358
1      -1.326647    0.816387   -2.758712
1      -3.291422    2.248330   -2.743424
```

1	-3.108184	3.570639	-0.695318
6	-1.399648	-3.161492	1.015908
6	-1.248350	-2.511500	-0.364080
6	-0.721790	-1.080984	-0.272996
6	-0.784253	-0.293043	1.095169
6	-1.252037	-1.028535	2.342830
6	-2.132202	-2.231002	1.986799
1	-0.612591	-3.126651	-1.009777
1	-2.235278	-2.491232	-0.838874
1	-3.069267	-1.892502	1.527984
1	-0.410968	-3.398537	1.431679
1	-1.777653	-0.342781	3.016493
1	-0.390384	-1.410187	2.900990
1	-2.399938	-2.769860	2.900539
1	-1.934005	-4.111004	0.916044

(Hartree/Particle)
Thermal correction to Energy=
0.529342
Thermal correction to Enthalpy=
0.530287
Thermal correction to Gibbs Free Energy=
0.461837
Sum of electronic and zero-point Energies=
-933.182622
Sum of electronic and thermal Energies=
-933.162407
Sum of electronic and thermal Enthalpies=
-933.161463
Sum of electronic and thermal Free Energies=
-933.229912

Bb

TS1

6	-2.634083	3.106542	0.337365
6	-3.132472	1.823135	1.047857
6	-2.293053	0.684691	0.583878
6	-0.857641	0.805409	0.041725
6	-0.682203	2.025682	-0.858106
6	-1.998032	2.802305	-1.026626
1	-3.079933	1.952332	2.134449
1	-4.181948	1.629093	0.802269
1	-2.701204	2.224474	-1.638108
1	-1.879895	3.598365	0.963385
1	-0.269658	1.735041	-1.830099
1	0.048202	2.698536	-0.396665
1	-1.804679	3.735955	-1.562989
1	-3.458767	3.815347	0.228269
6	-1.990575	-2.430161	-1.934846
6	-1.062758	-1.206242	-1.856834
6	-1.056892	-0.685755	-0.435512
6	-2.458421	-0.568119	0.157421
6	-3.496510	-1.612403	-0.026849
6	-3.424547	-2.107087	-1.487698
1	-0.051408	-1.451692	-2.191401
1	-1.448231	-0.422975	-2.522899
1	-3.830638	-1.327441	-2.143637
1	-1.584890	-3.229766	-1.301519
1	-4.498358	-1.247038	0.217101
1	-3.284679	-2.456159	0.643860
1	-4.060570	-2.988513	-1.610181
1	-2.007946	-2.820114	-2.956840
6	4.587409	0.328516	-1.583134
6	4.176613	-1.022430	-0.945206
6	2.781065	-0.875436	-0.429455
6	2.191844	0.211509	-0.292382
6	2.596372	1.607748	-0.568112
6	4.137411	1.539221	-0.753746
1	4.275860	-1.833037	-1.672803
1	4.843653	-1.273954	-0.112406
1	4.603278	1.486688	0.237011
1	4.136489	0.395542	-2.580226
1	2.343590	2.302911	0.238876
1	2.115040	1.982943	-1.476316
1	4.484653	2.464203	-1.224783
1	5.673268	0.359945	-1.721151
6	1.402500	-1.882456	2.434054
6	0.773115	-2.158130	1.042939
6	-0.004112	-1.049263	0.586453
6	0.253004	0.245070	0.940502
6	0.819702	0.619418	2.281858
6	0.816786	-0.653397	3.150501
1	1.677058	-2.051814	0.286143
1	0.339071	-3.149468	0.910952
1	-0.221014	-0.868140	3.429016
1	2.480126	-1.735176	2.308405
1	0.196937	1.393143	2.745568
1	1.832089	1.028665	2.206831
1	1.371114	-0.479612	4.077857
1	1.276255	-2.758499	3.075751

(Hartree/Particle)
Thermal correction to Energy=
0.523348
Thermal correction to Enthalpy=
0.524292
Thermal correction to Gibbs Free Energy=
0.452935
Sum of electronic and zero-point Energies=
-933.053449
Sum of electronic and thermal Energies=
-933.032176
Sum of electronic and thermal Enthalpies=
-933.031232
Sum of electronic and thermal Free Energies=
-933.102589

TS2

6	-2.155186	3.289524	0.147394
6	-2.648746	2.054767	0.946613
6	-1.912252	0.860502	0.455713
6	-0.505155	0.869301	-0.162948
6	-0.274368	2.091156	-1.041450
6	-1.566259	2.904745	-1.217625
1	-2.484303	2.207991	2.018607
1	-3.723790	1.903844	0.808845
1	-2.304287	2.333339	-1.793464
1	-1.375883	3.805007	0.719893
1	0.157582	1.803942	-2.004229
1	0.458329	2.738012	-0.550112
1	-1.349645	3.809238	-1.792477
1	-2.975356	4.000818	0.025921
6	-1.966175	-2.366123	-1.967069
6	-0.957689	-1.206802	-2.006150
6	-0.855219	-0.593396	-0.632820
6	-2.202865	-0.382670	0.065724
6	-3.297603	-1.380125	-0.010774
6	-3.346981	-1.933910	-1.450625
1	0.029446	-1.535589	-2.337164
1	-1.311787	-0.435467	-2.700478
1	-3.746638	-1.157377	-2.113602
1	-1.571030	-3.165978	-1.328183
1	-4.258129	-0.947794	0.282685
1	-3.088431	-2.205077	0.683520
1	-4.041127	-2.777426	-1.494355
1	-2.069530	-2.793590	-2.967963
6	4.352043	0.046257	-1.508901
6	3.656621	-1.262176	-1.103355
6	2.332055	-1.127398	-0.381766
6	1.963401	0.108074	0.021404
6	2.755364	1.396304	-0.149276
6	4.231077	1.075894	-0.387602
1	3.524436	-1.901167	-1.985170
1	4.324297	-1.837380	-0.444988
1	4.668696	0.664926	0.530618
1	3.873831	0.453640	-2.409576
1	2.641039	2.040528	0.733889
1	2.391984	1.982814	-1.001898
1	4.782325	1.990948	-0.628411
1	5.402965	-0.132161	-1.763012
6	0.559744	-1.892083	2.723839
6	0.166752	-2.229900	1.275800
6	0.015705	-1.078528	0.462666
6	0.610644	0.240383	0.763466
6	0.696516	0.609619	2.252702
6	0.079565	-0.490860	3.131317
1	1.148025	-2.372509	0.633861
1	-0.531071	-3.047650	1.106701
1	-1.013728	-0.455367	3.047032
1	1.649511	-1.941841	2.824508

```
1       0.192304    1.564185    2.438870
1       1.747429    0.740622    2.526314
1       0.326508   -0.305126    4.180452
1       0.140096   -2.643679    3.395712
(Hartree/Particle)
 Thermal correction to Energy=
0.523348
 Thermal correction to Enthalpy=
0.524292
 Thermal correction to Gibbs Free Energy=
0.452935
 Sum of electronic and zero-point Energies=
-933.053449
 Sum of electronic and thermal Energies=
-933.032176
 Sum of electronic and thermal Enthalpies=
-933.031232
 Sum of electronic and thermal Free Energies=
-933.102589
```

Intermediate

