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Potential Energy Surface Around the Tropylium Ion

A thesis
presented to
the faculty of the Department of Chemistry
East Tennessee State University

In partial fulfillment
of the requirements for the degree
Master of Science in Chemistry

by
Kenneth Wayne Bullins
August 2005

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Dr. Hamid Kasmai
Dr. Scott Kirkby

Keywords: Tropylium Ion, Benzylium Ion, PES, *Ab initio* Calculation, DFT, HF

ABSTRACT

Potential Energy Surface Around the Tropylium Ion

by

Kenneth Wayne Bullins

The formation of the tropylium ion, $C_7H_7^+$, in the mass spectrum of toluene is a chemical process that has been studied extensively in the past. The advances in computational power of personal computers have made the investigation of the pathway to form this ion and its subsequent decomposition feasible at a fairly high level of theory. The calculations that we performed were at the HF/6-31G (d, p) and the B3LYP/6-311++G (2d) levels. This work will show areas of the potential energy surface around the highly symmetric tropylium ion to give a glance of possible mechanisms for its formation and decomposition. Our results have confirmed some of the mechanisms reported in the literature, and in addition new areas are explored in the report.

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CONTENTS

| | Page |
|--|------|
| ABSTRACT | 2 |
| ACKNOWLEDGMENTS | 3 |
| LIST OF TABLES | 6 |
| LIST OF FIGURES | 7 |
| Chapter | |
| 1. INTRODUCTION | 8 |
| 2. THEORETICAL BACKGROUND | 22 |
| Model Chemistries | 27 |
| Hartree-Fock Self Consistent Field..... | 27 |
| Density Functional Theory | 32 |
| Basis Sets | 36 |
| Potential Energy Minima | 38 |
| Transition States..... | 39 |
| 3. RESULTS AND DISCUSSION | 41 |
| Computation Details | 41 |
| Production of the Tropylium Ion | 42 |
| Decomposition of the Tropylium Ion | 52 |
| Comparison of Data with Experimental Results | 55 |
| Summary of Results and Future Work | 57 |
| BIBLIOGRAPHY | 59 |
| APPENDICES | 62 |
| Appendix A: Structural Details of Scheme 3.1 | 62 |
| Appendix B: Structural Details of Scheme 3.2 | 69 |

| | |
|--|----|
| Appendix C: Structural Details of Scheme 3.3 | 74 |
| VITA | 80 |

LIST OF TABLES

| Table | Page |
|--|------|
| 1. Representative Input File for Gaussian 03 in Cartesian Coordinates. | 42 |
| 2. Energies of Scheme 3.1 with HF/6-31G(d, p). | 44 |
| 3. Energies of Scheme 3.1 with B3LYP/6-311++G(2d). | 44 |
| 4. Comparison of Our Hartree-Fock Data with Data from the Literature. | 46 |
| 5. Comparison of Our Density Functional Theory Data with Data from the Literature.. | 47 |
| 6. Energies of Scheme 3.2 with HF/6-31G(d, p). | 50 |
| 7. Energies of Scheme 3.2 with B3LYP/6-311++G(2d). | 50 |
| 8. Comparison of Our Hartree-Fock Data with Data from the Literature. | 51 |
| 9. Comparison of Our Density Functional Theory Data with Data from the Literature.. | 51 |
| 10. Energies of Scheme 3.3 with HF/6-31G(d, p). | 53 |
| 11. Energies of Scheme 3.3 with B3LYP/6-311++G(2d). | 53 |
| 12. Data Calculated with HF/6-31G(d, p) for the Purpose of Comparison with Experimental Results. | 55 |
| 13. Data Calculated with B3LYP/6-311G++(2d) for the Purpose of Comparison with Experimental Results. | 56 |

LIST OF FIGURES

| Figure | Page |
|--|------|
| 1. Reaction Mechanism for the Production of Tol ⁺ | 10 |
| 2. Representative Mass Spectrum of Toluene Based on the Data Provided by Rod Beavon. | 11 |
| 3. Representation of a) the Tropylium Ion and b) the Benzylium Ion. | 12 |
| 4. Irreversible Isomerization of Tol ⁺ to Cycloheptatriene Radical Cation..... | 13 |
| 5. ΔH_f Values Reported by Dewar and Landmann for Scheme 1.1. | 15 |
| 6. ΔH_f Values Reported by Cone, Dewar, and Landmann for Scheme 1.2. | 17 |
| 7. Potential Energy Surface Calculated by Lifshitz <i>et al.</i> | 19 |
| 8. Potential Energy Surface Calculated by Moon <i>et al.</i> | 20 |
| 9. Representative Potential Energy Surface. | 39 |
| 10. Energies of Scheme 3.1 for the Formation of the Tropylium Ion. | 45 |
| 11. Energies of Scheme 3.2 for the Formation of the Tr ⁺ ion Through Bz ⁺ | 49 |
| 12. Energies of Scheme 3.3 for the Formation of C ₅ H ₅ ⁺ | 54 |
| 13. Overall Potential Energy Surface Calculated in this Study. | 58 |

CHAPTER 1

INTRODUCTION

Despite many years of effort by several research groups resulting in a considerable number of publications, there is still debate as to the structure and reaction pathways for the $C_7H_7^+$ species formed in a mass spectrometric studies of compounds such as toluene. The $C_7H_7^+$ species ($m/e=91$) gives the most prominent peak in the mass spectrum of toluene.

Mass spectrometry is a tool used by chemists to identify the molecular weight, molecular formula and predict molecular structure of an unknown sample. In mass spectrometry, the sample is injected into the mass spectrometer where it is vaporized. The sample is then bombarded with a high energy (electron or photon) beam. When the beam hits a molecule of the sample, an electron is ejected and a radical cation (molecular ion) is produced. The molecular ion is known as the parent ion. The parent ion can undergo further fragmentation to produce smaller charged fragments known as daughter ions. The daughter ions show up down field from the parent ion in the mass spectrum. All of the positively charged ions are accelerated by passing them between two negatively charged plates. The particles then enter a curved analyzer tube where the unionized and negatively charged molecules are pumped out of the system by a vacuum pump. The analyzer tube is surrounded by a magnet that imposes a magnetic field on all of the positively charged molecules. This causes the positively charged fragments to travel in a circular path. For a given magnetic field, the radius of the path traveled is a function of the charge to mass ratio of the ion. When the fragments path matches the curvature of the analyzer tube, the fragment passes through an exit slit where a collector

records the relative number of particles with a particular mass to charge ratio. The strength of the magnetic field is slowly increased, allowing fragments with progressively increasing mass to charge ratio to travel through the analyzer tube and out of the exit slit. The mass spectrum is a plot of the relative abundance of the charged species versus the mass to charge ratio (m/z), where m is the mass of the ion and z is the charge of the ion. Because the charge on essentially all of the fragments that reach the collector plate is plus one, m/z is the molecular weight of the ion.⁴

There are several prominent peaks in the mass spectrum of toluene that give the relative abundance and mass to charge ratio of the species produced when toluene is subjected to a high energy electron beam. There have been many papers written that discuss the molecular structure of the most abundant peak that is at a mass to charge ratio of 91. This peak must correspond to the species $C_7H_7^+$, but no evidence as to the structure of the $C_7H_7^+$ species can be drawn from the spectra. It is now known that there are competing pathways for the production of two forms of this species, namely benzylium (Bz^+) and tropylium (Tr^+). The mass spectrum of toluene also contains a prominent peak at the mass to charge ratio of 65. This peak corresponds to the species $C_5H_5^+$, but it is not known how the $C_5H_5^+$ is produced. The structure of this species is also not known. Loss of acetylene from the tropylium or benzylium ions could produce this species. We will examine the potential energy surface around the tropylium ion to determine the feasibility of producing $C_5H_5^+$. A prominent peak at a mass to charge ratio of 51 corresponds to $C_4H_3^+$. There is also a noticeable peak at a mass to charge ratio of 39 that corresponds to the $C_3H_3^+$ species.

The toluene molecular ion (Tol^+) is formed in mass spectrometry when toluene (C_7H_8) is ionized by an electron beam. This results in the reaction shown in Figure 1.

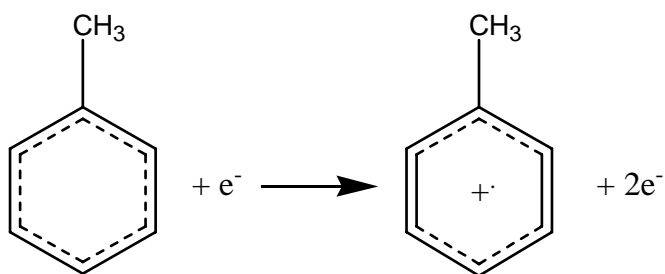


Figure 1. Reaction Mechanism for the Production of Tol^+ .

A representative mass spectrum of toluene is shown in Figure 2. The mass spectrum obtained for this process illustrates that there are many carbocations formed when toluene is subjected to a high energy electron beam.

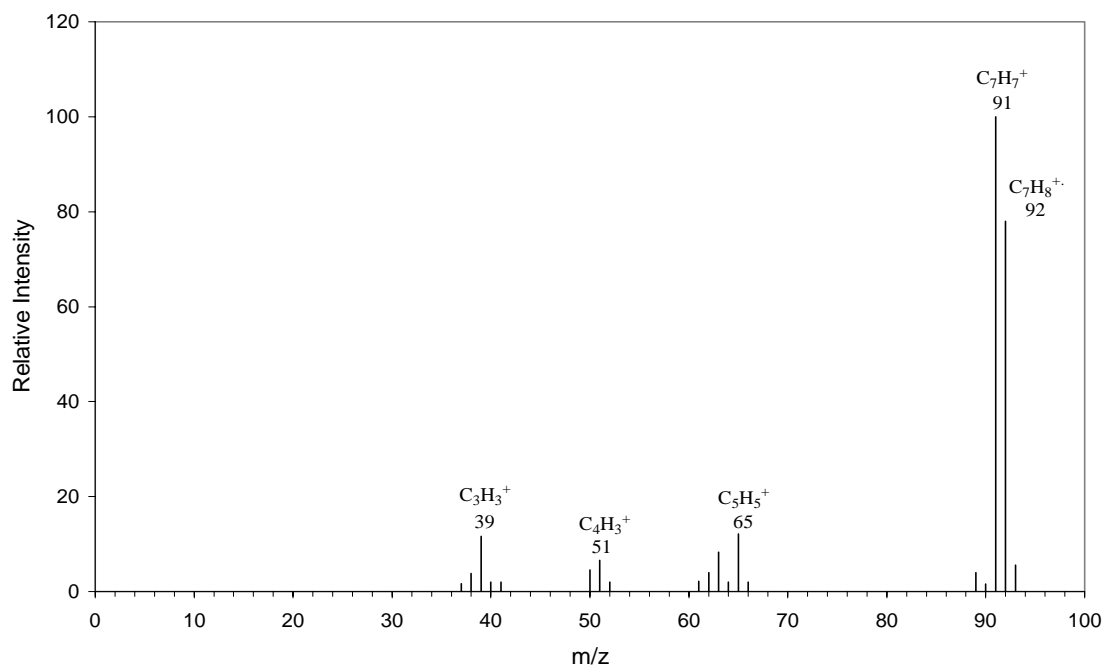
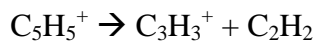


Figure 2. Representative Mass Spectrum of Toluene Based on the Data Provided by Rod Beavon.¹

Tol⁺ is known as the parent ion of the toluene molecule and shows up in the mass spectrum at a mass to charge ratio of 92. The most intense peak in the spectrum is at 91 (m/z). This peak can be accounted for by hydrogen cleavage from the Tol⁺ molecular ion to produce the C₇H₇⁺ ion. There is also a prominent peak at a mass to charge ratio of 65. This peak can be accounted for by the decomposition of C₇H₇⁺ reaction to C₅H₅⁺ and a neutral acetylene molecule:



Another noticeable peak occurs at a mass to charge ratio of 39. This peak may be similarly accounted for by the following reaction:



The production of C_7H_7^+ in mass spectrometry is a chemical reaction that has been the focus of many studies. The structure of the C_7H_7^+ molecule has also been intensively studied. In the early days of mass spectrometry it was generally accepted that upon electron impact, the C_7H_7^+ formed from toluene proceeded via the benzylium ion (Bz^+) channel², see Figure 1.3. In the early 30s Erich Huckel predicted that the tropylium ion (Tr^+), see Figure 3, is a stable structure.³

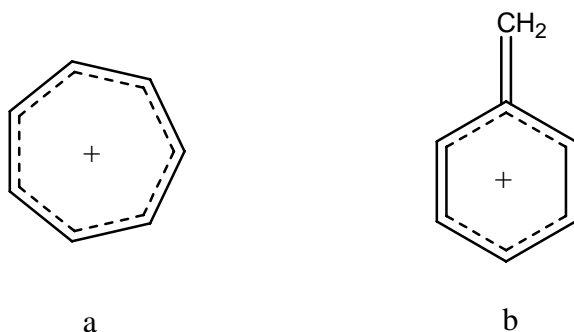


Figure 3. Representation of a) the Tropylium Ion and b) the Benzylium Ion.

Tropylium is an organic cation that has six π electrons distributed over a seven carbon ring. Even though tropylium is a carbocation, the species is remarkably unreactive because it is an aromatic system.⁴

In the late 50s, Rylander, Meyerson, and Grubb showed that the seven hydrogens in the C_7H_7^+ structure were indistinguishable (hydrogen scrambling) by investigating deuterated forms of the toluene molecule. Consecutive acetylene elimination from deuterated toluene also supported the notion that the hydrogens in this system are indistinguishable. Their results implied that the C_7H_7^+ produced in the mass spectrometer is the highly symmetrical Tr^+ structure. This was a landmark in organic mass

spectrometry because this proposal could explain known appearance energies and thermochemical data that were previously anomalous. It was suggested that the mechanism involved an irreversible isomerization from Tol⁺ to a cycloheptatriene radical cation.² Figure 4 is a representation of this isomerization.

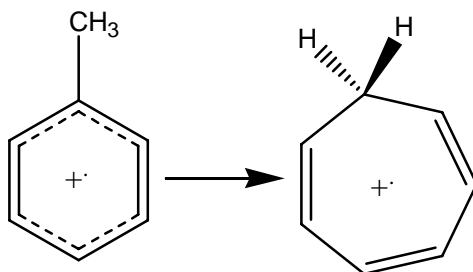
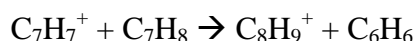


Figure 4. Irreversible Isomerization of Tol⁺ to Cycloheptatriene Radical Cation.

Many studies were performed in the 60s on C₇H₈ isomers.^{5, 6, 7} These studies showed that all isomers underwent loss of a hydrogen atom to form C₇H₇⁺ via the cycloheptatriene intermediate. In 1961 Meyerson, Mccollum, and Rylander found that bicycloheptadiene gave the same peaks as toluene and cycloheptatriene, but the peak at 66 (m/z) (C₅H₆⁺) was much more prominent in the spectrum of bicycloheptadiene. They proposed that pentadiene was produced from a reverse Diels Alder reaction of bicycloheptadiene. They also suggested that all C₇H₈ isomers probably decompose by the same mechanism.⁵

In the early days of mass spectrometry, techniques were limited to spectral fragmentation patterns, appearance energies, isotope labeling and metastable peaks.^{8, 9} Two methods were developed in the late sixties and early seventies that could be used to elucidate ion structures. Ion/molecule reactions were demonstrated to be sensitive to the structure of the ion. It was shown in an ion cyclotron resonance (ICR) study that the non-

decomposing Tol⁺ ions retain the toluene structure.¹⁰ Gas phase radiolysis studies of toluene showed that the C₇H₇⁺ produced underwent reactions that were characteristic of Bz⁺.¹¹ Collisional activation spectra of the C₇H₇⁺ ions produced from various precursors showed that both Tr⁺ and Bz⁺ ions are produced in the gas phase.^{12,13} An ICR study of the photodissociation of Tol⁺ established the formation of a C₇H₇⁺ species that reacts with neutral toluene.



This reaction is characteristic of the Bz⁺ structure because it proceeds through methylene (CH₂) transfer. It was concluded that both Tr⁺ and Bz⁺ are stable species that can exist for seconds as separate entities in the gas phase. Photodissociation spectroscopy of Tol⁺ produced from toluene in an ICR study demonstrated that a species of C₇H₇⁺ was produced that underwent the previous ion/molecule reaction.^{14,15} Dunbar's photodissociation spectroscopy study of Tol⁺ isomer showed that Tol⁺ and the cycloheptatriene radical cation are produced without interconversion on a time scale of seconds.¹⁶

The earliest theoretical calculations found on this system were performed by Dewar and Landmann in the mid 70s.^{17,18} These calculations were performed at the MINDO/3 level of theory. Three mechanisms were proposed. One is the McLafferty rearrangement where the cycloheptatriene intermediate (Int3) is formed from Tol⁺.¹⁷ Scheme 1.1 is the scheme of Dewar and Landmann and Figure 5 is a summary of the results for this mechanism to demonstrate the relative energies.

Scheme 1.1 Reaction mechanism proposed by Dewar and Landmann for Tol⁺ to Int3.¹⁷

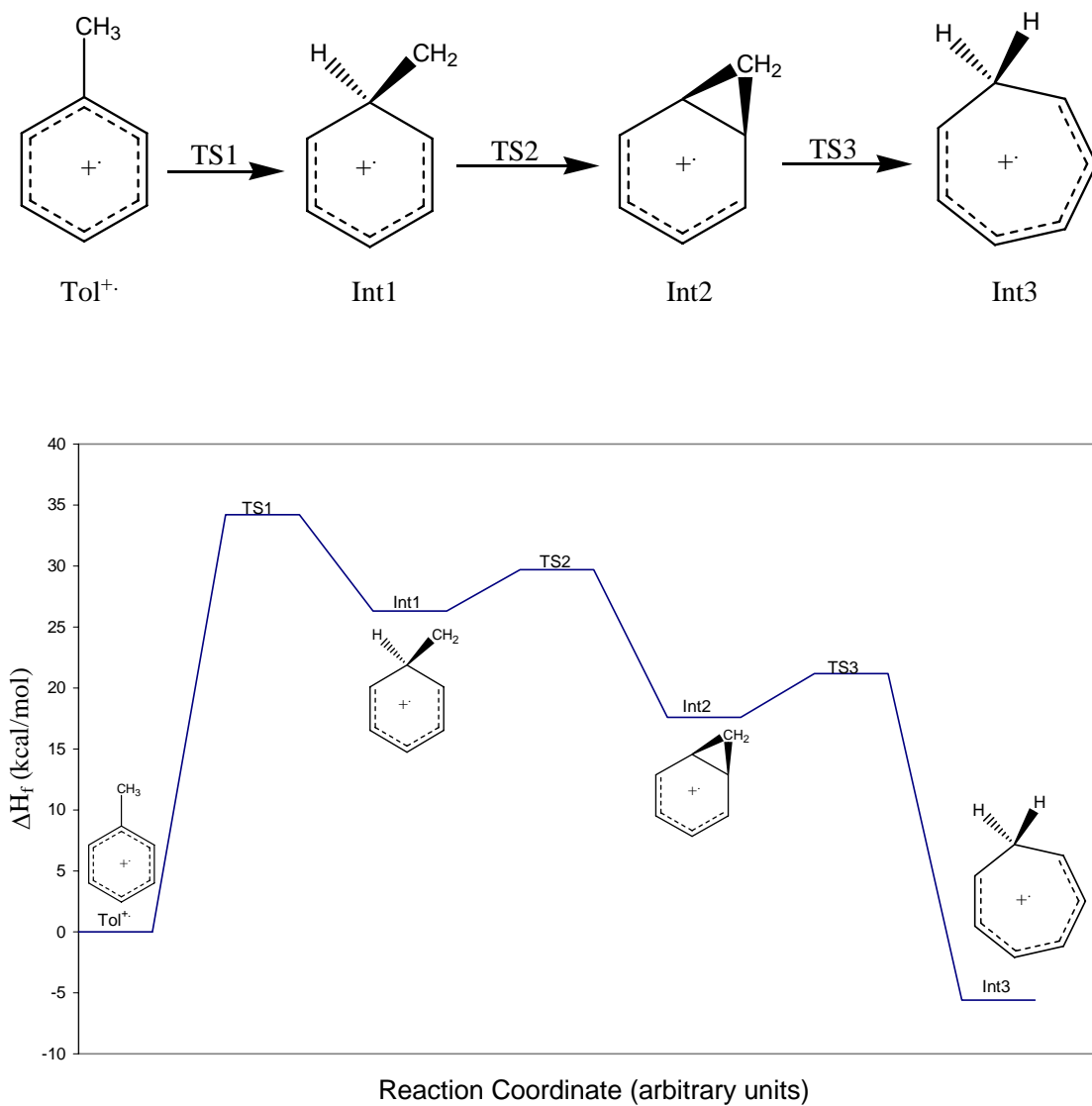


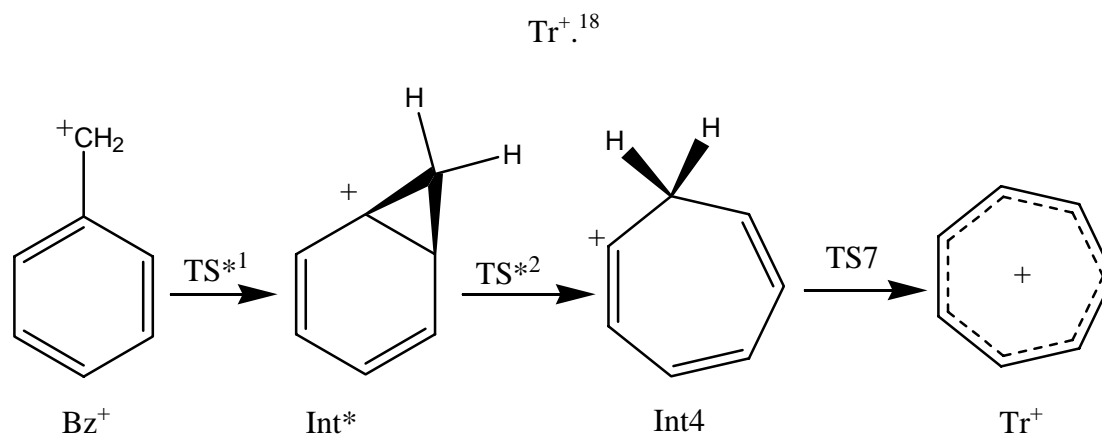
Figure 5. ΔH_f Values Reported by Dewar and Landmann for Scheme 1.1.¹⁷

This mechanism begins with a hydrogen migration from the methyl carbon to the ipso position of the six-membered ring to form Int1. The methyl carbon then bonds to the alpha carbon of the six-membered ring to form the norcaradienyl radical cation (Int2)

followed by a ring expansion to form Int3. There is a mistake in the original paper. The literature values for the heat of formation of Int2 and TS3 should be interchanged to correct this mistake.

Another mechanism proposed in the mid 70s by Cone, Dewar, and Landmann is for the interconversion between Tr^+ and Bz^+ ions.¹⁸ This mechanism is shown in Scheme 1.2. This mechanism was also performed at MINDO/3 level of theory. Figure 6 is a summary of the results obtained for this mechanism.

Scheme 1.2 Reaction mechanism proposed by Cone, Dewar, and Landmann for Bz^+ to



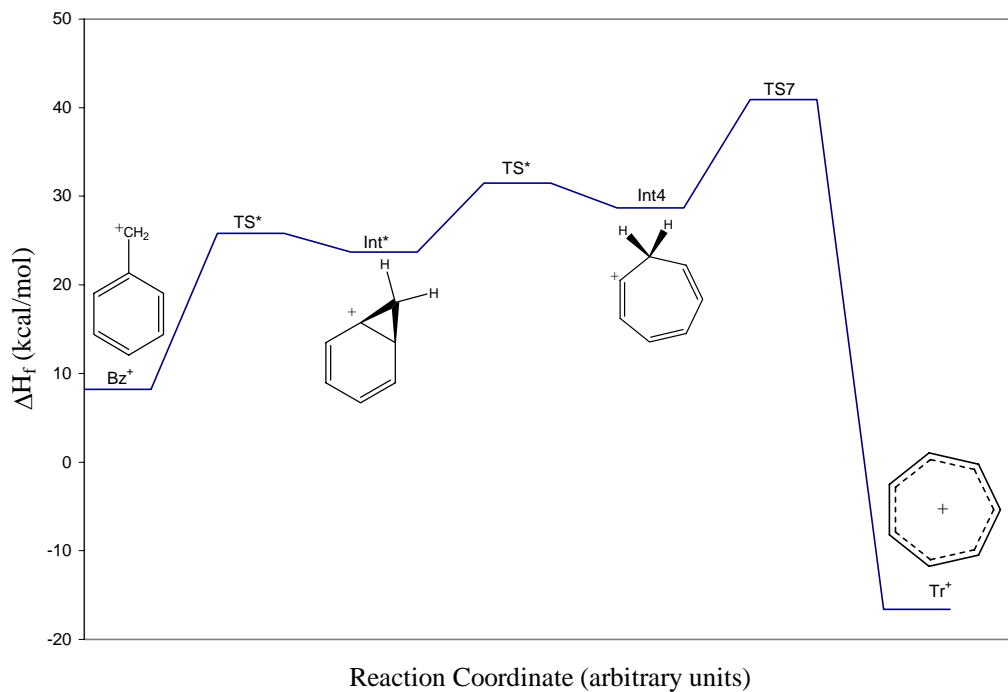


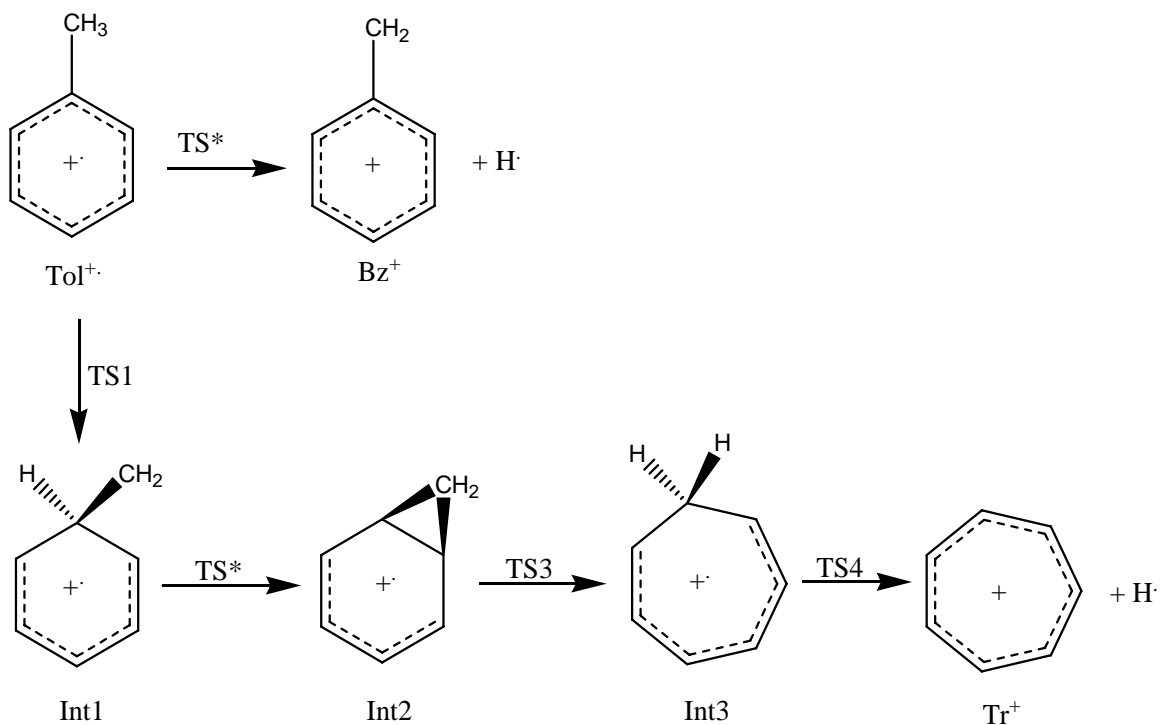
Figure 6. ΔH_f Values Reported by Cone, Dewar, and Landmann for Scheme 1.2.¹⁸

This mechanism begins with the Bz^+ ion. The methyl carbon bonds with the alpha carbon of the six-membered ring to give the norcaradienyl structured intermediate (Int^*). This intermediate undergoes ring expansion to give a structure similar to $Int3$. A hydrogen transfer to the carbon with the formal charge yields Tr^+ . Details of two of these mechanisms will be discussed in the results and discussion section.

Theoretical calculations have been improved in both structure and energy determination throughout recent years and there are many different types of higher level calculations that are now feasible. Modern computers have made it practical to study this system at these levels of theory. A review paper by Lifshitz *et al* was published in 1994 that discusses how the benzylium versus tropylium story has evolved throughout the

years.¹⁹ The data given in the paper are the arithmetic mean of values calculated by PMP3, MP4SDTQ, and QCISD(T)//HF/3-21G. Figure 7 is the data published in this paper.

Scheme 1.3 Reaction mechanism of Lifshitz *et al.*^{19, 20}



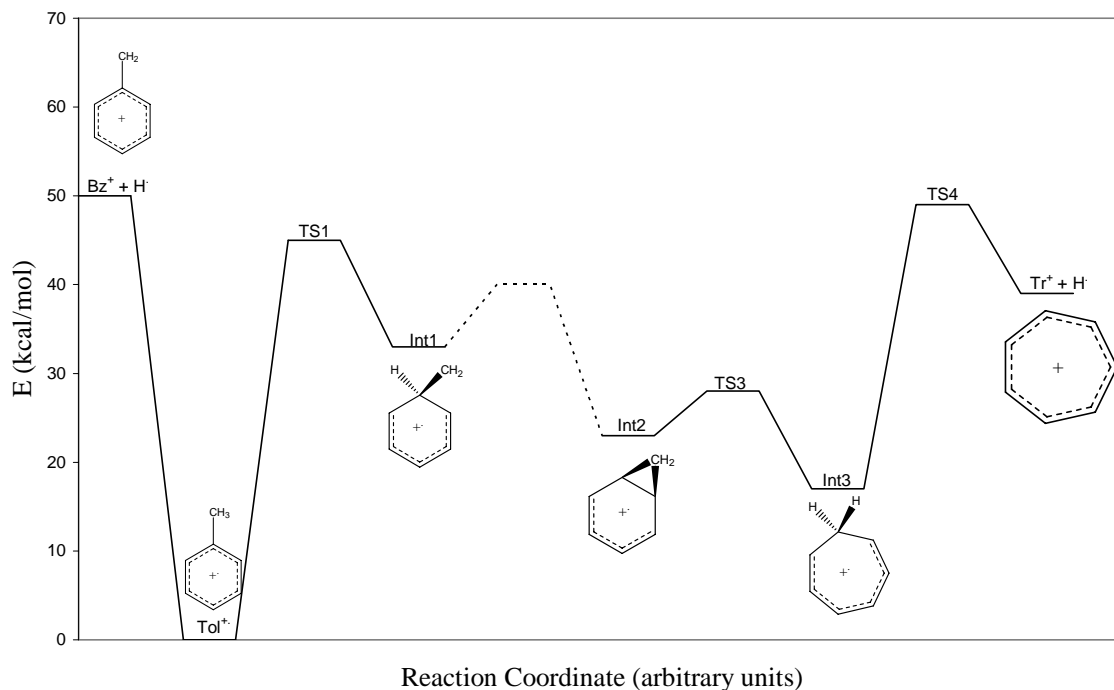


Figure 7. Potential Energy Surface Calculated by Lifshitz *et al.*^{19, 20}

This mechanism produces both Bz^+ and Tr^+ . The data to the left of Tol^+ are for the production of Bz^+ with no transition state for this reaction. The data to the right of Tol^+ are for the production of Tr^+ . This part of the mechanism is similar to Dewar and Landmann's Scheme 1, except the mechanism does not stop at the cycloheptatriene intermediate (Int3). This mechanism has a hydrogen cleavage from Int3 to produce Tr^+ and H. A transition state between Int1 and Int2 was not found in their study.