```
6      -1.868062    3.333459    0.648915
6      -2.344031    2.082807    1.442121
6      -1.827404    0.876559    0.741113
6      -0.506970    0.784247   -0.022264
6      -0.236563    2.067129   -0.804560
6      -1.459019    2.998194   -0.793916
1      -1.992197    2.139856    2.477649
1      -3.436953    2.040545    1.480783
1      -2.299132    2.532574   -1.321700
1      -0.999118    3.773521    1.151479
1       0.094871    1.846505   -1.824807
1       0.577534    2.612638   -0.319508
1      -1.219597    3.922119   -1.328966
1      -2.649793    4.097207    0.655353
6      -2.582394   -1.871948   -2.103400
6      -1.405147   -0.882629   -2.059316
6      -1.104868   -0.550437   -0.614585
6      -2.342548   -0.230357    0.198394
6      -3.596731   -1.014463    0.090155
6      -3.836057   -1.323581   -1.403139
1      -0.527400   -1.290496   -2.567627
1      -1.690981    0.037962   -2.584925
1      -4.147156   -0.401429   -1.909113
1      -2.279551   -2.810760   -1.622053
1      -4.452460   -0.495736    0.531774
1      -3.472581   -1.960809    0.634132
1      -4.660137   -2.035418   -1.505854
1      -2.824877   -2.117261   -3.141629
6       4.522362    0.379882   -1.470113
6       3.799869   -0.966777   -1.534478
6       2.460893   -0.964840   -0.848121
6       1.976276    0.034962   -0.108328
6       2.793598    1.302002    0.069915
6       4.288022    1.048950   -0.118205
1       3.677461   -1.282429   -2.576634
1       4.418489   -1.743781   -1.064875
1       4.656741    0.399955    0.685339
1       4.137855    1.040109   -2.256568
1       2.597786    1.748856    1.049189
1       2.479538    2.046987   -0.668500
1       4.840016    1.991225   -0.053125
1       5.590254    0.245196   -1.663953
6       0.833115   -2.550724    2.080809
6      -0.057794   -2.484564    0.862845
6      -0.125151   -1.311858    0.251136
6       0.650471   -0.075088    0.650773
6       0.902471    0.015042    2.181493
6       0.562316   -1.289917    2.926535
1       1.881828   -1.878697   -0.937087
1      -0.704634   -3.317871    0.603995
1      -0.499992   -1.294329    3.191128
1       1.893196   -2.592105    1.800756
1       0.324121    0.840814    2.607951
1       1.956101    0.244748    2.363010
1       1.127640   -1.328380    3.862860
1       0.623195   -3.447615    2.668862
(Hartree/Particle)
 Thermal correction to Energy=
0.528944
 Thermal correction to Enthalpy=
0.529888
 Thermal correction to Gibbs Free Energy=
0.458920
 Sum of electronic and zero-point Energies=
-933.180672
 Sum of electronic and thermal Energies=
-933.159701
 Sum of electronic and thermal Enthalpies=
-933.158757
 Sum of electronic and thermal Free Energies=
-933.229724
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Product

```
6       2.624445   -2.810157   -0.801522
6       3.000449   -1.733223    0.242809
6       2.005759   -0.628671    0.141094
6       0.614250   -0.763671   -0.461803
6       0.589841   -1.617554   -1.729745
6       1.980276   -2.192063   -2.050928
1       3.016128   -2.171391    1.247436
1       4.006715   -1.345261    0.050661
1       2.631739   -1.399116   -2.437967
1       1.908456   -3.512350   -0.356760
1       0.200205   -1.046928   -2.579722
1      -0.101316   -2.455082   -1.575532
1       1.895667   -2.944580   -2.840376
1       3.508493   -3.393811   -1.070486
6       1.208399    3.094184   -1.083771
6       0.498260    1.795497   -1.500294
6       0.560999    0.807807   -0.354609
6       1.960727    0.704035    0.217725
6       2.842440    1.874319    0.468615
6       2.680053    2.854064   -0.713279
1      -0.530437    1.991240   -1.815639
1       1.021391    1.368767   -2.366963
1       3.197476    2.440469   -1.587397
1       0.683514    3.531885   -0.224358
1       3.888077    1.578047    0.593942
1       2.538176    2.383911    1.392222
1       3.166843    3.804439   -0.475864
1       1.153487    3.829296   -1.892322
6      -3.876319    0.717844   -1.422627
6      -3.023257    1.509865   -0.414636
6      -1.945597    0.603367    0.080346
6      -1.900454   -0.719333   -0.070918
6      -2.924557   -1.562844   -0.751965
6      -4.191966   -0.707019   -0.935010
1      -2.610386    2.411082   -0.880866
1      -3.642610    1.856166    0.422987
1      -4.714823   -0.642666    0.026563
1      -3.326730    0.652108   -2.369549
1      -3.150746   -2.466481   -0.174843
1      -2.547421   -1.904088   -1.725025
1      -4.876433   -1.193544   -1.635719
1      -4.808065    1.250955   -1.632466
6      -0.771559    0.318228    3.194667
6      -0.424184    1.331644    2.095238
6      -0.575690    0.705108    0.717767
6      -0.533719   -0.878195    0.571265
6      -0.389796   -1.771068    1.800180
6       0.045869   -0.968481    3.035605
1      -1.048446    2.227767    2.184401
1       0.611282    1.650518    2.248673
1       1.106098   -0.702418    2.945968
1      -1.841313    0.076604    3.157091
1       0.322876   -2.580718    1.603927
1      -1.351363   -2.248901    2.019016
1      -0.052552   -1.593262    3.928596
1      -0.582016    0.765238    4.175131
(Hartree/Particle)
 Thermal correction to Energy=
0.529442
 Thermal correction to Enthalpy=
0.530386
 Thermal correction to Gibbs Free Energy=
0.462243
 Sum of electronic and zero-point Energies=
-933.193913
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 Sum of electronic and thermal Energies=
-933.173672
 Sum of electronic and thermal Enthalpies=
-933.172728
 Sum of electronic and thermal Free Energies=
-933.240871
```

Af

TS1

```
  6       2.122053   -2.988117   -1.091130
  6       1.052240   -2.667217   -0.022254
  6       0.833535   -1.181767    0.055058
  6       1.296857   -0.145250   -1.045036
  6       2.467418   -0.622996   -1.888213
  6       3.141286   -1.859245   -1.280168
 1       0.137831   -3.219566   -0.251427
 1       1.382423   -3.012257    0.963045
 1       3.596529   -1.603239   -0.315633
 1       1.627833   -3.160751   -2.054959
 1       3.184257    0.193050   -2.029131
 1       2.097053   -0.890515   -2.886296
 1       3.951157   -2.196685   -1.933603
 1       2.626857   -3.922108   -0.830020
 6       2.079333    2.106498    2.137259
 6       2.563446    1.670492    0.737712
 6       1.415286    0.870131    0.158484
 6       1.113569   -0.298231    1.057838
 6       0.969711   -0.217761    2.468854
 6       1.784899    0.930054    3.089700
 1       2.811980    2.541599    0.124707
 1       3.465066    1.051981    0.825460
 1       2.742119    0.512193    3.423101
 1       1.171337    2.707573    2.013177
 1       1.095100   -1.165096    3.000237
 1      -0.218679   -0.079649    2.475744
 1       1.288070    1.308260    3.987365
 1       2.820944    2.758751    2.607943
 6      -4.032527   -0.751189    0.880247
 6      -3.127665   -0.525380    2.115557
 6      -1.704596   -0.576892    1.657395
 6      -1.339150   -1.043897    0.558512
 6      -2.099446   -1.607622   -0.580732
 6      -3.522165   -1.880033   -0.023996
 1      -3.378698    0.421645    2.602463
 1      -3.296517   -1.309219    2.863020
 1      -3.500113   -2.813845    0.549187
 1      -4.070739    0.178857    0.299996
 1      -1.673943   -2.529429   -0.987335
 1      -2.143781   -0.891527   -1.403517
 1      -4.211803   -2.031413   -0.860385
 1      -5.056407   -0.968866    1.201690
 6      -1.433271    3.048220   -1.533521
 6      -0.677085    2.720819   -0.232795
 6       0.262613    1.602121   -0.517218
 6       0.225636    0.790639   -1.574373
 6      -0.732735    0.886505   -2.715017
 6      -1.903442    1.787387   -2.278097
 1      -0.158477    3.610534    0.140571
 1      -1.374184    2.406262    0.555930
 1      -2.559837    1.216841   -1.609991
 1      -0.769873    3.621601   -2.191720
 1      -1.092682   -0.098346   -3.031060
 1      -0.230416    1.318124   -3.590342
 1      -2.503712    2.073862   -3.146526
 1      -2.293496    3.687770   -1.316093
(Hartree/Particle)
 Thermal correction to Energy=
0.522953
 Thermal correction to Enthalpy=
0.523898
 Thermal correction to Gibbs Free Energy=
0.452713
 Sum of electronic and zero-point Energies=
-933.052937
 Sum of electronic and thermal Energies=
-933.031730
 Sum of electronic and thermal Enthalpies=
-933.030786
 Sum of electronic and thermal Free Energies=
-933.101971
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TS2

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 6       1.897263   -2.019049   -2.509567
 6       0.653496   -2.205196   -1.613297
 6       0.334718   -1.035831   -0.688450
 6       0.883651    0.446322   -1.049925
 6       1.992094    0.452666   -2.082149
 6       2.788257   -0.852696   -2.085906
 1      -0.227090   -2.386121   -2.235385
 1       0.749716   -3.087390   -0.974352
 1       3.206970   -1.040559   -1.089871
 1       1.576975   -1.833930   -3.540917
 1       2.642595    1.313395   -1.890241
 1       1.557001    0.603198   -3.079051
 1       3.638116   -0.768385   -2.769264
 1       2.477653   -2.945363   -2.532318
 6       2.338311    0.426013    2.643188
 6       2.550346    0.857192    1.183982
 6       1.225734    0.603856    0.478777
 6       0.845919   -0.839474    0.636379
 6       1.362908   -1.763850    1.629564
 6       2.114629   -1.094515    2.800065
 1       2.824973    1.913514    1.121245
 1       3.362455    0.277951    0.730560
 1       3.089282   -1.580862    2.900453
 1       1.467869    0.967717    3.030517
 1       1.999318   -2.493551    1.113017
 1       0.452674   -2.375335    1.873632
 1       1.587313   -1.278620    3.739099
 1       3.188714    0.728167    3.260108
 6      -3.846259   -1.688905    0.719506
 6      -2.747446   -2.721170    1.016429
 6      -1.337130   -2.285333    0.758273
 6      -1.113344   -1.204310   -0.015813
 6      -2.194342   -0.242924   -0.498640
 6      -3.538635   -0.971233   -0.586267
 1      -2.844647   -3.101836    2.039359
 1      -2.894289   -3.605501    0.376719
 1      -3.501976   -1.703963   -1.402193
 1      -3.884390   -0.952944    1.532534
 1      -1.942857    0.153462   -1.483901
 1      -2.298489    0.612959    0.173873
 1      -4.324420   -0.250989   -0.837362
 1      -4.828773   -2.170861    0.682244
 6      -0.996132    3.853188    0.573330
 6      -0.421893    2.689008    1.403516
 6       0.208203    1.730654    0.455310
 6      -0.007129    1.658291   -0.858990
 6      -0.872897    2.578278   -1.653521
 6      -1.756059    3.379660   -0.677885
 1       0.295624    3.062478    2.141725
 1      -1.217296    2.184646    1.968901
 1      -2.595701    2.749708   -0.365111
 1      -0.167456    4.499642    0.261913
 1      -1.492283    2.041775   -2.378558
 1      -0.237106    3.256122   -2.237582
 1      -2.187686    4.243820   -1.190479
 1      -1.658368    4.463805    1.193233
(Hartree/Particle)
 Thermal correction to Energy=
0.524529
 Thermal correction to Enthalpy=
0.525473
 Thermal correction to Gibbs Free Energy=
0.455491
 Sum of electronic and zero-point Energies=
-933.043497
 Sum of electronic and thermal Energies=
-933.022614
 Sum of electronic and thermal Enthalpies=
-933.021669
 Sum of electronic and thermal Free Energies=
-933.091652
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Intermediate

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6       0.380391   -3.400666   -0.917136
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6        0.382001   -2.663944    0.422269
6        0.088661   -1.136904    0.338288
6        0.585854   -0.463129   -1.044892
6        0.858537   -1.338361   -2.249247
6        1.348590   -2.739340   -1.894032
1       -0.323873   -3.125358    1.120096
1        1.373178   -2.795922    0.863781
1        2.344800   -2.684965   -1.437162
1       -0.622012   -3.411135   -1.361358
1        1.571300   -0.823001   -2.902656
1       -0.074104   -1.433266   -2.822363
1        1.448986   -3.338113   -2.804124
1        0.659616   -4.445045   -0.746608
6        3.685554    0.973752    1.027275
6        3.202033    0.336943   -0.288795
6        1.691223    0.329494   -0.220412
6        1.196550   -0.348987    1.029012
6        1.881236   -0.444388    2.158993
6        3.247958    0.186291    2.277877
1        3.571234    0.903220   -1.148857
1        3.582274   -0.688116   -0.373023
1        3.967276   -0.621536    2.470061
1        3.277973    1.989367    1.081768
1        1.536182   -1.067881    2.980756
1       -0.829984    0.638330    2.105462
1        3.301031    0.839231    3.156292
1        4.774332    1.076115    1.028230
6       -4.031917    0.181694    0.811208
6       -3.039096    0.609054    1.889909
6       -1.642444    0.142380    1.582046
6       -1.342057   -0.807218    0.695003
6       -2.418721   -1.557625   -0.055740
6       -3.829625   -1.292847    0.474776
1       -3.038823    1.699774    1.994963
1       -3.355126    0.216440    2.865952
1       -3.986496   -1.884395    1.384670
1       -3.871424    0.788085   -0.088252
1       -2.217667   -2.632088   -0.008343
1       -2.354224   -1.299411   -1.121716
1       -4.570547   -1.632971   -0.254343
1       -5.058392    0.365585    1.140862
6       -0.294813    3.674894   -0.978911
6        0.832454    2.997041   -0.177542
6        0.887439    1.562702   -0.575619
6       -0.036775    0.898651   -1.268379
6       -1.307494    1.476185   -1.799539
6       -1.560315    2.806150   -1.068955
1        1.785555    3.508802   -0.350864
1        0.636075    3.064293    0.901303
1       -1.908389    2.578176   -0.054522
1        0.066818    3.877416   -1.993962
1       -2.149802    0.795964   -1.651328
1       -1.228569    1.642276   -2.881700
1       -2.358237    3.366480   -1.565094
1       -0.540298    4.642713   -0.532661
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Product

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6        2.582040   -1.134435   -2.400711
6        1.863426   -1.792196   -1.221846
6        0.738862   -0.951072   -0.610319
6        0.704559    0.612065   -0.934761
6        1.713927    1.157915   -1.928407
6        2.971357    0.303465   -2.068896
1        1.466201   -2.765239   -1.526503
1        2.610223   -2.004316   -0.447152
1        3.551180    0.319234   -1.137129
1        1.930385   -1.128892   -3.283736
1        1.961938    2.191046   -1.658179
1        1.229594    1.209830   -2.912713
1        3.615664    0.720027   -2.848792
1        3.463798   -1.726356   -2.664064
6        2.581725    1.135064    2.400599
6        1.862857    1.792489    1.221705
6        0.738552    0.950916    0.610317
6        0.704897   -0.612227    0.934779
6        1.714555   -1.157665    1.928363
6        2.971634   -0.302683    2.068808
1        1.465315    2.765426    1.526283
1        2.609563    2.004780    0.446973
1        3.551437   -0.318233    1.137024
1        1.930056    1.129272    3.283613
1        1.962999   -2.190682    1.658099
1        1.230291   -1.209809    2.912688
1        3.616132   -0.718971    2.848692
1        3.463236    1.727354    2.663950
6       -3.031718   -1.856258    1.007403
6       -1.794302   -1.506674    1.853783
6       -0.654821   -1.272116    0.921665
6       -0.615195   -1.583992   -0.373375
6       -1.701545   -2.248826   -1.147032
6       -2.709087   -2.831569   -0.137911
1       -1.988174   -0.626646    2.476737
1       -1.558449   -2.325203    2.546275
1       -2.287716   -3.749378    0.288788
1       -3.432473   -0.930477    0.578449
1       -1.311061   -3.037973   -1.799262
1       -2.196306   -1.521985   -1.804693
1       -3.632565   -3.115780   -0.650442
1       -3.817676   -2.278068    1.640416
6       -2.709285    2.831485    0.137956
6       -1.702040    2.248348    1.147136
6       -0.615727    1.583431    0.373489
6       -0.655377    1.271535   -0.921545
6       -1.794801    1.506247   -1.853693
6       -3.032148    1.856297   -1.007402
1       -1.311480    3.037265    1.799592
1       -2.197095    1.521482    1.804552
1       -3.433315    0.930675   -0.578490
1       -2.287546    3.749154   -0.288679
1       -1.988944    0.626205   -2.476539
1       -1.558676    2.324609   -2.546294
1       -3.817885    2.278396   -1.640499
1       -3.632718    3.116000    0.650400
```

```
(Hartree/Particle)
 Thermal correction to Energy=
0.529318
 Thermal correction to Enthalpy=
0.530262
 Thermal correction to Gibbs Free Energy=
0.462117
 Sum of electronic and zero-point Energies=
-933.191051
 Sum of electronic and thermal Energies=
-933.170747
 Sum of electronic and thermal Enthalpies=
-933.169803
 Sum of electronic and thermal Free Energies=
-933.237948
```