The most recent theoretical calculations published on this system were by Moon, Choe, and Kim in 2000.²¹ Their mechanism is the same as the one shown in Figure 8, but less detail is given about the interconversion between Tol^+ and Int3. Their study was at the HF/6-31G** and G2(MP2,-SVP) levels of theory.

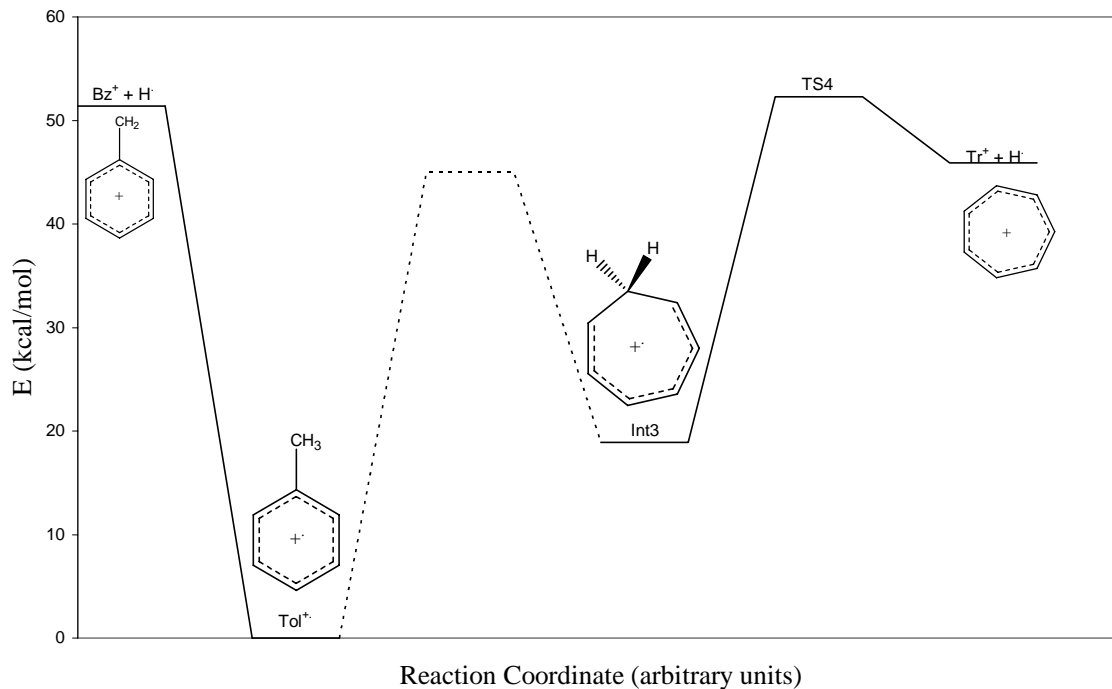


Figure 8. Potential Energy Surface Calculated by Moon *et al.*²¹

This study was performed to compare various theoretical methods that are used to solve the Schrödinger equation and to elaborate on the current mechanism for the formation of the tropylium ion from toluene. Calculations performed at HF/6-31G(d, p) are compared with data calculated at HF/6-31G** and calculations performed using B3LYP/6-311++G(2d) are compared to some expensive calculations. This work examined the pathways for the production of the two most likely possibilities, namely the benzylium (Bz^+) and tropylium (Tr^+) ions. Further, the potential energy surface around the Tr^+ ion was investigated to determine the feasibility of producing the $C_5H_5^+$ species. An existing reaction path for the interconversion of benzylium and tropylium will also be examined and compared to literature values.

The second chapter of this report discusses the theoretical background for the types of calculations that will be used to perform our calculations. This will begin with the time independent Schrödinger equation for a single particle that is developed into the time independent Schrödinger equation for a single particle. This equation is then applied to a many body system where the Schrödinger equation can not be exactly solved. The Born-Oppenheimer approximation is used to separate the Schrödinger equation into nuclear and electronic parts. Basis sets and model chemistries are then introduced. Details of the Hartree-Fock Self Consistent Field method and Density Functional Theory are discussed. The chapter is concluded with the requirements for a structure to be a potential energy minima or a transition state.

The third chapter contains the results obtained for two reaction mechanisms for the formation of the tropylium ion as well as results obtained for the decomposition of the tropylium ion. The structures and energies of all molecules in these mechanisms will be compared with those given in literature. Conclusions are drawn and recommendations for further work are given.

CHAPTER 2

THEORETICAL BACKGROUND

Quantum Mechanics describes how particles like electrons and nuclei have both wave and particle characteristics. The time dependent Schrödinger equation is a mathematical description of the wave function of a particle and is given by Equation 1.

$$\left\{ \frac{-\hbar^2}{2m} \nabla^2 + V \right\} \Psi(r,t) = i\hbar \frac{\partial \Psi(r,t)}{\partial t} \quad (1)$$

In this equation $\Psi(r,t)$ is the wave function in spherical polar coordinates and is a function of the position of the particle and time. $\Psi(r,t)$ is called the wavefunction because it is based on the differential equation for a macroscopic wave. Electrons and protons behave like particles or waves, depending on the type of experiment that is being performed, but in any case it is impossible to measure both the wave and particle behavior simultaneously. These wave and particle characteristics are known as complementary observables. The wavefunction contains all the information that can be known about a particle. \hbar is a form of Planck's constant, m is the mass of the particle, and ∇^2 is the differential operator known as the Laplacian operator and is given by Equation 2.

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (2)$$

The term V is the potential field in which the particle is moving. When the potential field is not a function of time, the wave function may be written as a product of a spatial function and a time function, see Equation 3.

$$\Psi(r,t) = \psi(r)\tau(t) \quad (3)$$

This substitution allows the Schrödinger equation to be simplified by the separation of variables technique. The term in parentheses on the left hand side of Equation 1 is known as the Hamiltonian operator H . The Hamiltonian operator is the quantum mechanical equivalent of the classical Hamiltonian, which is the sum of the kinetic and potential energies of the system being described.

$$H = T + V \quad (4)$$

In Equation 4 the term T is the kinetic energy of the particle and the term V is the potential energy term that is the coulombic repulsion or attraction between charged particles for an isolated system. When these substitutions are made, it is possible to obtain an equation that is a function of the position of the particle and an equation that is a function of time. This leads us to one of the most famous equations of Quantum Mechanics in Chemistry.

The fundamental equation of quantum mechanics is an eigenvalue equation that is the time independent Schrödinger and is shown in Equation 5.

$$H\psi = E\psi \quad (5)$$

An eigenvalue equation is defined as an equation that when an operator acts on the equation, it produces a numerical multiple of the equation called the eigenvalue. In this equation ψ is known as the wave function of the system and is an eigenfunction of the Hamiltonian operator and is composed of the kinetic and potential energies. The energy, E , is the eigenvalue of the Hamiltonian operator. The kinetic energy term for a system of particles is the sum of the kinetic energy of all the particles in the system:

$$T = -\frac{\hbar^2}{2} \sum_k \frac{1}{m_k} \nabla^2 \quad (6)$$

and the potential energy term for a system of particles is the summation of the coulombic repulsion and attraction between all of the particles in the system:

$$V = \frac{1}{4\pi\epsilon_0} \sum_j \sum_{k < j} \frac{q_j q_k}{r_{ij}} \quad (7)$$

where ϵ_0 is the permittivity of vacuum and q_j and q_k are the charges on the two particles.

The charge for an electron is $-e$ and the charge for a nuclei is Ze . Z is the atomic number of the atom and r_{ij} is the distance between the two particles.

The Schrödinger equation works perfectly when describing atomic hydrogen or hydrogen-like atoms. However, when the system being described is a many electron atom or molecule, the Schrödinger equation can not be separated and approximations must be used because of the electron-electron repulsion terms.

The Schrödinger equation for a system containing many particles is similar to Equation 1. For this particular case, ψ is a function of the positions of all of the particles in the system. The wave function does have a physical significance. The product of the wave function and its complex conjugate ($\psi^*\psi$) is interpreted as the probability density of the particle in a particular volume of space. This is known as the Born interpretation.²² Max Born proposed this interpretation in 1925 and was awarded the 1954 Nobel Prize for this interpretation. When the Schrödinger equation is subjected to the appropriate boundary conditions, many physical properties may be obtained from the solution of ψ . A stationary state is obtained when ψ is a solution to the Schrödinger equation. Many stationary states may be obtained from the many different solutions for ψ . Quantum Mechanics requires that restrictions be placed on these wave functions. Because ($\psi^*\psi$) is the probability density of the particle, it is necessary to normalize these wave functions.

This is achieved by multiplying the wave function by a constant and setting the integral of $(\psi^*\psi)$ over all space equal to the number of particles in the system as shown in Equation 8.

$$\int_{-\infty}^{\infty} |\psi|^2 dv = n_{particles} \quad (8)$$

The Pauli principle requires the wave functions to be antisymmetric with respect to the interchanging any two identical fermions in the system. This can be expressed mathematically as Equation 9.

$$\psi(r_1, r_2) = -\psi(r_2, r_1) \quad (9)$$

Protons and electrons are fermions; therefore, their quantum mechanical description must obey the Pauli principle.

The fundamental equations of Quantum Mechanics are more easily solved by eliminating fundamental constants. This is achieved by writing the equations in terms of atomic units. The atomic unit of length is the Bohr radius (a_0). The magnitude of the Bohr radius is shown in Equation 10.

$$a_0 = \frac{h^2}{4\pi^2 m_e e^2} = 0.52917725 \text{ Angstroms} \quad (10)$$

The atomic unit of mass is specified in terms of the electron rest mass ($m_e=1$). The atomic unit of energy is the hartree. One hartree is defined as the Coulomb repulsion between two electrons separated by a distance of one Bohr, see Equation 11.

$$1 \text{ hartree} = \frac{e^2}{a_0} \quad (11)$$

The Born-Oppenheimer approximation simplifies the solution of the Schrödinger equation by separating the nuclear and electronic motions within the molecule. This

approximation is reasonable because the masses of the nuclei are far greater than the masses of the electrons. The nuclei are slowly moving with respect to the electrons, which allow the electronic motion to be described as occurring in a field of fixed nuclei. The full Hamiltonian for a molecular system may be written as Equation 12.

$$H = T^{elec}(r) + T^{nucl}(R) + V^{nucl-elec}(R, r) + V^{elec}(r) + V^{nucl}(R) \quad (12)$$

In this equation R and r represent the position of the nuclei and the electrons respectively. The Born-Oppenheimer approximation assumes that the kinetic energies of the nuclei are zero so that we may construct a polyatomic electronic Hamiltonian as seen in Equation 13.

$$H^{elec} = -\frac{1}{2} \sum_i^{elec} \nabla_i^2 - \sum_i^{elec} \sum_I^{nucl} \frac{Z_I}{R_I - r_i} + \sum_i^{elec} \sum_{j < i}^{elec} \frac{1}{r_i - r_j} + \sum_I^{nucl} \sum_{J < I}^{nucl} \frac{Z_I Z_J}{R_I - R_J} \quad (13)$$

This Hamiltonian can be substituted into the Schrödinger equation to describe the motion of the electrons in a field of fixed nuclei:

$$H^{elec} \psi^{elec}(r, R) = E^{eff}(R) \psi^{elec}(r, R) \quad (14)$$

The complete (nonrelativistic) electronic Hamiltonian in atomic units for a molecule with N electrons and M nuclei is shown in Equation 15.

$$H_{el} = \sum_{i=1}^N \left\{ -\frac{1}{2} \nabla_i^2 - \sum_{\alpha=1}^M \frac{Z_\alpha}{r_{i\alpha}} + \sum_{j>i} \frac{1}{r_{ij}} \right\} \quad (15)$$

The first term in the summation is the kinetic-energy operator for the electrons. The second term is the coulomb attraction of the electrons to the nuclei and the third term describes the repulsion between electrons. The indices i and j represent the N electrons and α represents the M nuclei. The term Z_α is the charge on nucleus α and the distance from electron i to the nucleus α is $r_{i\alpha}$. The term r_{ij} is the distance between electron i and

electron j . Since the Schrödinger equation can not be solved for many electron molecules, we must employ model chemistries that make further approximations.

Model Chemistries

Model chemistries are solutions of the Schrödinger equation that are obtained by applying mathematical approximations to the system being described. The first applied is the Born-Oppenheimer approximation. This eliminates the kinetic energy of the nuclei by assuming that because the nuclei are much heavier than the electrons their positions can be considered as fixed parameters compared to the electrons. The other contributions to the energy of a many electron atom or molecule are the kinetic energy of each electron, the mutual potential energy of the nuclei, and each electron and the mutual potential energy of each pair of electrons. The potential energy of the electron-electron interaction is not analytically solvable for molecules and many electron atoms because the Schrödinger equation contains multi-variable terms that cannot be separated. The electron-electron potential energy is calculated (approximated) by applying model chemistries to the system being described.

Hartree-Fock Self Consistent Field

The Hartree-Fock Self Consistent Field theory assumes that there is no instantaneous electron-electron interaction and that each electron sees all of the other electrons as an average distribution. This assumption seems to be reasonable for calculating molecular geometries and frequencies of stable molecules but sometimes fails when describing chemical processes such as bond dissociation. This method is purely

mathematical and employs no experimental data. Models of this type are known as *ab initio* methods. These methods get their name from the latin translation of “from the beginning”. The Hartree-Fock Self Consistent Field theory is an *ab initio* method that allows the Pauli Principle to be satisfied while letting each electron have its own orbital. The Pauli Principle for multi-electron atoms and molecules states that the wavefunction must be antisymmetric upon interchanging two electrons in the system. The wave function in this theory is assumed to be in the form of a Slater determinant of molecular orbitals. Antisymmetric wave functions are formed automatically and the Pauli principle is obeyed when the wave function is written in this form. This is true because when any two rows or columns of a matrix are interchanged, the sign of the determinant also changes. When the spatial orbitals are all doubly occupied, the Slater determinant has the form of Equation 16.

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1)\alpha_1 & \phi_1(1)\beta_1 \dots & \phi_N(1)\alpha_1 & \phi_N(1)\beta_1 \\ \phi_1(2)\alpha_2 & \phi_1(2)\beta_2 \dots & \phi_N(2)\alpha_2 & \phi_N(2)\beta_2 \\ \dots & \dots & \dots & \dots \\ \phi_1(N)\alpha_N & \phi_1(N)\beta_N \dots & \phi_N(N)\alpha_N & \phi_N(N)\beta_N \end{vmatrix} \quad (16)$$

In the Linear Combination of Atomic Orbitals-Molecular Orbital-Self Consistent Field theory (LCAO-MO-SCF) the ϕ_k 's ($k=1, 2, N/2$) are the molecular orbitals written as a linear combination of atomic orbitals b_v by the formula

$$\phi_k = \sum_v c_{kv} b_v . \quad (17)$$

The ϕ_k 's are chosen to be a normalized orthogonal set of molecular orbitals to fulfill some of the restrictions on ψ . The index v represents the basis function. The coefficients c_{kv} are

treated as variational parameters in this equation. The ϕ_k 's are obtained by the Hartree-Fock approach by solving the following equation:

$$f_k \phi_k = \varepsilon_k \phi_k. \quad (18)$$

The term f_k is known as the Fock operator and is given by:

$$f_k = -\frac{1}{2} \nabla_k^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{k\alpha}} + \sum_j (2J_j(k) - K_j(k)). \quad (19)$$

The terms J_j and K_j are the coulomb and exchange operators respectively. Combining Equations 17 and 19 yields the following equation:

$$\sum_{\nu} f b_{\nu} c_{\nu} = \varepsilon \sum_{\nu} b_{\nu} c_{\nu} \quad (20)$$

The set of functions b_{μ} used to represent the atomic orbitals is known as the basis set for the calculation. The most commonly used basis set is a sum of primitive gaussian orbitals (g_p)

$$b_{\mu} = \sum_p k_{\mu p} g_p, \quad (21)$$

where the coefficients $k_{\mu p}$'s are chosen to make the orbitals resemble Slater type orbitals.