Ab

TS1

```
6       -0.551972   -3.062332   -0.557710
6       -0.907342   -1.743751   -1.296745
6       -0.558065   -0.592021   -0.395266
6        0.462545   -0.838727    0.709932
6        0.113166   -1.933755    1.698322
6       -0.732879   -3.015357    0.972595
1       -0.353574   -1.682813   -2.239086
1       -1.969725   -1.728868   -1.554490
1       -1.787419   -2.846278    1.197920
1        0.485391   -3.327081   -0.778648
1       -0.463276   -1.515127    2.521566
1        1.031143   -2.375382    2.099284
1       -0.489899   -4.002809    1.374770
1       -1.162407   -3.872667   -0.965526
6        0.803480    3.154234    1.027494
6        0.521108    1.842275    1.800164
6        0.712959    0.731984    0.796487
6       -0.243353    0.917667   -0.401904
6        0.151581    2.088695   -1.263031
6        0.039856    3.302129   -0.306943
1        1.202762    1.757068    2.651915
1       -0.502642    1.820086    2.179848
1       -1.023195    3.457334   -0.086915
1        1.877420    3.221058    0.822429
1       -0.481564    2.246250   -2.137238
```

1	1.176158	1.969912	-1.623654
1	0.388241	4.205734	-0.816413
1	0.561722	4.012500	1.661606
6	-3.989151	0.386154	-1.252816
6	-2.625048	1.079718	-1.279960
6	-1.695868	0.679762	-0.134516
6	-2.034341	-0.084923	0.974803
6	-3.429383	-0.669944	0.932384
6	-4.464985	0.168403	0.177107
1	-2.134766	0.895149	-2.240496
1	-2.758925	2.166661	-1.215281
1	-4.590332	1.135330	0.679835
1	-3.916655	-0.589692	-1.747515
1	-3.762180	-0.867050	1.956400
1	-3.367738	-1.660233	0.456082
1	-5.442739	-0.322849	0.187622
1	-4.710202	0.971252	-1.830623
6	4.473047	0.048131	-0.253387
6	3.390166	1.117564	-0.029344
6	2.109096	0.413727	0.283920
6	1.873694	-0.884669	0.117215
6	2.803145	-1.873210	-0.505541
6	3.974951	-1.101940	-1.140331
1	3.681762	1.784222	0.789351
1	3.289058	1.752719	-0.918929
1	3.641506	-0.686103	-2.098797
1	4.774141	-0.357616	0.719391
1	2.300920	-2.472978	-1.271492
1	3.167026	-2.582624	0.249066
1	4.798639	-1.786435	-1.361637
1	5.362905	0.502453	-0.697934

(Hartree/Particle)
Thermal correction to Energy=
0.526780
Thermal correction to Enthalpy=
0.527724
Thermal correction to Gibbs Free Energy=
0.461797
Sum of electronic and zero-point Energies=
-933.065577
Sum of electronic and thermal Energies=
-933.045785
Sum of electronic and thermal Enthalpies=
-933.044840
Sum of electronic and thermal Free Energies=
-933.110768

TS2

6	-0.049581	-3.166126	-0.601563
6	-0.331089	-1.939893	-1.498136
6	-0.058352	-0.708460	-0.699400
6	0.724005	-0.802416	0.606404
6	0.228432	-1.850244	1.595975
6	-0.542820	-2.957394	0.839215
1	0.301988	-1.959120	-2.392756
1	-1.365237	-1.966282	-1.849011
1	-1.602055	-2.685187	0.806538
1	1.026957	-3.371182	-0.589220
1	-0.427556	-1.390084	2.333389
1	1.087049	-2.283557	2.118582
1	-0.469834	-3.899339	1.389243
1	-0.526543	-4.047522	-1.037940
6	0.163918	3.169719	0.648766
6	0.249018	1.888092	1.504563
6	0.731378	0.788965	0.583990
6	-0.068871	0.665599	-0.709308
6	-0.266486	1.885162	-1.538011
6	-0.722351	3.024441	-0.602453
1	0.939055	2.036644	2.340558
1	-0.730788	1.627783	1.905903
1	-1.751957	2.825456	-0.287145
1	1.174183	3.463086	0.333435
1	-0.946828	1.750344	-2.379969
1	0.716023	2.139412	-1.959573
1	-0.727934	3.968108	-1.155631
1	-0.219172	3.992135	1.259828
6	-4.250394	-0.321624	-1.005536
6	-2.848233	0.198239	-1.388229
6	-2.036939	0.073821	-0.146643
6	-2.302237	-0.038897	1.092207
6	-3.759791	-0.101671	1.479595
6	-4.714330	0.271909	0.327562
1	-2.459106	-0.352174	-2.249747
1	-2.926749	1.247218	-1.697763
1	-4.750856	1.364314	0.230190
1	-4.213772	-1.414585	-0.924198
1	-3.958758	0.523641	2.355968
1	-3.956722	-1.129776	1.811901
1	-5.733854	-0.059038	0.552594
1	-4.957983	-0.077625	-1.803767
6	4.658865	0.651524	0.041433
6	3.393880	1.529057	-0.003288
6	2.227250	0.654218	0.304733
6	2.222271	-0.674449	0.315745
6	3.370088	-1.564281	-0.021383
6	4.464483	-0.696529	-0.672972
1	3.475638	2.355677	0.710882
1	3.277734	1.988266	-0.994371
1	4.181765	-0.503459	-1.714799
1	4.917601	0.463306	1.089797
1	3.067187	-2.366710	-0.703243
1	3.752499	-2.056887	0.881549
1	5.412319	-1.241474	-0.697691
1	5.503012	1.186032	-0.403128

```
(Hartree/Particle)
 Thermal correction to Energy=
0.525474
 Thermal correction to Enthalpy=
0.526418
 Thermal correction to Gibbs Free Energy=
0.457269
 Sum of electronic and zero-point Energies=
-933.044925
 Sum of electronic and thermal Energies=
-933.024053
 Sum of electronic and thermal Enthalpies=
-933.023109
 Sum of electronic and thermal Free Energies=
-933.092258
```

Intermediate

```
6      -0.408136   -3.120402   -0.437413
6      -0.497109   -1.882583   -1.373099
6      -0.356925   -0.647609   -0.523267
6       0.518366   -0.784071    0.724598
6       0.018713   -1.804527    1.736323
6      -0.872768   -2.834267    1.001350
1       0.305078   -1.916456   -2.117514
1      -1.438268   -1.891891   -1.926063
1      -1.903577   -2.466376    0.970925
1       0.625324   -3.479970   -0.402172
1      -0.555384   -1.309123    2.519094
1       0.869770   -2.315783    2.198532
1      -0.898136   -3.770677    1.565197
1      -0.999850   -3.936113   -0.860956
6       0.554581    3.248764    0.759194
6       0.435137    1.971155    1.620719
6       0.697950    0.806199    0.695070
6      -0.196409    0.818271   -0.548232
6      -0.046139    2.022030   -1.431755
6      -0.310001    3.235908   -0.517112
1       1.154929    2.006207    2.444567
1      -0.566422    1.877175    2.045018
1      -1.368981    3.222557   -0.230483
1       1.602393    3.390220    0.466765
1      -0.717524    2.030334   -2.292281
1       0.978078    2.055159   -1.819338
1      -0.144786    4.163224   -1.073850
1       0.284418    4.121755    1.360929
6      -3.878070   -0.350676   -1.199144
6      -2.574982    0.406177   -1.438252
6      -1.638969    0.289889   -0.231139
6      -2.123316    0.236639    1.103604
6      -3.594452    0.060088    1.260012
6      -4.542711    0.196126    0.059831
1      -2.086817    0.066573   -2.356752
1      -2.815115    1.464993   -1.600200
1      -4.786411    1.253283   -0.099685
1      -3.668025   -1.420993   -1.071344
1      -3.931753    0.653645    2.117656
1      -3.636489   -0.972747    1.652572
1      -5.488235   -0.315885    0.263633
1      -4.540277   -0.255308   -2.064340
6       4.527341    0.228477   -0.153264
6       3.371595    1.243247   -0.095130
6       2.135132    0.503175    0.293341
6       1.981832   -0.817120    0.295812
6       2.993120   -1.821479   -0.147899
6       4.127305   -1.070592   -0.870284
1       3.600793    2.040171    0.620739
1       3.241229    1.733593   -1.069071
1       3.790627   -0.821803   -1.883978
1       4.835531   -0.011879    0.870887
1       2.552286   -2.566686   -0.818565
1       3.384180   -2.378038    0.713561
1       5.000882   -1.719921   -0.976921
1       5.394020    0.673845   -0.649741
(Hartree/Particle)
 Thermal correction to Energy=
0.527045
 Thermal correction to Enthalpy=
0.527989
 Thermal correction to Gibbs Free Energy=
0.460472
 Sum of electronic and zero-point Energies=
-933.076295
 Sum of electronic and thermal Energies=
-933.055925
 Sum of electronic and thermal Enthalpies=
-933.054981
 Sum of electronic and thermal Free Energies=
-933.122497
```

Product

```
 6       0.234838    3.220704    0.739422
 6      -0.054662    1.935248    1.582058
 6      -0.444710    0.823136    0.632598
 6       0.444702    0.823168   -0.632472
 6       0.054748    1.935475   -1.581744
 6      -0.234702    3.220809   -0.738897
 1       0.843527    1.663339    2.144369
 1      -0.844907    2.120189    2.314905
 1      -1.307884    3.415966   -0.752378
 1       1.308029    3.415822    0.752952
 1      -0.843424    1.663739   -2.144167
 1       0.845050    2.120511   -2.314508
 1       0.222313    4.086376   -1.226123
 1      -0.222170    4.086223    1.226741
 6       0.264867   -3.206948   -0.728552
 6       0.024588   -1.915003   -1.556308
 6       0.434341   -0.779709   -0.648117
 6      -0.434447   -0.779709    0.648215
 6      -0.024564   -1.915018    1.556313
 6      -0.265049   -3.206917    0.728559
 1       0.618103   -1.956583   -2.475329
 1      -1.025289   -1.826811   -1.849218
 1      -1.340676   -3.397716    0.703839
 1       1.340465   -3.397882   -0.703800
 1      -0.617910   -1.956593    2.475443
 1       1.025380   -1.826837    1.849002
 1       0.176321   -4.061869    1.250227
 1      -0.176594   -4.061843   -1.250240
 6      -4.377555   -0.676340    0.207298
 6      -3.110277   -1.544196    0.144719
 6      -1.922388   -0.655847    0.337481
 6      -1.926152    0.671600    0.287605
 6      -3.108628    1.525359   -0.042828
 6      -4.227050    0.623308   -0.591644
 1      -3.154622   -2.315314    0.920699
 1      -3.052998   -2.077913   -0.813116
 1      -3.992486    0.371319   -1.632976
 1      -4.581553   -0.426725    1.255198
 1      -2.868543    2.290532   -0.785017
 1      -3.448463    2.063317    0.852087
 1      -5.175301    1.168256   -0.603406
 1      -5.238692   -1.243136   -0.157912
 6       4.377422   -0.676617   -0.207666
 6       3.110099   -1.544346   -0.144301
 6       1.922261   -0.655950   -0.337170
 6       1.926158    0.671525   -0.287649
 6       3.108737    1.525303    0.042316
 6       4.227335    0.623325    0.590906
 1       3.154157   -2.315859   -0.919897
 1       3.053050   -2.077558    0.813833
 1       3.993224    0.371678    1.632422
 1       4.581026   -0.427387   -1.255734
 1       2.868893    2.290542    0.784520
 1       3.448250    2.063197   -0.852762
 1       5.175618    1.168231    0.602088
 1       5.238649   -1.243364    0.157412
(Hartree/Particle)
 Thermal correction to Energy=
0.530425
 Thermal correction to Enthalpy=
0.531369
 Thermal correction to Gibbs Free Energy=
0.464071
 Sum of electronic and zero-point Energies=
-933.160514
 Sum of electronic and thermal Energies=
-933.140380
 Sum of electronic and thermal Enthalpies=
-933.139435
```

```
 Sum of electronic and thermal Free Energies=
-933.206734
```