The primitive gaussians have the following form:

$$g_p = x^a y^b z^c e^{-\alpha r^2} Y_{lm}(\theta, \phi), \quad (22)$$

where a, b, and c are integers and the parameter α is usually fixed. $Y_{lm}(\theta, \phi)$ is the spherical harmonic of a three dimensional rigid rotor. The Gaussian functions must be normalized such that

$$\int_{all-space} g^2 d\tau = 1. \quad (23)$$

This implies that $k_{\mu\rho}$ is a function of a , b , c , and α . Multiplying Equation 20 by b_μ and integrating results in the following equation:

$$\sum_v (f_{\mu v} - \varepsilon S_{\mu v}) c_v = 0, \quad (24)$$

where

$$S_{\mu v} = \langle b_\mu | b_v \rangle \quad (25)$$

and

$$f_{\mu v} = \langle b_\mu | f | b_v \rangle. \quad (26)$$

The notation in equations 25 and 26 is known as Dirac notation. Paul Dirac invented this notation to shorten quantum mechanical equations. An example of how this works is Equation 25 in spherical polar coordinates:

$$\langle b_\mu | b_v \rangle = \int_0^{2\pi} \int_0^\pi \int_0^\infty b_\mu b_v r^2 dr \sin(\theta) d\theta d\phi \quad (27)$$

Equation 24 is a set of linear homogenous equations with solutions that must satisfy the secular equation

$$|F - \varepsilon S| = 0. \quad (28)$$

F and S are matrices that are formed from Equations 25 and 26. The Fock matrix can be expressed as follows

$$f_{\mu v} = h_{\mu v} + 2J_{\mu v} - K_{\mu v}. \quad (29)$$

In this equation the one-electron part of the Fock operator is given by

$$h_{\mu v} = \left\langle b_\mu \left| -\frac{1}{2} \nabla^2 - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} \right| b_v \right\rangle \quad (30)$$

and the two-electron coulomb and exchange terms are given by $J_{\mu\nu}$ and $K_{\mu\nu}$ respectively.

The two-electron coulomb term is given by:

$$J_{\mu\nu} = \langle \mathbf{b}_\mu | \sum_j J_j | \mathbf{b}_\nu \rangle = \sum_j \sum_{\sigma\lambda} \langle \mu\nu | \sigma\lambda \rangle c_{j\lambda} c_{j\sigma}, \quad (31)$$

and the two-electron exchange term is given by:

$$K_{\mu\nu} = \langle \mathbf{b}_\mu | \sum_j K_j | \mathbf{b}_\nu \rangle = \sum_j \sum_{\sigma\lambda} \langle \mu\lambda | \sigma\nu \rangle c_{j\lambda} c_{j\sigma} \quad (32)$$

where $\langle \mu\lambda | \sigma\nu \rangle$ is the two electron repulsion integral. The two electron terms depend on the orbital coefficients; therefore, an initial guess for the orbital coefficients must be assumed and then Equation 20 must be solved to get new coefficients. This process is continued until a self-consistent field has been achieved. The HF-SCF method produces the best wavefunctions that can be expressed as a single Slater determinant. The wavefunction describes electron-electron repulsion in an average sense but it does not include electron correlation. The correlation may be defined as the difference between the exact energy of the system (E_{exact}) and the energy calculated by the HF-SCF theory (E_{HF}):

$$E_C^{\text{HF}} = E_{\text{exact}} - E_{\text{HF}}, \quad (33)$$

where the exact energy is determined experimentally or in some cases from more accurate calculations. The Hartree-Fock method is available in Gaussian by using the HF keyword in the route section of the input.

Density Functional Theory

Density functional theory methods are ultimately derived from the Thomas-Fermi-Dirac model of the 1920s and Slater's work in quantum chemistry in the 1950s. This approach is based on modeling electron correlation by general functionals of the electron density. This method is a semiempirical method that parametrizes the equations to reproduce key experimental data. Most modern Density functional theories are based on the Hohenberg-Kohn theorem of the 1960s. A functional is a function of a function. This assumes that the ground state of a many electron atom or molecule can be exactly expressed as a functional of the electron density. Unfortunately, this theorem does not provide the exact form of the functional. In this method the electronic energy is partitioned into several terms:

$$E = E^T + E^V + E^J + E^{XC} . \quad (34)$$

In this equation, E^T is the kinetic energy of the electrons, E^V is the sum of the potential energy from the nuclear-electron attraction and the nuclear-nuclear repulsion and E^J is the electron-electron repulsion term. E^{XC} is the exchange-correlation term that contains the remaining part of the electron-electron interactions. These electron-electron interactions include the exchange energy, E^X , from the antisymmetry of the wave function and the dynamic correlation, E^C , in the motions of the individual electrons. All terms in Equation 34 except the nuclear-nuclear term are functions of the electron density (ρ).

The electron density is obtained from the coordinates of the electrons. The kinetic energy term can be expressed as a functional of the electron density but the general expression is complicated and not completely known. An expression for the kinetic energy of electrons in boxlike potentials has the following form:

$$T = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}} d\tau. \quad (35)$$

This expression and improvements of this equation that take into account the gradient of ρ are rarely used for the electronic structure and the more traditional expression for the kinetic energy that involves wave functions is normally used.

$$T = -\frac{1}{2} \sum_i \int \psi_i \nabla^2 \psi_i d\tau \quad (36)$$

Both potential energy terms are written as functionals of the electron density and have the following form.

$$V_{nuc} = -\sum_{\alpha} \frac{Z_{\alpha} \rho(1)}{r_{1\alpha}} d\tau_1 \quad (37)$$

$$V_{rep} = \frac{1}{2} \iint \frac{\rho(1)\rho(2)}{r_{12}} d\tau_1 d\tau_2. \quad (38)$$

The exchange-correlation term is normally written as a sum of exchange functional and correlation functional:

$$E^{XC}(\rho) = E^X(\rho) + E^C(\rho) \quad (39)$$

Both components of the exchange-correlation term can be written as local functionals that depend on the electron density or gradient-corrected functionals that depend on the electron density and the gradient of electron density. The local density approximation (LDA) is used to indicate any density functional where the E_{XC} term at some position r can be calculated exclusively from the value of ρ at that position. The only requirement on ρ is that it be single valued at every position and can otherwise be ill-behaved (there are cusps in the density at the nucleus). The local exchange functional that was developed to reproduce the exchange energy of a uniform free electron gas is of the following form:

$$E_{LDA}^x = -\frac{9\alpha}{8} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int \rho^{\frac{4}{3}} d^3r \quad (40)$$

where α is an empirical constant for the type of system being described and has a value of 2/3 for a uniform free electron gas. This functional by itself has problems when describing molecular systems. In 1988 Becke formulated the following gradient corrected exchange functional that improves the LDA functional:

$$E_{Becke88}^x = E_{LDA}^x - \gamma \int \frac{\rho^{\frac{4}{3}} x^2}{(1 + 6\gamma \sinh^{-1} x)} d^3r \quad (41)$$

where $x = \rho^{-\frac{4}{3}} |\nabla \rho|$ and γ is a parameter that is chosen to fit the known exchange energies of an inert gas atom.

The electron density may also be expressed in terms of an effective radius where one electron is contained within a sphere defined by a radius where it would have the same density throughout as its center.

$$r_s(r) = \left(\frac{3}{4\pi\rho(r)}\right)^{\frac{1}{3}} \quad (42)$$

The spin of the electrons is dealt with by using individual functionals for the α and β spins. The spin densities at any position are expressed in terms of the normalized spin density (ζ).

$$\zeta(r) = \frac{\rho^\alpha(r) - \rho^\beta(r)}{\rho(r)} \quad (43)$$

ζ is zero everywhere for an unpolarized system (closed-shell system, RB3LYP) and has a value between zero and one for a polarized system (open-shell, UB3LYP). The spin density $\rho(r)$ is equal to zero for a closed-shell system and is one for an open-shell

system. The α spin density is one-half the product of the total spin density ρ and $(\zeta+1)$ and the β spin density is the difference between the total spin density and the α spin density. The LDA method can be extended to the spin-polarized regime by using:

$$\varepsilon_X[\rho(r), \zeta] = \varepsilon_X^0[\rho(r)] + \left\{ \varepsilon_X^1[\rho(r)] - \varepsilon_X^0[\rho(r)] \right\} \left[\frac{(1+\zeta)^{\frac{4}{3}} + (1-\zeta)^{\frac{4}{3}} - 2}{2 \left(2^{\frac{1}{3}} - 1 \right)} \right] \quad (44)$$

where the superscript-zero exchange energy density is from Equation 40 with the appropriate value of α and the superscript 1 represents the analogous expression for a uniform free electron gas. This is known as the local spin density approximation (LSDA).

The relevant theory for the correlation functional is from Vosko, Wilk, and Nusair (VWN). They designed a local functional that is dependent on r_s .

$$\varepsilon_C^i(r_s) = \frac{A}{2} \left\{ \begin{array}{l} \ln \left(\frac{r_s}{r_s + b\sqrt{r_s} + c} \right) + \frac{2b}{\sqrt{4c-b^2}} \tan^{-1} \left(\frac{\sqrt{4c-b^2}}{2\sqrt{r_s} + b} \right) \\ - \frac{bx_0}{x_0^2 + bx_0 + c} \left[\ln \left(\frac{(\sqrt{r_s} - x_0)^2}{r_s + b\sqrt{r_s} + c} \right) + \frac{2(b+2x_0)}{\sqrt{4c-b^2}} \tan^{-1} \left(\frac{\sqrt{4c-b^2}}{2\sqrt{r_s} + b} \right) \right] \end{array} \right\} \quad (45)$$

where there are different sets of empirical constants A, x_0 , b, and c for $i=1$ and $i=0$.

The B3LYP exchange-correlation functional is a hybrid functional and is written as follows:

$$E_{B3LYP}^{XC} = (1-a)E_{LSDA}^X + aE_{HF}^X + b\Delta E_{B88}^X + (1-c)E_{LSDA}^C + cE_{LYP}^C \quad (46)$$

where a, b, and c were optimized to 0.20, 0.72, and 0.81 respectively. These are known as hybrid functionals because they incorporate both HF and DFT exchange terms.

The energy can be expressed in terms of the electron density without determination of the wavefunctions, but it is difficult to obtain high accuracy on the basis

of this approach. The electron density is determined from wavefunctions that are obtained from self consistent field calculations. The theory of Kohn and Sham involves solving the following equation:

$$F\psi = \varepsilon\psi \quad (47)$$

where

$$F(\mathbf{1}) = -\frac{1}{2}\nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} + \sum_j J_j(\mathbf{1}) + V_{xc} \quad (48)$$

and

$$V_{xc} = \frac{\partial E_{xc}}{\partial \rho}. \quad (49)$$

When the Kohn-Sham orbitals ψ_i are obtained, the electron density may be obtained from the sum over the occupied orbitals:

$$\rho = \sum_i |\psi_i|^2 \quad (50)$$

The best known Density Functional Method is Becke's three-parameter hybrid functional with the Lee-Young-Parr correlation functional. This density functional method is available in Gaussian by using the keyword B3LYP in the route section of the input.

Basis Sets

The solution of the Schrödinger equation for many electron molecules requires that the wave functions for the molecular orbitals be approximated as a linear combination of molecular orbitals. These types of wave functions are known as basis sets. The two most commonly used basis sets are slater-type orbitals and gaussian-type orbitals. The methods used in this study contain gaussian-type orbitals. These basis sets

are a sum of gaussian wave functions that define more realistic atomic orbital functions. The 6-31G(d, p) basis set is a fixed linear combination of six primitive gaussians for the inner shell orbitals, a linear combination of three gaussians for the inner part of the valence shell orbital and one gaussian for the outer part of the valence shell orbital. This type of basis set is known as a “double zeta quality” basis function because the outer shell functions are separated into two subsets. Polarization functions are added to this method and are represented by the notation (d, p). The d represents a polarization function that will allow the p orbitals of the carbons to have d orbital characteristics. The p allows the hydrogen orbitals to behave as p type orbitals. Polarization functions are sometimes denoted by the symbol *. Polarization functions are added to the wave function to describe distortions from the spherically symmetric atomic environment of a molecular orbital caused by other atomic centers. The 6-311++G(2d) basis set contains a fixed linear combination of six gaussians for the inner shells, a fixed linear combination of gaussians to describe the inner part of the valence shell and two separate gaussians to represent the outer part of the valence shell. This type of basis set is known as a “triple zeta quality” because the valence orbital functions are separated into three subsets. The (2d) term indicates that two polarization functions have been added to the basis set. Diffuse functions are Gaussian orbitals that have very small α parameters that allow the wave function to extend far from the nucleus. These functions are used for describing weakly bound states and are denoted by the + symbol. The term ++ indicates that two diffuse functions have been included for each valence orbital.

Basis sets may either be restricted or unrestricted basis sets. A molecular system that contains only paired electrons is a closed-shell system. Closed-shell systems are

better modeled with a restricted basis set in which there is only one molecular orbital for each pair of alpha and beta spins. A molecular system that contains unpaired electrons is an open-shell system. An unrestricted method works better when investigating an open-shell system. In this method the alpha and beta electrons are allowed to occupy two different orbitals.

Potential Energy Minima

A potential energy surface describes how the energy of a molecular system changes with a small change in structure. The potential energy surface for a diatomic molecule is a two-dimensional plot of energy versus the internuclear separation of the atoms. Non-linear polyatomic molecules have $3N-6$ degrees of freedom plus one degree of freedom for the energy, where N is the number of atoms in the molecule. The potential energy surface in a normal coordinate system for such a molecule will have as many orthogonal dimensions as the number of degrees of freedom plus an energy dimension. The potential energy surface for a molecule with many nuclei becomes complicated and many local minima and one global minimum exist. Multivariable Calculus states that a minimum of a function is obtained when the first derivative of the function is zero and the second derivative is positive. An energy minima is expressed mathematically when all first derivatives of the electronic energy with respect to the coordinates are zero and the second derivatives are positive; therefore, an optimized structure that yields no imaginary frequencies is a minimum on the potential energy surface. A representative potential energy surface that depicts a reactant that has two minimum energy reaction paths to form Product A and Product B is shown in Figure 9.

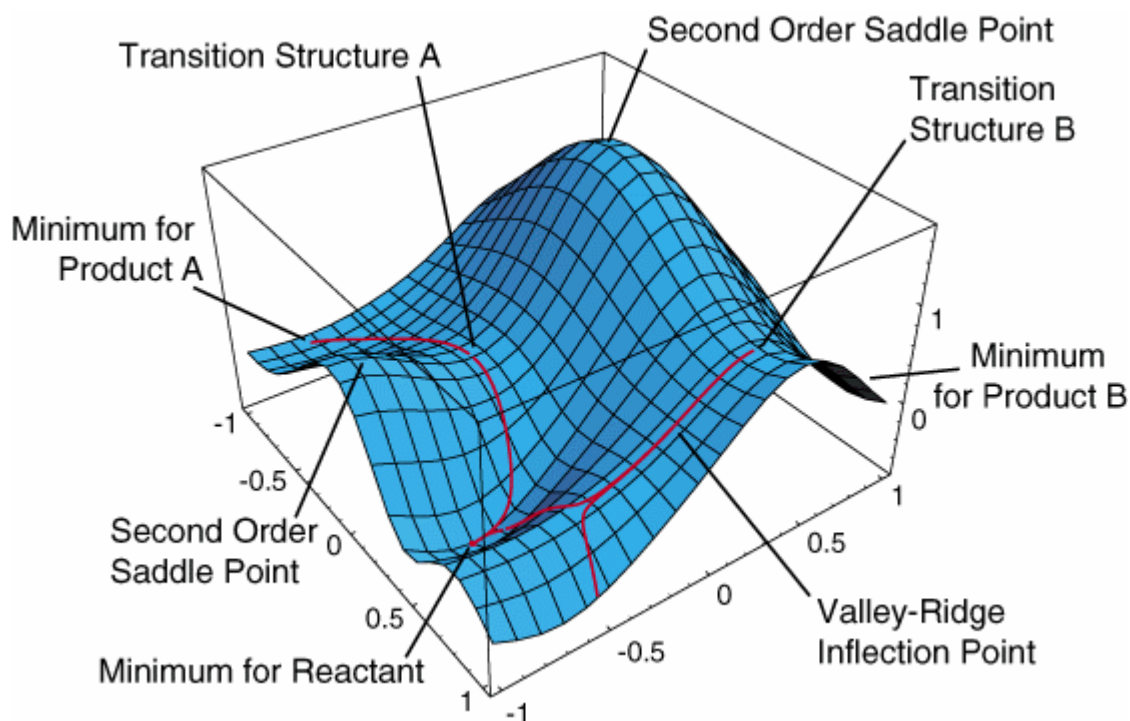


Figure 9. Representative Potential Energy Surface.²³

Transition States

Collision Theory is inadequate for predicting reaction rates of chemical reactions. Transition state theory was developed in the 1930s by Wigner and Pitzer to remedy this dilemma. This theory was later extended by Eyring.²⁴ A transition state is the molecular structure that connects the products and reactants of a chemical reaction. This structure can be considered as a point of unstable equilibrium. An example of unstable equilibrium is a pencil balanced on its sharpened tip where the slightest perturbation will cause the pencil to fall. A transition state occurs when the structure of the system is at a first order saddle point on the potential energy surface. There are two mathematical requirements that must be satisfied to define a transition state. All first derivatives of the electronic energy with respect to the internal coordinates must be zero and one of the second

derivatives must be negative while all other second derivatives must be positive. The second derivatives are the force constants of the molecule and are eigenvalues of the Hessian Matrix which can be used to calculate vibrational spectra data. Consequently, a frequency calculation that yields one imaginary frequency confirms that the structure is a transition state. The program Gaussview was used to animate the imaginary frequency to ensure that the transition state connects the desired equilibrium structures. The QST2 command requires structural data for the reactant and product for a particular chemical reaction. The QST3 function requires data for a product, reactant, and a guess value for what the transition state may be. All atoms in the input of the reactant, product, and guess structures are required to be consistent in these types of calculations. Because Density Functional calculations are much more time consuming than Hartree-Fock calculations, all transition states were found at the HF/6-31G(d, p) level of theory before proceeding to the B3LYP/6-311++G(2d) level of theory.