Pathway III

First Step: Addition of cyclohexyne onto Starting Material(SM)

SM

```
 6      -2.612762    0.230585   -0.241624
 6      -1.699454    1.430574    0.077209
 6      -0.202828    1.208864   -0.095668
 6       0.144028   -0.066234   -0.155316
 6      -0.661895   -1.340927   -0.087206
 6      -2.073529   -1.035749    0.420955
 1      -2.023020    2.286336   -0.533732
 1      -1.885156    1.747385    1.117341
 1      -2.033074   -0.870526    1.506088
 1      -2.632557    0.075976   -1.329464
 1      -0.168788   -2.067602    0.572617
 1      -0.716092   -1.823450   -1.076424
 1      -2.740207   -1.891048    0.250803
 1      -3.649075    0.420450    0.074241
 8       1.544832   -0.473489   -0.344594
 8       3.657029    0.066229    0.082580
 6       2.471839    0.282171    0.205997
 1       2.040689    1.124859    0.768553
(Hartree/Particle)
 Thermal correction to Energy=
0.154684
 Thermal correction to Enthalpy=
0.155628
 Thermal correction to Gibbs Free Energy=
0.112724
 Sum of electronic and zero-point Energies=
-422.391067
 Sum of electronic and thermal Energies=
-422.382655
 Sum of electronic and thermal Enthalpies=
-422.381711
 Sum of electronic and thermal Free Energies=
-422.424614
```

TS

```
6      -3.320331   -2.068161    0.385859
6      -1.836190   -1.943696   -0.006343
6      -1.239122   -0.548508    0.075332
6      -2.131815    0.427588    0.131577
6      -3.640754    0.410340    0.130030
6      -4.143384   -0.973527   -0.291302
1      -1.247756   -2.637088    0.610455
1      -1.706746   -2.312312   -1.036359
1      -4.031677   -1.076270   -1.378827
1      -3.413851   -1.954886    1.474869
1      -4.028936    1.178882   -0.551842
1      -4.034694    0.666029    1.126283
1      -5.212030   -1.080915   -0.066502
1      -3.717568   -3.061000    0.131843
8      -1.706602    1.821768    0.238501
8      -0.159697    3.267044   -0.443263
6      -0.699736    2.187754   -0.528419
1      -0.404535    1.399889   -1.239251
6       4.525670   -0.036597    0.285458
6       4.369046   -1.264629   -0.664225
6       2.936497   -1.257852   -1.090984
6       2.080472   -0.604640   -0.526898
6       1.952246    0.346876    0.572633
6       3.349345    0.161455    1.264449
1       5.083328   -1.192924   -1.491364
1       4.596862   -2.196920   -0.133977
1       3.286597   -0.712301    1.923417
1       4.614026    0.861648   -0.336849
1       1.109798    0.115688    1.224808
1       1.814883    1.368277    0.207134
1       3.550604    1.032207    1.897706
1       5.460428   -0.126907    0.853552
(Hartree/Particle)
 Thermal correction to Energy=
0.284554
 Thermal correction to Enthalpy=
0.285498
 Thermal correction to Gibbs Free Energy=
0.222779
 Sum of electronic and zero-point Energies=
-655.591351
 Sum of electronic and thermal Energies=
-655.576164
 Sum of electronic and thermal Enthalpies=
-655.575220
 Sum of electronic and thermal Free Energies=
-655.637939
```

Product

```
 6      -3.665220   -0.294651   -0.117606
 6      -2.969982   -0.036816    1.231145
 6      -1.443450    0.009991    1.235684
 6      -0.847763   -0.465794    0.120372
 6      -1.512331   -1.068336   -1.120654
 6      -2.970695   -1.436940   -0.854734
 1      -3.360129    0.897913    1.658238
 1      -3.278589   -0.817928    1.946495
 1      -3.003420   -2.335548   -0.222965
 1      -3.597931    0.611491   -0.735249
 1      -0.963853   -1.958439   -1.467220
 1      -1.461388   -0.352277   -1.957370
 1      -3.488811   -1.681944   -1.791548
 1      -4.735234   -0.511079    0.016715
 6       2.741990   -1.978172    0.035044
 6       1.272700   -1.837107    0.426647
 6       0.646074   -0.510780    0.051616
 6       1.436217    0.514070   -0.270073
 6       2.941293    0.498983   -0.289183
 6       3.512677   -0.721622    0.430134
 1       0.679356   -2.639442   -0.026321
 1       1.145439   -1.950476    1.511363
 1       3.416288   -0.576252    1.512828
 1       2.818521   -2.117386   -1.051257
 1       3.304635    1.421604    0.178123
 1       3.295065    0.528361   -1.329714
 1       4.581443   -0.825766    0.211313
 1       3.181366   -2.865910    0.504717
 8       0.955477    1.763862   -0.674102
 8      -0.224734    3.553584   -0.119746
 6       0.148956    2.452806    0.173838
 1      -0.121483    1.879722    1.079256
(Hartree/Particle)
 Thermal correction to Energy=
0.287508
 Thermal correction to Enthalpy=
0.288452
 Thermal correction to Gibbs Free Energy=
0.232260
 Sum of electronic and zero-point Energies=
-655.694636
 Sum of electronic and thermal Energies=
-655.680684
 Sum of electronic and thermal Enthalpies=
-655.679740
 Sum of electronic and thermal Free Energies=
-655.735932
```

Electrocyclizations

Anion

TS

```
6      -3.331316   -0.146366    0.348956
6      -2.311275    0.125028    1.471394
6      -0.884780   -0.320840    1.181015
6      -0.641808   -0.895334   -0.053099
6      -1.689599   -1.511265   -0.954991
```

```
6      -3.065383   -1.515945   -0.280805
1      -2.271276    1.202892    1.683767
1      -2.659669   -0.342021    2.406553
1      -3.084789   -2.279746    0.508398
1      -3.224570    0.620387   -0.430116
1      -1.402248   -2.533542   -1.243987
1      -1.756965   -0.941817   -1.895406
1      -3.847018   -1.779545   -1.004417
1      -4.363404   -0.083486    0.721412
6       3.181103   -1.096183   -0.562367
6       1.768633   -1.585900   -0.907726
6       0.724863   -0.625196   -0.399505
6       1.023608    0.474673    0.396076
6       2.383339    0.696190    1.000040
6       3.222005   -0.576215    0.876662
1       1.696667   -1.750712   -1.994278
1       1.619724   -2.575997   -0.444086
1       2.809542   -1.343108    1.543226
1       3.467504   -0.279993   -1.239237
1       2.262018    0.986430    2.049248
1       2.892304    1.534685    0.499806
1       4.252631   -0.382002    1.196202
1       3.909150   -1.903156   -0.707718
8       0.413192    1.793034    0.243469
8      -0.666450    3.164854   -1.129854
6      -0.100038    2.119343   -0.927177
1       0.050357    1.335684   -1.689133
(Hartree/Particle)
 Thermal correction to Energy=
0.284899
 Thermal correction to Enthalpy=
0.285843
 Thermal correction to Gibbs Free Energy=
0.230786
 Sum of electronic and zero-point Energies=
-655.642963
 Sum of electronic and thermal Energies=
-655.629429
 Sum of electronic and thermal Enthalpies=
-655.628485
 Sum of electronic and thermal Free Energies=
-655.683541
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Product