CHAPTER 3

RESULTS AND DISCUSSION

Computation Details

All quantum mechanical calculations were performed using the Gaussian 03²⁵ program on a Dell workstation, model Optiplex GX 260 with Pentium 4 two GHz processor with 256 MB of memory on Windows XP professional operating system. The molecular structures were input into Gaussian 03 via PCMODEL. The Gaussian program requires a model chemistry, basis set, and the type of calculation to be performed in the route section of the input. The program also requires the initial structure of the molecule in three dimensional coordinates or internal coordinates (z-matrix) as well as the charge and spin multiplicity of the species. Stationary states were optimized and frequency calculations were performed for all minima in the proposed schemes by using the keywords OPT and FREQ respectively. A representative input file for Gaussian 03 in Cartesian Coordinates is shown in Table 1.

Table 1. Representative Input File for Gaussian 03 in Cartesian Coordinates.

```
# HF/6-31G(d,p) Opt Freq

Tol+.

  1  2
C -0.253600  0.957650  0.000000
C -1.315500  0.035050  0.000000
C -1.067600 -1.346850  0.000000
C  0.251600 -1.824450  0.000000
C  1.319100 -0.914150  0.000000
C  1.064000  0.466250  0.000000
C -0.504900  2.442850  0.000000
H -2.358400  0.392650  0.000000
H -1.910300 -2.058550  0.000000
H  0.448400 -2.909750  0.000000
H  2.358400 -1.283550  0.000000
H  1.910200  1.173250  0.000000
H -1.591100  2.687650  0.000000
H -0.051900  2.909750  0.903900
H -0.051900  2.909750 -0.903900
```

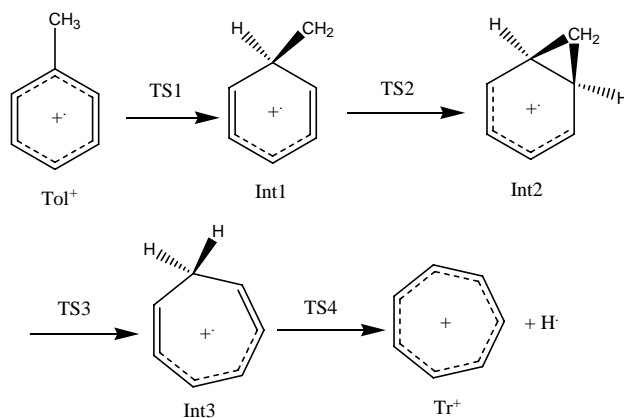
The QST2 and QST3 keywords were used to find the transition structures that connect two minima. Intrinsic reaction coordinate calculations were performed to make sure that each transition structure connects two particular minima. The negative vibrational frequencies of the transition states were animated in Gaussview to see if the motion connected the reactant and products.

Production of the Tropylium Ion

We know from the mass spectrum of toluene that $C_7H_7^+$ is produced in the mass spectrometer. The first scheme that will be discussed is a reaction mechanism that accounts for the formation of Tr^+ . Scheme 3.1 is similar to the mechanism that was proposed by Dewar and Landmann (Scheme 1.1) for the formation of Tr^+ and $H\cdot$ from the

Tol⁺ molecule, but this scheme has the hydrogen cleavage from the cycloheptatriene intermediate.

Scheme 3.1 Formation of Tr⁺ from Tol⁺.



The Tol⁺ ion and all intermediates and transition states in this mechanism have a single positive charge and a spin multiplicity of two. All structures of species, including transition states, for Scheme 3.1 are listed in Appendix A. The product Tr⁺ has a plus one charge and spin multiplicity of one and H[•] has no charge and a spin multiplicity of two. This mechanism begins with a hydrogen migration in the Tol⁺ molecular ion from the methyl group to the ipso position of the six-member ring to form the first intermediate (Int1). Formation of a bond between the methyl carbon and an alpha carbon produces the second intermediate (Int2). This intermediate is composed of a six-member ring and a three-member ring (norcaradienyl ion). Dissociation of the bond common to the rings in a disrotatory fashion produces a cycloheptatriene intermediate (Int3). The last step in the formation of the tropylium ion and atomic hydrogen is a hydrogen cleavage from the former methyl carbon in the cycloheptatriene intermediate. The energetics of this proposed scheme at the HF/6-31G(d, p) and B3LYP/6-311++G(2d) levels of theory are

given in Table 2 and Table 3 respectively and are shown graphically in Figure 10. All energy values have been corrected for zero point energies so that these values may be compared with experimental results. All relative energy values are with respect to the energy of the Tol⁺ ion.

Table 2. Energies of Scheme 3.1 with HF/6-31G(d, p).

| Species | E (hartree) | ΔE (hartree) | ΔE (kcal/mol) |
|----------------------------------|-------------|----------------------|-----------------------|
| Tol ⁺ | -269.353237 | 0.000000 | 0.00000000 |
| TS1 | -269.283089 | 0.070148 | 44.01853641 |
| Int1 | -269.297672 | 0.055565 | 34.86756537 |
| TS2 | -269.295548 | 0.057689 | 36.20039555 |
| Int2 | -269.310254 | 0.042983 | 26.97224084 |
| TS3 | -269.297260 | 0.055977 | 35.12609928 |
| Int3 | -269.323046 | 0.030191 | 18.94513931 |
| TS4 | -269.270569 | 0.082668 | 51.87495535 |
| Tr ⁺ + H [·] | -269.280995 | 0.072242 | 45.33254130 |

Table 3. Energies of Scheme 3.1 with B3LYP/6-311++G(2d).

| Species | E (hartree) | ΔE (hartree) | ΔE (kcal/mol) |
|----------------------------------|-------------|----------------------|-----------------------|
| Tol ⁺ | -271.190114 | 0.000000 | 0.00000000 |
| TS1 | -271.130888 | 0.059226 | 37.16487765 |
| Int1 | -271.133438 | 0.056676 | 35.56472842 |
| TS2 | -271.130512 | 0.059602 | 37.40082122 |
| Int2 | -271.153783 | 0.036331 | 22.79804764 |
| TS3 | -271.141514 | 0.048600 | 30.49696170 |
| Int3 | -271.166518 | 0.023596 | 14.80671416 |
| TS4 | -271.115215 | 0.074899 | 46.99983404 |
| Tr ⁺ + H [·] | -271.120267 | 0.069847 | 43.82965605 |

The relative energies of most of the species in this scheme are consistent between the two methods that were employed. The largest deviation occurs for TS1 where the energy calculated with the Hartree-Fock method is almost seven kcal/mol higher than the energy calculated with density functional theory. It is not certain why the energy of the Hartree-Fock calculation is so much higher than the density functional theory energy while the structural details calculated by both methods are very similar. Conversely, the

energy values calculated for Int1 and TS2 are similar for the two methods but there are significant differences between bond angles calculated by the two methods. These differences might be accounted for by the addition of electron correlation in density functional theory. The structures of Int2, TS3, Int3, TS4, and Tr^+ are similar between the two methods that were employed in this work except that the distances between two atoms that are relevant for a transition state are smaller for the Hartree-Fock calculations. For example, in TS4 the distance between the methylene carbon and the hydrogen that is being ejected is 1.854 angstroms with Hartree-Fock while the distance with density functional theory is 2.030 angstroms.

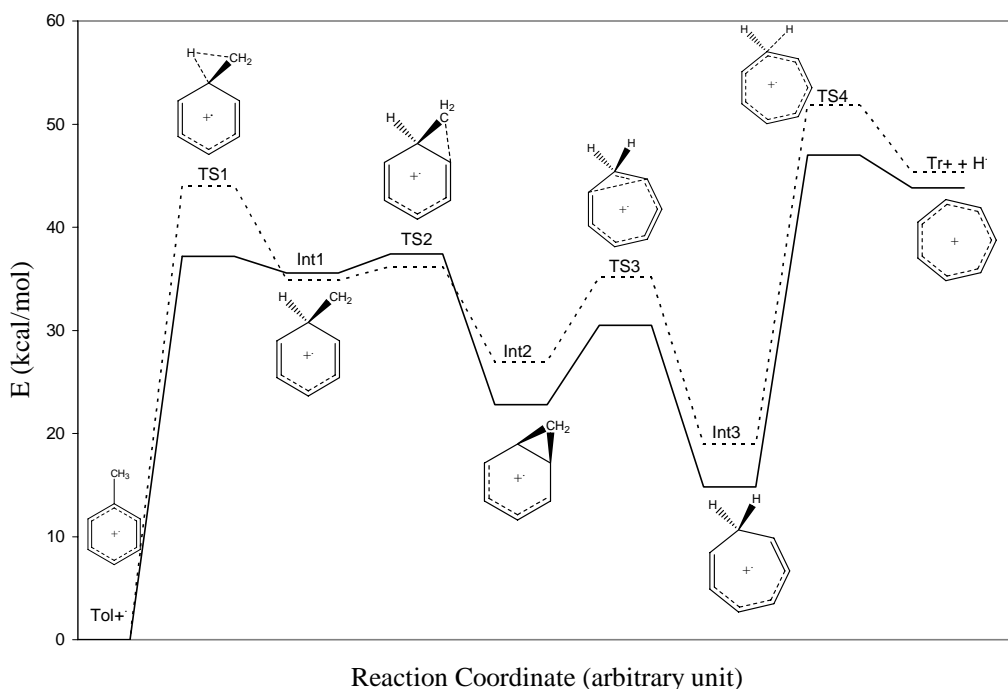


Figure 10. Energies of Scheme 3.1 for the Formation of the Tropylium Ion. The dashed line is with HF/6-31G(d, p) and the solid line is with B3LYP/6-311++G(2d).

The energy values for Scheme 3.1 at the HF/6-31G(d, p) level of theory are compared with literature values in Table 4.

Table 4. Comparison of Our Hartree-Fock Data with Data from the Literature. All values are in kcal/mol.

| Species | Our HF Data | Mindo/3 ¹⁷ | HF/6-31G ^{**21} |
|----------------------------------|-------------|-----------------------|--------------------------|
| Tol ⁺ | 0.0 | 0.0 | 0.0 |
| TS1 | 44.0 | 34.2 | |
| Int1 | 34.9 | 26.3 | |
| TS2 | 36.2 | 29.7 | |
| Int2 | 27.0 | 21.2 | |
| TS3 | 35.1 | 17.6 | |
| Int3 | 18.9 | -5.6 | 18.9 |
| TS4 | 51.9 | | 52.3 |
| Tr ⁺ + H ⁺ | 45.3 | | 45.9 |

The energies that we have calculated are in decent agreement with the values calculated by Dewar and Landmann considering the lack of rigor of the method that they used. The mean absolute error for the heat of formation calculated with MINDO/3 was found to be 11 kcal/mol.²⁶ Taking this into consideration, all values that we have calculated are in good agreement with MINDO/3 except for the values for TS3 and Int3. The energies that we have calculated are in excellent agreement with the energies calculated by Moon, Choe, and Kim at the HF/6-31G^{**} level of theory. The differences between what we have calculated and what Moon *et al* have calculated can be attributed to the polarization functions. We have also completed this mechanism at this level of theory. The energy values for Scheme 3.1 at the B3LYP/6-311++G(2d) level of theory are compared with literature values in Table 5.

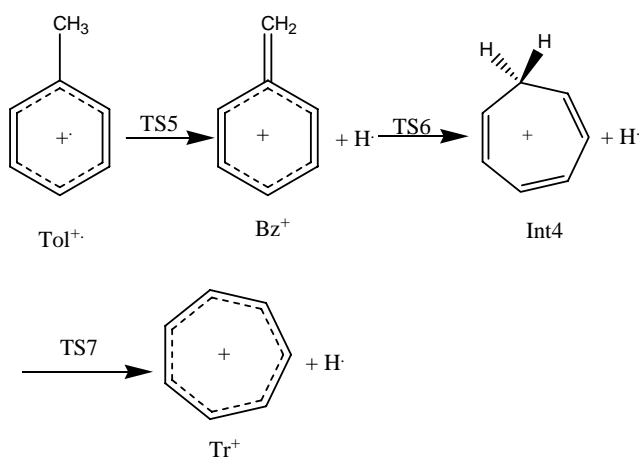
Table 5. Comparison of Our Density Functional Theory Data with Data from the Literature. All values are in kcal/mol.

| Species | Our DFT Data | G2(MP2,SVP) ²¹ | Lifshitz ^{19, 20} |
|----------------------------------|--------------|---------------------------|----------------------------|
| Tol ⁺ | 0.0 | 0.0 | 0.0 |
| TS1 | 37.2 | | 45.0 |
| Int1 | 35.6 | | 33.0 |
| TS2 | 37.4 | | |
| Int2 | 22.8 | | 23.0 |
| TS3 | 30.5 | | 28.0 |
| Int3 | 14.8 | | 17.0 |
| TS4 | 47.0 | 48.2 | 49.0 |
| Tr ⁺ + H ⁺ | 43.8 | 42.0 | 39.0 |

The energies calculated with B3LYP/6-311++(2d) are comparable with the values calculated with G2(MP2, SVP) by Moon, Choe, and Kim. Energies calculated by Lifshitz *et al* are the arithmetic mean of values calculated by PMP3, MP4SDTQ, and QCISD(T)//HF/3-21G. The energies calculated with density functional theory are also comparable with most of the energies calculated by Lifshitz *et al*. TS2 was not found in the literature. Lifshitz's paper states that there is some uncertainty about the exact energy of TS2, but it is definitely considerably lower than the energy of TS1.²⁰ Our data are contrary to this statement in that the TS2 energy is slightly higher than the energy of TS1 with density functional theory. The largest deviations between these two sets of data is for TS1 and Tr⁺ + H⁺. Scheme 3.1 has also been completed with density functional theory.

An alternative process for the formation of the tropylium ion is shown in Scheme 3.2. This scheme is like the scheme proposed by Cone, Dewar, and Landmann (Scheme 1.2), except it begins with the Tol⁺ ion and produces Tr⁺ ion through the Bz⁺ ion.

Scheme 3.2 Formation of Tr^+ from Tol^+ .



All structures of species, including transition states, for Scheme 3.2 are listed in Appendix B. This scheme begins with a hydrogen cleavage from the methyl carbon of Tol^+ to produce the Bz^+ ion and $\text{H} \cdot$ molecule through TS5. TS5 was not calculated in the literature. Even though the barrier is small, a transition state does exist. The hydrogen being ejected must be in the plane of the ring where the coulombic repulsion between the hydrogen and the neighboring nuclei is at a maximum. Formation of a bond between the methyl carbon and the α carbon produces the norcaradienyl cation (Int4). A hydrogen shift from the former methyl carbon to the carbon that was at the ipso position of the six-member ring produces the tropylium ion. The energetics of this Scheme 3.2 is shown graphically in Figure 11. Scheme 3.1 is clearly a better mechanism than Scheme 3.2 for the formation of the tropylium ion because the highest energy barrier is 80 kcal/mol lower in Scheme 3.1. The structures involved in Scheme 3.1 have symmetry properties that maximize the π interactions within the systems. The rings of the structures involved in Scheme 3.2 are slightly contorted which decreases the stability of the π interactions of the systems. A minima for the structure Int^* in Scheme 1.2 proposed by Cone, Dewar,

and Landmann could not be found. Every attempt resulted in minimization to the Bz^+ structure.

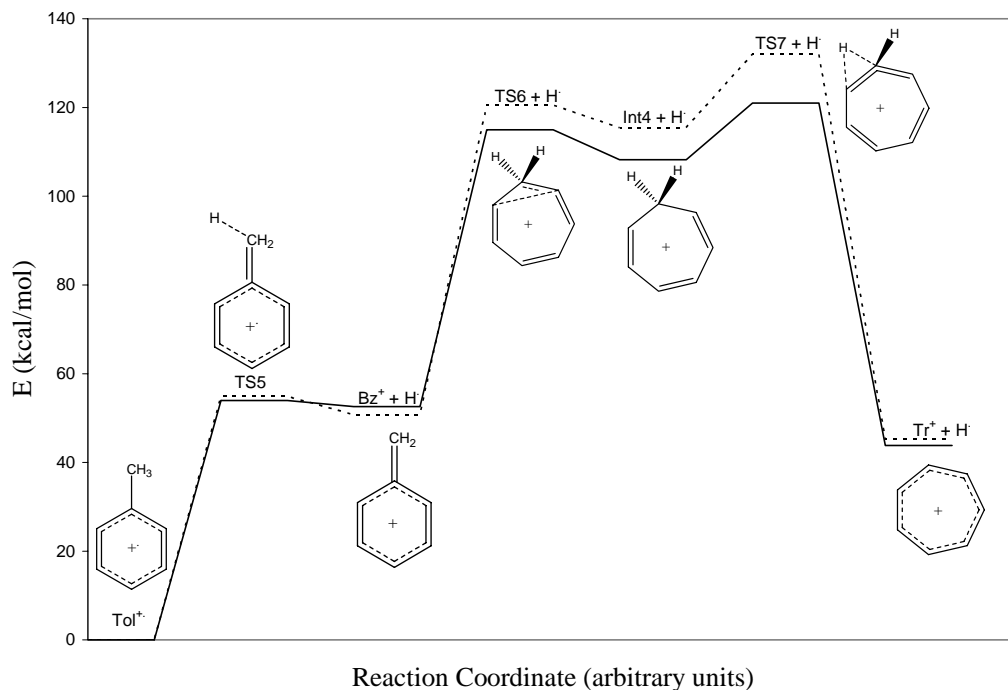


Figure 11. Energies of Scheme 3.2 for the Formation of the Tr^+ ion Through Bz^+ . The dashed line is with HF/6-31G(d, p) and the solid line is with B3LYP/6-311++G(2d).

Table 6 and Table 7 are the energetics of this scheme at HF/6-31G(d, p) and B3LYP/6-311++G(2d) respectively. The energies and structures between these two methods are very similar between the computational methods until we get to TS6. The difference between the energy calculated with Hartree-Fock is about 5 kcal/mol higher than the energy calculated with density functional theory for TS6. This can be accounted for by the structure of this transition state. The bond lengths are similar, but the species calculated with density functional theory has a planar seven-member ring that will

maximize the π interactions while the species calculated with Hartree-Fock has a puckered ring. Int4 is about 7 kcal/mol higher with Hartree-Fock than with density functional theory. The overall structure of the species calculated with Hartree-Fock is similar to the species calculated with density functional theory. It is not certain why this deviation occurs unless it has something to do with electron correlation. The energy of TS7 is almost 11 kcal/mol higher with Hartree-Fock. This deviation might be accounted for by small differences in the structures calculated by the two methods.

Table 6. Energies of Scheme 3.2 with HF/6-31G(d, p).

| Species | E(hartree) | ΔE (hartree) | ΔE (kcal/mol) |
|----------------------------------|-------------|----------------------|-----------------------|
| Tol ⁺ | -269.353237 | 0.000000 | 0.00000000 |
| TS5 | -269.265735 | 0.087502 | 54.90833627 |
| Bz ⁺ + H [·] | -269.272266 | 0.080971 | 50.81007172 |
| TS6 + H [·] | -269.161092 | 0.192145 | 120.57281288 |
| Int4 + H [·] | -269.169328 | 0.183909 | 115.40464464 |
| TS7 + H [·] | -269.142998 | 0.210239 | 131.92696977 |
| Tr ⁺ + H [·] | -269.280995 | 0.072242 | 45.33254130 |

Table 7. Energies of Scheme 3.2 with B3LYP/6-311++G(2d).

| Species | E(hartree) | ΔE (hartree) | ΔE (kcal/mol) |
|----------------------------------|-------------|----------------------|-----------------------|
| Tol ⁺ | -271.190114 | 0.000000 | 0.00000000 |
| TS5 | -271.104115 | 0.085999 | 53.96518949 |
| Bz ⁺ + H [·] | -271.106356 | 0.083758 | 52.55894070 |
| TS6 + H [·] | -271.006836 | 0.183278 | 115.00868614 |
| Int4 + H [·] | -271.017727 | 0.172387 | 108.17448018 |
| TS7 + H [·] | -270.997285 | 0.192829 | 121.00202938 |
| Tr ⁺ + H [·] | -271.120267 | 0.069847 | 43.82965605 |

The energies that we have calculated with Hartree-Fock are compared with literature values in Table 8. The values that we have calculated are not comparable with

the MINDO/3 calculations performed by Cone, Dewar, and Landmann. This is probably because they are looking at the heat of formation of the species without including the data for the hydrogen that are lost at the beginning of the reaction. There was not much found on recent calculations for this mechanism in the literature. The values that were found are in excellent agreement with the values we have calculated.

Table 8. Comparison of our Hartree-Fock Data with Data from the Literature. All values are in kcal/mol.

| Species | Our HF Data | Mindo/3 ¹⁸ | Literature HF ²¹ |
|----------------------------------|-------------|-----------------------|-----------------------------|
| Tol ⁺ | 0.0 | 0.0 | 0.0 |
| TS5 | 54.9 | | |
| Bz ⁺ + H [·] | 50.8 | 8.2 | 51.4 |
| TS* + H [·] | | 25.8 | |
| Int* + H [·] | | 23.7 | |
| TS6 + H [·] | 120.6 | 31.5 | |
| Int4 + H [·] | 115.4 | 28.7 | |
| TS7 + H [·] | 131.9 | 40.9 | |
| Tr ⁺ + H [·] | 45.3 | -16.6 | |

Table 9 is a comparison of our density functional theory with literature values. The small amount of data that was found on this mechanism are in excellent agreement with the values that we have calculated.

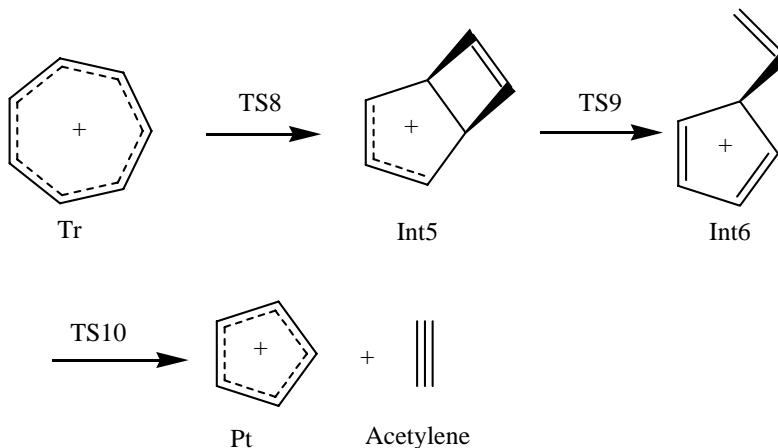
Table 9. Comparison of our Density Functional Theory Data with Data from the Literature. All values are in kcal/mol.

| Species | Our DFT Data | G2(MP2,SVP) ²¹ | Lifshitz ^{19, 20} |
|----------------------------------|--------------|---------------------------|----------------------------|
| Tol ⁺ | 0.0 | 0.0 | 0.0 |
| TS5 | 54.0 | | |
| Bz ⁺ + H [·] | 52.6 | 48.9 | 50.0 |
| TS* + H [·] | | | |
| Int* + H [·] | | | |
| TS6 + H [·] | 115.0 | | |
| Int4 + H [·] | 108.2 | | |
| TS7 + H [·] | 121.0 | | |
| Tr ⁺ + H [·] | 43.8 | | |

Decomposition of the Tropylium Ion

The mass spectrum of toluene shows that $C_5H_5^+$ is produced in the mass spectrometer. A proposed scheme for the decomposition of the Tropylium ion to form $C_5H_5^+$ is shown in Scheme 3.3.

Scheme 3.3 Decomposition of the Tropylium Ion to form $C_5H_5^+$ and acetylene.



All structures of species, including transition states, for Scheme 3.3 are listed in Appendix C. The mechanism begins by forming a bond between two carbon atoms to form an intermediate (Int5) that is a carbocation composed of a five-member ring and a four-member ring. Cleavage of a bond in the four-member ring produces an ethylene substituted pentadiene intermediate (Int6). Breaking another carbon bond in Int6 produces acetylene and a pentylium carbocation. Figure 12 is the potential energy surface of this proposed scheme. Table 10 and Table 11 contain the data calculated for this scheme using HF/6-31G(d, p) and B3LYP/6-311++G(2d).

Table 10. Energies of Scheme 3.3 with HF/6-31G(d, p).

| Species | E(hartree) | ΔE (hartree) | ΔE (kcal/mol) |
|---|-------------|----------------------|-----------------------|
| Tr ⁺ + H [·] | -269.280995 | 0.072242 | 45.3325413 |
| TS8 + H [·] | -269.160090 | 0.193147 | 121.2015774 |
| Int5 + H [·] | -269.201733 | 0.151504 | 95.07019929 |
| TS9 + H [·] | -269.132968 | 0.220269 | 138.2208901 |
| Int6 + H [·] | -269.138147 | 0.215090 | 134.9710184 |
| TS10 + H [·] | -269.125143 | 0.228094 | 143.1311519 |
| C ₅ H ₅ ⁺ + C ₂ H ₂ + H [·] | -269.149778 | 0.203459 | 127.6724554 |

Table 11. Energies of Scheme 3.3 with B3LYP/6-311++G(2d).

| Species | E(hartree) | ΔE (hartree) | ΔE (kcal/mol) |
|---|-------------|----------------------|-----------------------|
| Tr ⁺ + H [·] | -271.120267 | 0.069847 | 43.82965605 |
| TS8 + H [·] | -271.010461 | 0.179653 | 112.7339642 |
| Int5 + H [·] | -271.035678 | 0.154436 | 96.91005714 |
| TS9 + H [·] | -270.967927 | 0.222187 | 139.4244533 |
| Int6 + H [·] | -270.974830 | 0.215284 | 135.0927552 |
| TS10 + H [·] | -270.967926 | 0.222188 | 139.4250808 |
| C ₅ H ₅ ⁺ + C ₂ H ₂ + H [·] | -270.960654 | 0.229460 | 143.9883299 |

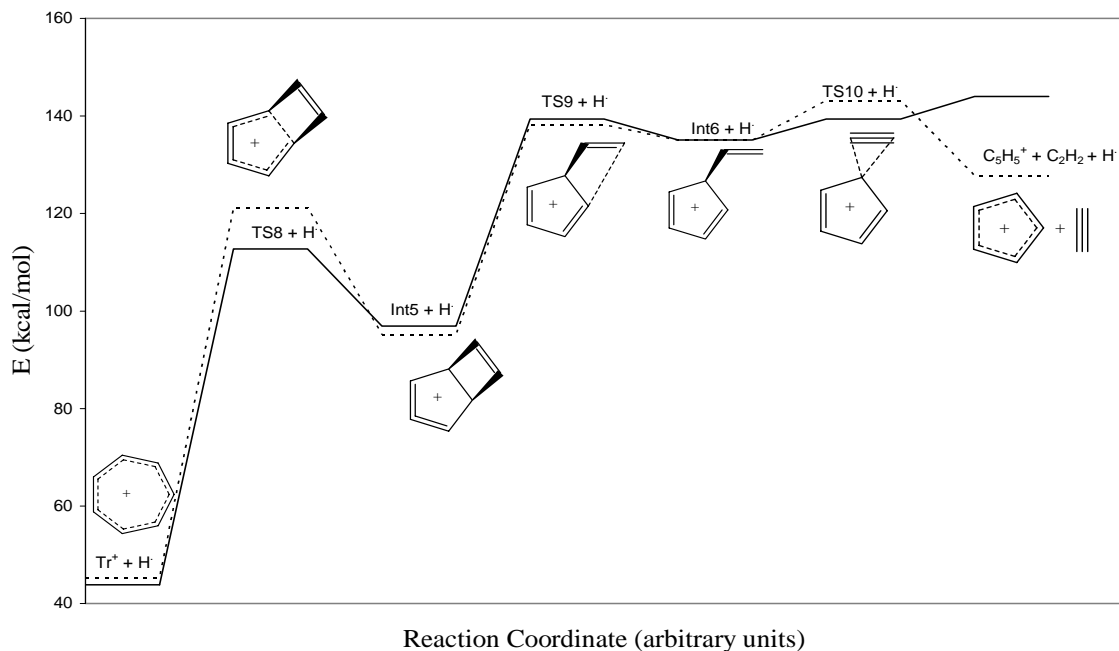


Figure 12. Energies of Scheme 3.3 for the Formation of $C_5H_5^+$. The dashed line is with HF/6-31G(d, p) and the solid line is with B3LYP/6-311++G(2d).

The energy values of most structures are similar between the two methods employed. The energy value for TS8 with HF/6-31G(d, p) is about 9 kcal/mol higher than the energy value calculated with B3LYP/6-311++G(2d). Hartree-Fock calculation of the energy of TS10 is about 4 kcal/mol higher than the value calculated with density functional theory. It is not certain why the energies of the products in Scheme 3.3 are so different between the two methods that were employed. The fact that this mechanism is failing at the last step with density functional theory warrants further study. The $C_5H_5^+$ species could have a different structure from what has been proposed or a different transition state for this step could exist.

Comparison of Data with Experimental Results

The fact that all of these calculations are producing results is wonderful if these values are comparable with experimental values. Consequently, it is necessary to compare some of our calculated values with some experimental results. In order to achieve this, calculations for normal toluene have been performed with both Hartree-Fock and density functional theory. The appearance energies (AE) of Tr^+ and Bz^+ can be determined from their respective highest energy barriers along the minimum energy reaction path. Table 12 contains the energy calculated for normal toluene, Tol^+ , and the highest energy barriers along the minimum energy reaction paths that produce Tr^+ and Bz^+ at the HF/6-31G(d, p) level of theory.

Table 12. Data Calculated with HF/6-31G(d, p) for the Purpose of Comparison with

Experimental Results.

| Species | E (hartree) | ΔE (hartree) | ΔE (eV) |
|----------------|-------------|----------------------|-----------------|
| Normal toluene | -269.617543 | 0.000000 | 0.000000 |
| Tol^+ | -269.353237 | 0.264306 | 7.192189 |
| TS4 | -269.270569 | 0.346974 | 9.441718 |
| TS5 | -269.265735 | 0.351808 | 9.573259 |

One of the more recent experimental determinations of the ionization potential (IP) of toluene to Tol^+ at zero degrees Kelvin yields: $\text{IP}=8.8276\pm 0.0006$ eV.²⁷

Calculating the percent relative error for IP (% R. E. IP) yields the following:

$$\% \text{ R. E. IP} = \frac{|7.19189\text{eV} - 8.8276\text{eV}|}{8.8276\text{eV}} * 100\% = 18.5295\% .$$

The value for IP calculated with Hartree-Fock is not in good agreement with experimental results. Another recent publication provides the data to calculate the appearance energy (AE) of C_7H_7^+ . This publication reports the critical energy (E_0) to be

2.11 eV and the intrinsic kinetic shift (IS) due to radiative decay in the infrared region to 0.19 eV.²⁸ With this data it is possible to calculate the AE of C₇H₇⁺ from the following formula:

$$AE = IP + E_0 + IS = 11.13 \text{ eV.}$$

After adding the intrinsic kinetic shift to my calculated data, the percent relative error for the appearance energies of both Tr⁺ (% R. E. Tr⁺) and Bz⁺ (% R. E. Bz⁺) are as then calculated respectively as follows:

$$\% \text{ R. E. Tr}^+ = \frac{|9.63172eV - 11.13eV|}{11.13eV} * 100\% = 13.46\%$$

$$\% \text{ R. E. Bz}^+ = \frac{|9.76326eV - 11.13eV|}{11.13eV} * 100\% = 12.28\%$$

These values calculated at the Hartree-Fock level of theory are not in good agreement with experimental values. These are good examples of how Hartree-Fock can sometimes fail when describing chemical processes.