```
6       2.628191   -1.798576    0.404672
6       1.279348   -1.623556    1.126572
6       0.344771   -0.934181    0.191198
6       0.744654   -0.107785   -0.843209
6       2.147723   -0.017761   -1.361233
6       3.106197   -0.496583   -0.256944
1       0.929806   -2.607373    1.474946
1       1.453956   -1.031083    2.049730
1       3.168281    0.280714    0.516521
1       2.515205   -2.566040   -0.372069
1       2.394703    1.003328   -1.677901
1       2.257198   -0.653912   -2.249944
1       4.119716   -0.627220   -0.657190
1       3.392279   -2.158985    1.104568
6      -0.393213    2.960820    0.049642
6      -0.493513    2.109411   -1.253602
6      -0.467594    0.620514   -1.014272
6      -0.859432   -0.015695    0.351483
6      -0.782842    0.962394    1.523901
6       0.140715    2.144430    1.229273
1      -1.385299    2.441069   -1.806298
1       0.356926    2.356038   -1.906149
1       1.149198    1.774804    1.006634
1      -1.390556    3.329527    0.326015
1      -0.473831    0.440515    2.440403
1      -1.794761    1.345658    1.704526
1       0.222932    2.780383    2.119900
1       0.227721    3.852062   -0.111521
8      -2.179188   -0.651748    0.483268
8      -3.468788   -2.135161   -0.553421
6      -2.446121   -1.493264   -0.503412
1      -1.652981   -1.525214   -1.265349
(Hartree/Particle)
 Thermal correction to Energy=
0.287414
 Thermal correction to Enthalpy=
0.288358
 Thermal correction to Gibbs Free Energy=
0.233467
 Sum of electronic and zero-point Energies=
-655.696704
 Sum of electronic and thermal Energies=
-655.683164
 Sum of electronic and thermal Enthalpies=
-655.682219
 Sum of electronic and thermal Free Energies=
-655.737110
```

Brominated

Reactant

```
6      -2.052822    1.978204   -1.121474
6      -1.028824    0.896938   -1.496491
6      -0.567410    0.155569   -0.243435
6      -0.195758    1.125929    0.833833
6      -1.032121    2.291817    1.208086
6      -1.495600    2.976249   -0.095839
1      -1.429244    0.209753   -2.245046
1      -0.154827    1.391016   -1.936779
1      -0.640735    3.502076   -0.537894
1      -2.953746    1.501845   -0.721454
1      -0.488036    2.989579    1.849125
1      -1.906824    1.940412    1.767527
1      -2.250204    3.732920    0.133500
1      -2.354224    2.515599   -2.024518
35      -1.970331   -1.145794    0.281868
6       3.414699    1.092351    0.273028
6       2.368675    1.260861    1.403704
6       1.074432    0.717434    0.914909
6       0.930395   -0.371068   -0.121585
6       1.898255   -0.170590   -1.309196
6       2.762993    1.084876   -1.116999
1       2.699903    0.737649    2.305314
1       2.245581    2.315405    1.668636
1       2.155572    1.989111   -1.245302
1       3.945188    0.144119    0.409079
1       1.368457   -0.142376   -2.264511
1       2.565339   -1.036389   -1.343359
1       3.532584    1.110250   -1.892595
1       4.162833    1.884976    0.340289
8       1.092685   -1.662395    0.463938
8       0.998493   -3.845995    0.064082
6       0.811524   -2.730081   -0.304459
1       0.403899   -2.466983   -1.296040
(Hartree/Particle)
 Thermal correction to Energy=
0.295163
 Thermal correction to Enthalpy=
0.296107
 Thermal correction to Gibbs Free Energy=
0.235459
 Sum of electronic and zero-point Energies=
-3229.916521
 Sum of electronic and thermal Energies=
-3229.901073
 Sum of electronic and thermal Enthalpies=
-3229.900129
 Sum of electronic and thermal Free Energies=
-3229.960777
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TS

```
 6       2.238845   -2.190832   -0.589805
 6       1.272788   -1.283143   -1.370457
 6       0.698833   -0.195105   -0.447698
 6       0.157281   -0.854410    0.743265
 6       0.989144   -1.733722    1.599306
 6       1.595195   -2.805121    0.660757
 1       1.765341   -0.839180   -2.236860
 1       0.430033   -1.882907   -1.731984
 1       0.794337   -3.488700    0.355630
 1       3.122586   -1.613593   -0.302065
 1       0.399913   -2.194590    2.394850
```

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 1       1.790186   -1.150726    2.064949
 1       2.332371   -3.399082    1.207001
 1       2.586010   -2.990531   -1.249861
 35       2.091980    1.162113   -0.200352
 6      -3.646059   -1.079492    0.224070
 6      -2.321788   -1.505942    0.868604
 6      -1.123471   -0.724362    0.401117
 6      -0.958122    0.250244   -0.791622
 6      -2.464810    0.655122   -1.104322
 6      -3.418279   -0.537083   -1.185687
 1      -2.386243   -1.461901    1.960669
 1      -2.128652   -2.557162    0.622157
 1      -3.021953   -1.314259   -1.848536
 1      -4.113395   -0.288329    0.820751
 1      -2.533436    1.292394   -1.987779
 1      -2.750532    1.254945   -0.246722
 1      -4.368906   -0.210103   -1.615739
 1      -4.343313   -1.920703    0.220983
 8      -0.645783    1.704212   -0.304009
 8      -0.794926    3.274364    1.257686
 6      -0.987186    2.149965    0.895274
 1      -1.462213    1.385147    1.538657
(Hartree/Particle)
 Thermal correction to Energy=
0.292029
 Thermal correction to Enthalpy=
0.292973
 Thermal correction to Gibbs Free Energy=
0.236276
 Sum of electronic and zero-point Energies=
-3229.784417
 Sum of electronic and thermal Energies=
-3229.770093
 Sum of electronic and thermal Enthalpies=
-3229.769149
 Sum of electronic and thermal Free Energies=
-3229.825846
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Product

```
6      -2.052822    1.978204   -1.121474
6      -1.028824    0.896938   -1.496491
6      -0.567410    0.155569   -0.243435
6      -0.195758    1.125929    0.833833
6      -1.032121    2.291817    1.208086
6      -1.495600    2.976249   -0.095839
1      -1.429244    0.209753   -2.245046
1      -0.154827    1.391016   -1.936779
1      -0.640735    3.502076   -0.537894
1      -2.953746    1.501845   -0.721454
1      -0.488036    2.989579    1.849125
1      -1.906824    1.940412    1.767527
1      -2.250204    3.732920    0.133500
1      -2.354224    2.515599   -2.024518
35     -1.970331   -1.145794    0.281868
6       3.414699    1.092351    0.273028
6       2.368675    1.260861    1.403704
6       1.074432    0.717434    0.914909
6       0.930395   -0.371068   -0.121585
6       1.898255   -0.170590   -1.309196
6       2.762993    1.084876   -1.116999
1       2.699903    0.737649    2.305314
1       2.245581    2.315405    1.668636
1       2.155572    1.989111   -1.245302
1       3.945188    0.144119    0.409079
1       1.368457   -0.142376   -2.264511
1       2.565339   -1.036389   -1.343359
1       3.532584    1.110250   -1.892595
1       4.162833    1.884976    0.340289
8       1.092685   -1.662395    0.463938
8       0.998493   -3.845995    0.064082
6       0.811524   -2.730081   -0.304459
1       0.403899   -2.466983   -1.296040
(Hartree/Particle)
 Thermal correction to Energy=
0.295159
 Thermal correction to Enthalpy=
0.296103
 Thermal correction to Gibbs Free Energy=
0.238488
 Sum of electronic and zero-point Energies=
-3229.899712
 Sum of electronic and thermal Energies=
-3229.885077
 Sum of electronic and thermal Enthalpies=
-3229.884133
 Sum of electronic and thermal Free Energies=
-3229.941748
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Neutral

Reactant