Table 13 contains the energy calculated for normal toluene, Tol⁺ and the highest energy barriers along the minimum energy reaction paths that produce Tr⁺ and Bz⁺ at the B3LYP/6-311G++(2d) level of theory.

Table 13. Data Calculated with B3LYP/6-311G++(2d) for the Purpose of Comparison with Experimental Results.

| Species | E (hartree) | ΔE (hartree) | ΔE (eV) |
|------------------|-------------|--------------|-----------|
| Normal toluene | -271.505676 | 0.000000 | 0.000000 |
| Tol ⁺ | -271.190114 | 0.315562 | 8.586947 |
| TS4 | -271.115215 | 0.390461 | 10.625069 |
| TS5 | -271.104115 | 0.401561 | 10.927117 |

Calculating the percent relative error for the ionization potential for density functional theory yields the following:

$$\% \text{ R. E. IP} = \frac{|8.586947eV - 8.8276eV|}{8.8276eV} * 100\% = 2.73\% .$$

After adding the experimental data for the intrinsic kinetic shift, the percent relative error for the appearance energies of Tr^+ and Bz^+ are respectively shown:

$$\% \text{ R. E. Tr}^+ = \frac{|10.815069eV - 11.13eV|}{11.13eV} * 100\% = 2.83\%$$

$$\% \text{ R. E. Bz}^+ = \frac{|11.117117eV - 11.13eV|}{11.13eV} * 100\% = 0.12\% .$$

The values calculated with density functional theory are in excellent agreement with the experimentally determined ionization potentials as well as the appearance energies of Tr^+ and Bz^+ .

Summary of Results and Future Work

Figure 13 is the overall potential energy surface calculated in this work. Most of the structures calculated with density functional theory have relative energies that are lower than the energies of the structures calculated with Hartree-Fock. This is probably a result of the electron correlation that included in density functional theory.

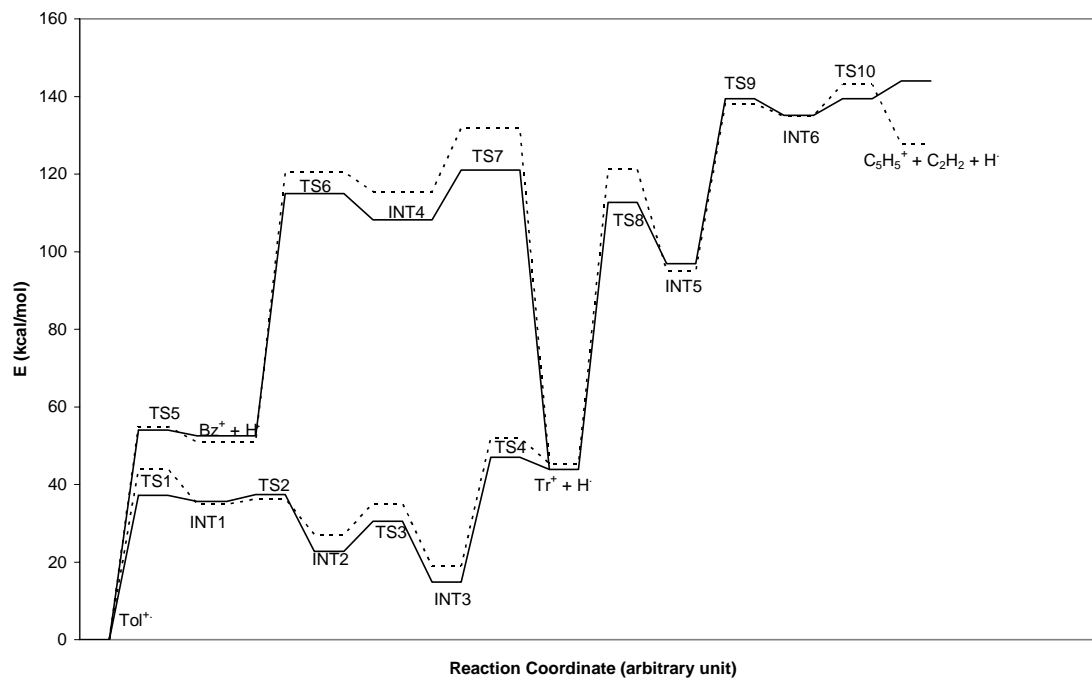


Figure 13. Overall Potential Energy Surface Calculated in this Study.

Future work for this system could be the investigation of alternative mechanisms for the production of $C_5H_5^+$, whether it be a mechanism that produces the structure proposed in this work or some other $C_5H_5^+$ isomer. Another minima and transition state between Bz^+ and Int4 in Scheme 3.2 warrants further study. Mechanisms that could account for the production of $C_5H_3^+$, $C_4H_3^+$, and $C_3H_3^+$ (or possibly $C_6H_6^{++}$) should also be investigated.

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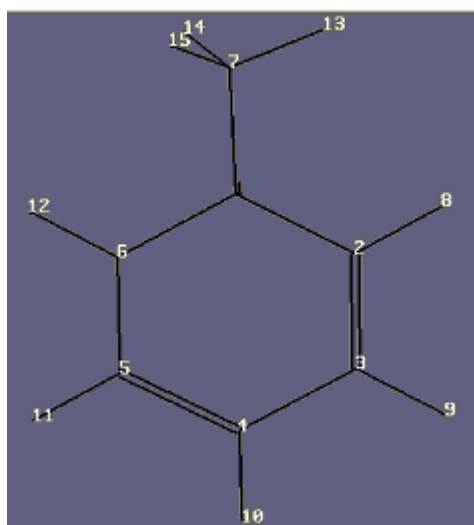
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APPENDICES

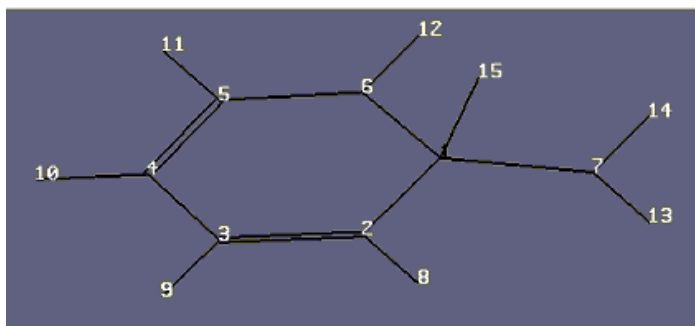
APPENDIX A: Structural Details of Scheme 3.1

Structural Details (Cartesian Coordinates) of Scheme 3.1 with HF/6-31G(d, p).



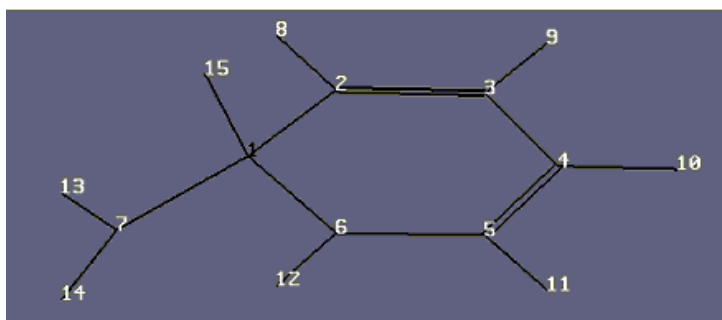
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|---|-----------|-----------|-----------|
| C | 0.013789 | 0.959782 | 0.000000 |
| C | -1.229527 | 0.267431 | 0.000000 |
| C | -1.245023 | -1.089746 | 0.000000 |
| C | -0.021873 | -1.826665 | 0.000000 |
| C | 1.222435 | -1.160251 | 0.000000 |
| C | 1.246915 | 0.203053 | 0.000000 |
| C | 0.078522 | 2.446760 | 0.000000 |
| H | -2.142460 | 0.832701 | 0.000000 |
| H | -2.176773 | -1.625027 | 0.000000 |
| H | -0.055993 | -2.900741 | 0.000000 |
| H | 2.134479 | -1.726748 | 0.000000 |
| H | 2.176773 | 0.742326 | 0.000000 |
| H | -0.901401 | 2.900740 | 0.000000 |
| H | 0.631695 | 2.784310 | 0.873398 |
| H | 0.631695 | 2.784310 | -0.873398 |

Tol⁺



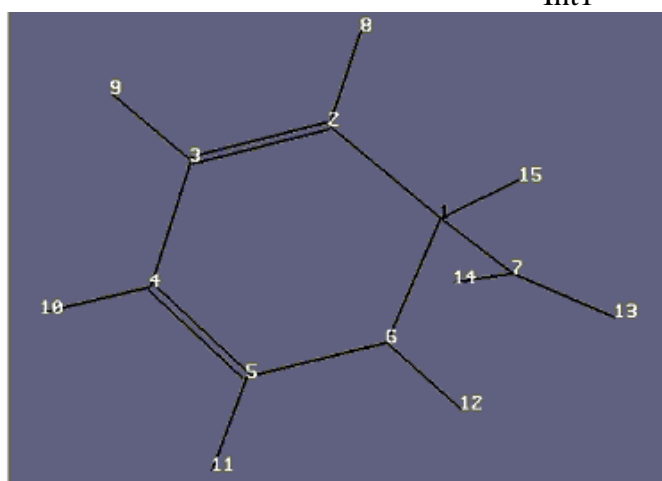
| | | | |
|---|-----------|-----------|-----------|
| C | 0.944269 | -0.000030 | -0.421236 |
| C | 0.194233 | -1.242843 | -0.468778 |
| C | -1.175503 | -1.225953 | -0.514907 |
| C | -1.862815 | -0.000072 | -0.546866 |
| C | -1.175439 | 1.225929 | -0.514968 |
| C | 0.194160 | 1.242870 | -0.468504 |
| C | 2.395759 | 0.000023 | -0.670627 |
| H | 0.734292 | -2.171873 | -0.436019 |
| H | -1.723289 | -2.149038 | -0.534480 |
| H | -2.936668 | -0.000010 | -0.585782 |
| H | -1.723393 | 2.148918 | -0.534539 |
| H | 0.734231 | 2.171872 | -0.435421 |
| H | 2.936669 | -0.926548 | -0.643872 |
| H | 2.936407 | 0.926783 | -0.645509 |
| H | 1.350314 | -0.001049 | 0.670628 |

TS1



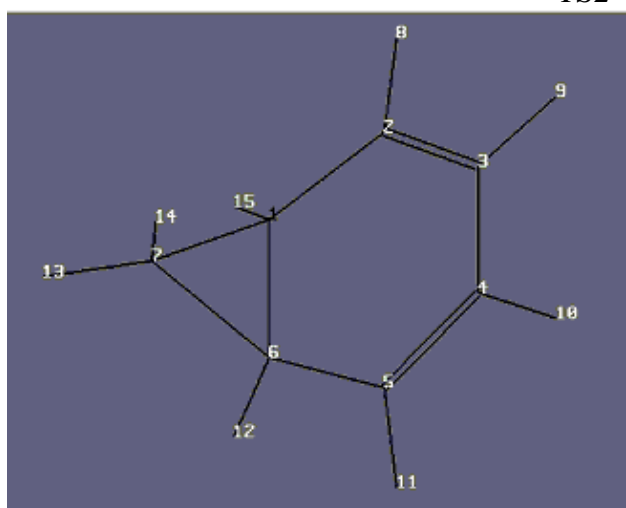
| | | | |
|---|-----------|-----------|-----------|
| C | -0.998433 | 0.000036 | -0.092247 |
| C | -0.215246 | 1.246550 | -0.270629 |
| C | 1.118586 | 1.240210 | -0.495652 |
| C | 1.776540 | 0.000318 | -0.610694 |
| C | 1.118936 | -1.239677 | -0.495414 |
| C | -0.214964 | -1.246319 | -0.270348 |
| C | -2.309286 | 0.000040 | -0.850761 |
| H | -0.748221 | 2.177645 | -0.185746 |
| H | 1.674424 | 2.151972 | -0.600652 |
| H | 2.836940 | 0.000425 | -0.798691 |
| H | 1.675042 | -2.151338 | -0.599900 |
| H | -0.747641 | -2.177646 | -0.185812 |
| H | -2.836940 | 0.924799 | -0.983821 |
| H | -2.834062 | -0.925517 | -0.989391 |
| H | -1.239787 | 0.000256 | 0.989391 |

Int1



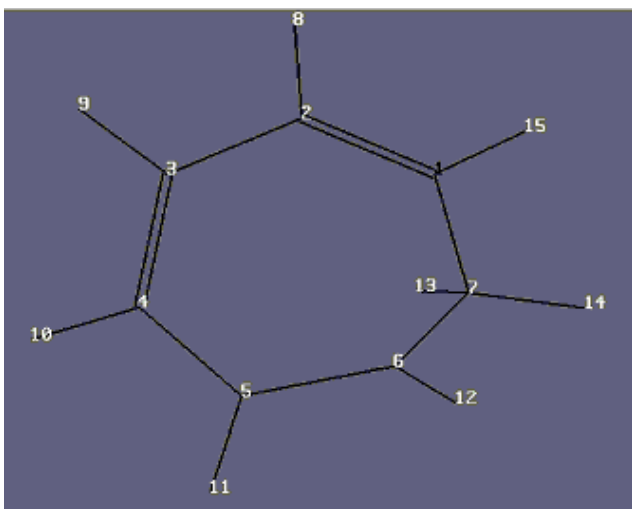
| | | | |
|---|-----------|-----------|-----------|
| C | 0.934453 | -0.312857 | -0.691374 |
| C | -0.103019 | -1.358904 | -0.490273 |
| C | -1.367146 | -1.035035 | -0.107963 |
| C | -1.730182 | 0.326002 | 0.055587 |
| C | -0.847430 | 1.365448 | -0.206050 |
| C | 0.425450 | 1.072539 | -0.659172 |
| C | 1.773407 | -0.089439 | 0.567554 |
| H | 0.187619 | -2.385657 | -0.619149 |
| H | -2.103124 | -1.797741 | 0.063492 |
| H | -2.730230 | 0.560792 | 0.374938 |
| H | -1.168545 | 2.385657 | -0.110427 |
| H | 1.094925 | 1.864005 | -0.942828 |
| H | 2.730231 | 0.387864 | 0.479875 |
| H | 1.341007 | -0.250472 | 1.536234 |
| H | 1.579822 | -0.518168 | -1.536234 |

TS2



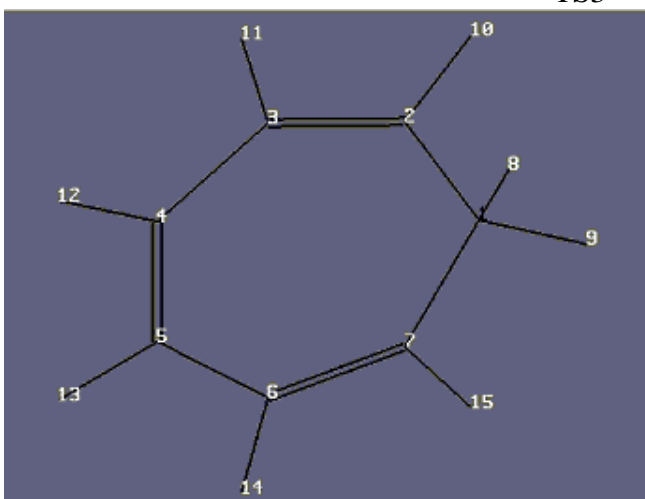
| | | | |
|---|-----------|-----------|-----------|
| C | -0.844865 | 0.760463 | -0.729057 |
| C | 0.444202 | 1.409512 | -0.528630 |
| C | 1.587986 | 0.696493 | -0.193112 |
| C | 1.587986 | -0.696493 | -0.193112 |
| C | 0.444202 | -1.409512 | -0.528630 |
| C | -0.844865 | -0.760462 | -0.729057 |
| C | -1.430090 | 0.000000 | 0.437317 |
| H | 0.506962 | 2.477166 | -0.646003 |
| H | 2.500425 | 1.226541 | 0.009670 |
| H | 2.500425 | -1.226541 | 0.009670 |
| H | 0.506962 | -2.477166 | -0.646003 |
| H | -1.544188 | -1.267144 | -1.368277 |
| H | -2.500424 | 0.000000 | 0.517731 |
| H | -0.894554 | 0.000000 | 1.368277 |
| H | -1.544188 | 1.267144 | -1.368277 |