```
6      -3.587423   -0.983480   -0.235955
6      -2.953320    0.006590   -1.212633
6      -1.454003    0.017659   -1.124452
6      -0.755306   -0.535860   -0.131023
6      -1.431381   -1.241278    1.026484
6      -2.914260   -0.887316    1.131294
1      -3.256165   -0.221916   -2.239711
1      -3.319451    1.022530   -1.012487
1      -3.014596    0.137314    1.508699
1      -3.468409   -2.002717   -0.622518
1      -0.913262   -0.979045    1.956614
1      -1.311721   -2.326981    0.914032
1      -3.405618   -1.544171    1.854275
1      -4.661393   -0.796939   -0.152898
6       2.902817   -1.795732   -0.342964
6       1.425038   -1.844173    0.038214
6       0.729329   -0.505238   -0.104912
6       1.447748    0.618386   -0.188016
6       2.944677    0.704223   -0.169997
6       3.586058   -0.597087    0.308163
1       0.898885   -2.572564   -0.587501
1       1.316266   -2.198736    1.071571
1       3.483889   -0.672929    1.396887
1       2.992549   -1.713748   -1.432317
1       3.234738    1.541725    0.472084
1       3.293930    0.959779   -1.178170
1       4.656341   -0.589140    0.087413
1       3.393528   -2.727858   -0.050541
8       0.856891    1.868581   -0.350393
8      -0.665429    3.271370    0.469407
6      -0.021778    2.279710    0.590583
1      -0.042301    1.611630    1.468394
1      -0.918073    0.535737   -1.914653
(Hartree/Particle)
 Thermal correction to Energy=
0.303600
 Thermal correction to Enthalpy=
0.304544
 Thermal correction to Gibbs Free Energy=
0.248405
 Sum of electronic and zero-point Energies=
-656.332181
 Sum of electronic and thermal Energies=
-656.318223
 Sum of electronic and thermal Enthalpies=
-656.317279
 Sum of electronic and thermal Free Energies=
-656.373419
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TS

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 6       3.204499    0.928659    0.851995
 6       2.222320    1.904304    0.196670
 6       1.138382    1.190534   -0.556199
 6       1.129133   -0.202428   -0.686719
 6       2.357990   -1.043226   -0.450106
 6       3.582274   -0.179257   -0.133236
 1       1.764026    2.558902    0.947204
 1       2.760762    2.572468   -0.489121
 1       3.962882    0.277104   -1.054763
 1       2.743202    0.476903    1.739042
 1       2.542736   -1.672655   -1.327375
 1       2.170822   -1.731043    0.384195
 1       4.384503   -0.803784    0.268023
 1       4.092009    1.466106    1.195690
 6      -0.910834   -2.466043    0.537155
 6      -0.705258   -2.049467   -0.955433
```

```
 6      -0.167561   -0.657441   -0.862948
 6      -1.002486    0.288202   -0.217128
 6      -1.085347    0.014620    1.270736
 6      -1.672692   -1.425620    1.378599
 1      -0.029175   -2.744799   -1.459013
 1      -1.662879   -2.066566   -1.480345
 1      -2.722416   -1.406414    1.068703
 1       0.077263   -2.625303    0.984804
 1      -1.703058    0.736146    1.806320
 1      -0.081855    0.034703    1.697723
 1      -1.660813   -1.734561    2.428265
 1      -1.433610   -3.426141    0.581493
 8      -2.294693    0.367302   -0.816151
 8      -2.895756    2.257718    0.278130
 6      -3.114549    1.370447   -0.493142
 1      -4.043294    1.261613   -1.071983
 1       0.507256    1.787444   -1.196160
(Hartree/Particle)
 Thermal correction to Energy=
0.300734
 Thermal correction to Enthalpy=
0.301679
 Thermal correction to Gibbs Free Energy=
0.248284
 Sum of electronic and zero-point Energies=
-656.248856
 Sum of electronic and thermal Energies=
-656.235811
 Sum of electronic and thermal Enthalpies=
-656.234867
 Sum of electronic and thermal Free Energies=
-656.288261
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Product

```
6       2.842340   -1.454627    0.666026
6       1.387838   -1.315383    1.141693
6       0.502203   -1.033676   -0.068729
6       1.076370    0.089711   -0.903431
6       2.511471    0.192279   -1.268547
6       3.348180   -0.180171   -0.026266
1       1.065577   -2.211961    1.680114
1       1.334576   -0.477465    1.847138
1       3.305321    0.649682    0.689187
1       2.918412   -2.300981   -0.028564
1       2.770370    1.189269   -1.635046
1       2.730590   -0.519567   -2.074425
1       4.397058   -0.300179   -0.310590
1       3.490574   -1.688433    1.515087
6      -1.167389    2.760587    0.180993
6      -0.387157    2.277594   -1.067399
6      -0.017867    0.853543   -0.846929
6      -0.770776   -0.112449    0.034791
6      -1.175481    0.528825    1.378041
6      -0.747158    2.003494    1.448871
1      -1.000445    2.401432   -1.964752
1       0.520620    2.872091   -1.212701
1       0.339735    2.073949    1.576306
1      -2.238880    2.597727    0.022283
1      -0.779917   -0.033766    2.228008
1      -2.266170    0.486819    1.448764
1      -1.199385    2.466586    2.329896
1      -1.027729    3.835807    0.313569
8      -1.931173   -0.654746   -0.635614
8      -3.401623   -2.321729   -0.577310
6      -2.428684   -1.790003   -0.138007
1      -1.846824   -2.188119    0.714788
1       0.305539   -1.959440   -0.622306
(Hartree/Particle)
 Thermal correction to Energy=
0.303705
 Thermal correction to Enthalpy=
0.304649
 Thermal correction to Gibbs Free Energy=
0.250303
 Sum of electronic and zero-point Energies=
-656.312319
 Sum of electronic and thermal Energies=
-656.298999
 Sum of electronic and thermal Enthalpies=
-656.298055
 Sum of electronic and thermal Free Energies=
-656.352402
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