Int2



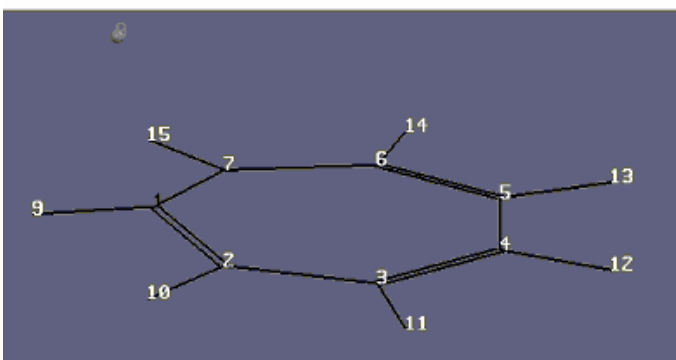
TS3

| | | | |
|---|-----------|-----------|-----------|
| C | 1.170393 | 0.870833 | -0.417164 |
| C | -0.051305 | 1.449468 | -0.485044 |
| C | -1.285884 | 0.872039 | -0.029820 |
| C | -1.546034 | -0.504601 | -0.042207 |
| C | -0.604872 | -1.421786 | -0.476447 |
| C | 0.805451 | -1.112519 | -0.574277 |
| C | 1.483909 | -0.356064 | 0.448911 |
| H | -0.116846 | 2.421081 | -0.944820 |
| H | -2.099894 | 1.543763 | 0.174461 |
| H | -2.547302 | -0.842440 | 0.148822 |
| H | -0.893224 | -2.421082 | -0.755579 |
| H | 1.368475 | -1.494772 | -1.410380 |
| H | 0.994721 | -0.332104 | 1.410380 |
| H | 2.547302 | -0.512738 | 0.517937 |
| H | 2.001820 | 1.313571 | -0.933292 |



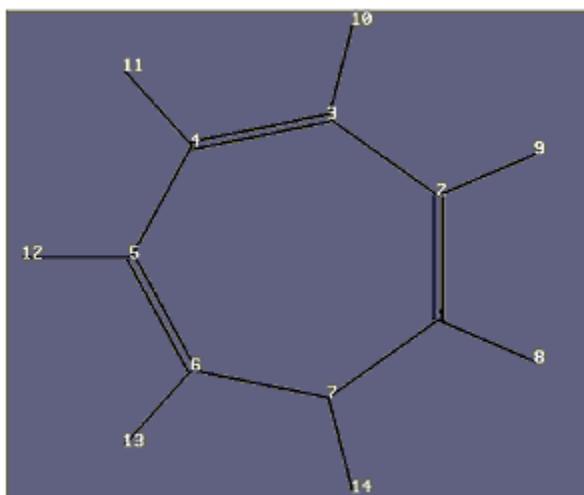
Int3

| | | | |
|---|-----------|-----------|-----------|
| C | 1.727279 | 0.000000 | 0.000000 |
| C | 0.997395 | 1.303482 | 0.000000 |
| C | -0.343292 | 1.588354 | 0.000000 |
| C | -1.429690 | 0.695834 | 0.000000 |
| C | -1.429690 | -0.695834 | 0.000000 |
| C | -0.343292 | -1.588354 | 0.000000 |
| C | 0.997395 | -1.303482 | 0.000000 |
| H | 2.403311 | 0.000000 | 0.857139 |
| H | 2.403311 | 0.000000 | -0.857139 |
| H | 1.654552 | 2.156488 | 0.000000 |
| H | -0.606239 | 2.630938 | 0.000000 |
| H | -2.403311 | 1.153908 | 0.000000 |
| H | -2.403311 | -1.153908 | 0.000000 |
| H | -0.606239 | -2.630938 | 0.000000 |
| H | 1.654552 | -2.156488 | 0.000000 |



TS4

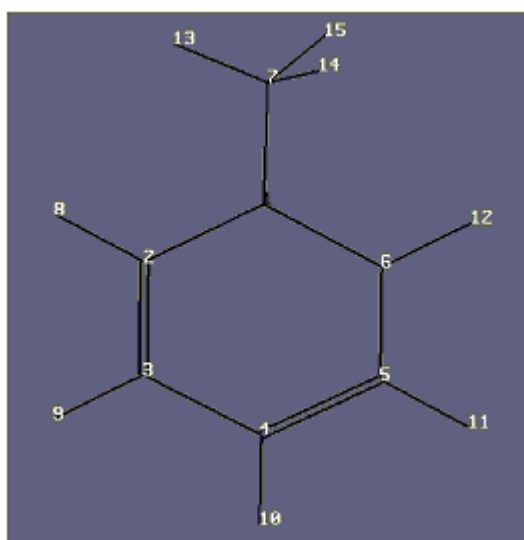
| | | | |
|---|-----------|-----------|-----------|
| C | -1.486111 | 0.000269 | -0.807721 |
| C | -0.858957 | -1.269271 | -0.873722 |
| C | 0.494238 | -1.569363 | -0.823083 |
| C | 1.578114 | -0.694569 | -0.724371 |
| C | 1.578274 | 0.694369 | -0.724425 |
| C | 0.494613 | 1.569432 | -0.823148 |
| C | -0.858651 | 1.269693 | -0.873599 |
| H | -1.970332 | -0.000095 | 0.981951 |
| H | -2.547011 | 0.000418 | -0.981951 |
| H | -1.525337 | -2.110164 | -0.945833 |
| H | 0.744622 | -2.614486 | -0.863835 |
| H | 2.546734 | -1.158862 | -0.665717 |
| H | 2.547011 | 1.158434 | -0.665885 |
| H | 0.745262 | 2.614486 | -0.864003 |
| H | -1.524869 | 2.110759 | -0.945213 |



| | | | |
|---|-----------|-----------|----------|
| C | 1.574247 | -0.694318 | 0.000000 |
| C | 1.574247 | 0.694318 | 0.000000 |
| C | 0.488568 | 1.560118 | 0.000000 |
| C | -0.865252 | 1.251118 | 0.000000 |
| C | -1.467759 | 0.000000 | 0.000000 |
| C | -0.865252 | -1.251118 | 0.000000 |
| C | 0.488568 | -1.560118 | 0.000000 |
| H | 2.543063 | -1.160875 | 0.000000 |
| H | 2.543063 | 1.160875 | 0.000000 |
| H | 0.727846 | 2.608463 | 0.000000 |
| H | -1.535694 | 2.091825 | 0.000000 |
| H | -2.543063 | 0.000000 | 0.000000 |
| H | -1.535694 | -2.091825 | 0.000000 |
| H | 0.727846 | -2.608463 | 0.000000 |

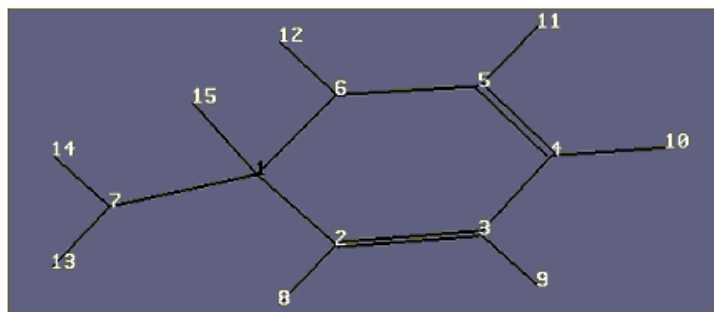
Tr⁺

Structural Details (Cartesian Coordinates) of Scheme 3.1 with B3LYP/6-311++G(2d).



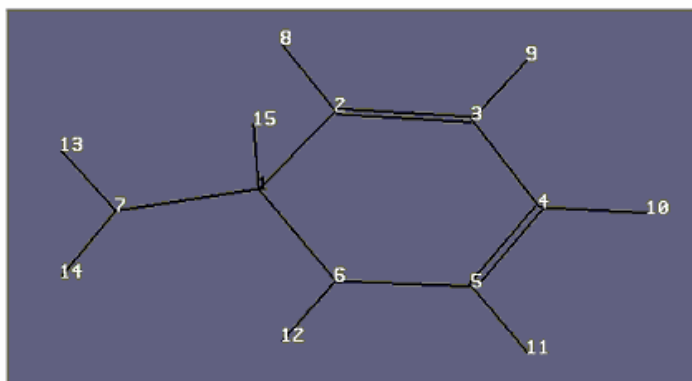
| | | | |
|---|-----------|-----------|-----------|
| C | 0.010135 | 0.970378 | 0.000000 |
| C | -1.231761 | 0.261598 | 0.000000 |
| C | -1.244692 | -1.102986 | 0.000000 |
| C | -0.016104 | -1.820216 | 0.000000 |
| C | 1.225804 | -1.141339 | 0.000000 |
| C | 1.241985 | 0.222462 | 0.000000 |
| C | 0.053372 | 2.442080 | 0.000000 |
| H | -2.156349 | 0.825918 | 0.000000 |
| H | -2.179195 | -1.650164 | 0.000000 |
| H | -0.033867 | -2.904078 | 0.000000 |
| H | 2.147494 | -1.709392 | 0.000000 |
| H | 2.179195 | 0.766955 | 0.000000 |
| H | -0.929577 | 2.904078 | 0.000000 |
| H | 0.623306 | 2.802959 | 0.866998 |
| H | 0.623306 | 2.802959 | -0.866998 |

Tol⁺



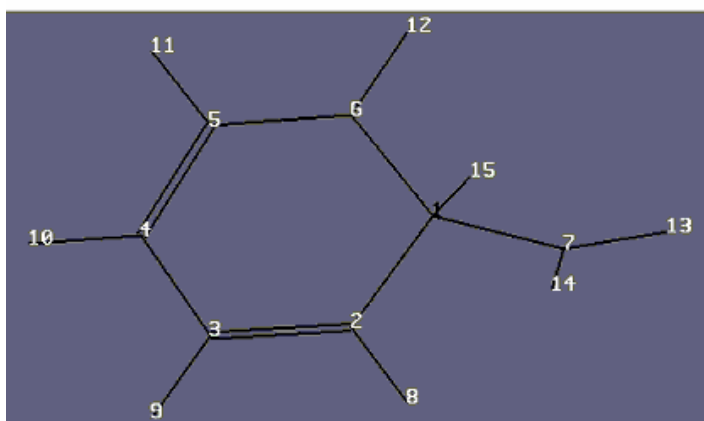
| | | | |
|---|-----------|-----------|-----------|
| C | -0.949736 | -0.000012 | -0.413311 |
| C | -0.192682 | 1.246353 | -0.452758 |
| C | 1.172787 | 1.224091 | -0.506775 |
| C | 1.860549 | 0.000042 | -0.540083 |
| C | 1.172835 | -1.224025 | -0.506683 |
| C | -0.192646 | -1.246334 | -0.452785 |
| C | -2.395414 | 0.000033 | -0.664338 |
| H | -0.734320 | 2.184683 | -0.421934 |
| H | 1.727695 | 2.153597 | -0.530039 |
| H | 2.943200 | 0.000046 | -0.582518 |
| H | 1.727804 | -2.153499 | -0.529729 |
| H | -0.734259 | -2.184682 | -0.422022 |
| H | -2.943184 | 0.931766 | -0.652204 |
| H | -2.943201 | -0.931705 | -0.653611 |
| H | -1.416845 | -0.000248 | 0.664337 |

TS1



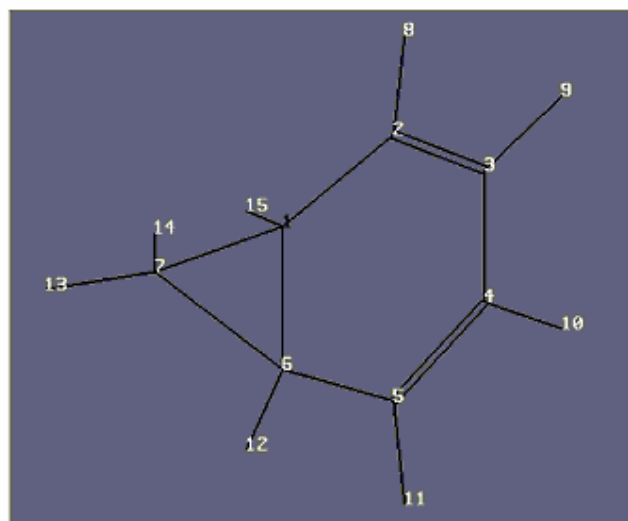
| | | | |
|---|-----------|-----------|-----------|
| C | -0.962751 | 0.000005 | -0.338114 |
| C | -0.189587 | 1.247187 | -0.447956 |
| C | 1.173805 | 1.227710 | -0.545540 |
| C | 1.850921 | -0.000002 | -0.605498 |
| C | 1.173983 | -1.227691 | -0.545651 |
| C | -0.189551 | -1.247215 | -0.447703 |
| C | -2.386229 | -0.000089 | -0.741985 |
| H | -0.731152 | 2.185312 | -0.397228 |
| H | 1.732191 | 2.154289 | -0.591611 |
| H | 2.932018 | 0.000036 | -0.691552 |
| H | 1.732469 | -2.154208 | -0.591810 |
| H | -0.731197 | -2.185312 | -0.396973 |
| H | -2.932018 | 0.929614 | -0.802350 |
| H | -2.931751 | -0.929870 | -0.803367 |
| H | -1.036999 | 0.000060 | 0.803367 |

Int1



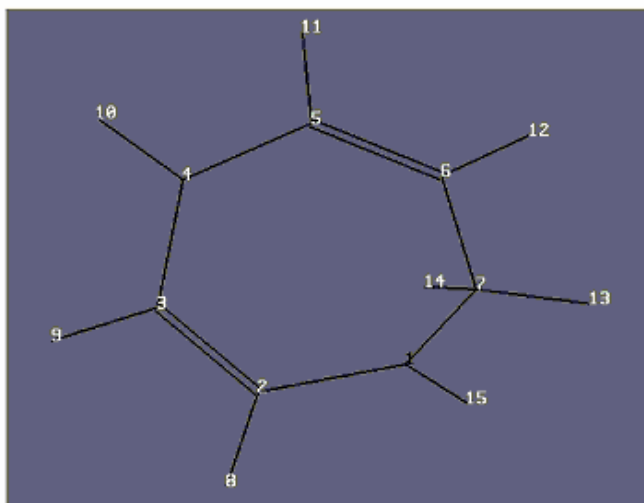
| | | | |
|---|-----------|-----------|-----------|
| C | 0.798204 | -0.000011 | -0.432247 |
| C | 0.021776 | -1.248537 | -0.280353 |
| C | -1.315299 | -1.235071 | -0.006470 |
| C | -1.972179 | 0.000033 | 0.137449 |
| C | -1.315245 | 1.235115 | -0.006433 |
| C | 0.021820 | 1.248551 | -0.280370 |
| C | 2.058284 | -0.000018 | 0.414041 |
| H | 0.558524 | -2.184067 | -0.390899 |
| H | -1.870940 | -2.157158 | 0.108734 |
| H | -3.032981 | 0.000057 | 0.367577 |
| H | -1.870856 | 2.157216 | 0.108815 |
| H | 0.558585 | 2.184067 | -0.390946 |
| H | 3.032981 | 0.000202 | -0.046934 |
| H | 1.967534 | -0.000207 | 1.489689 |
| H | 1.139239 | -0.000039 | -1.489689 |

TS2



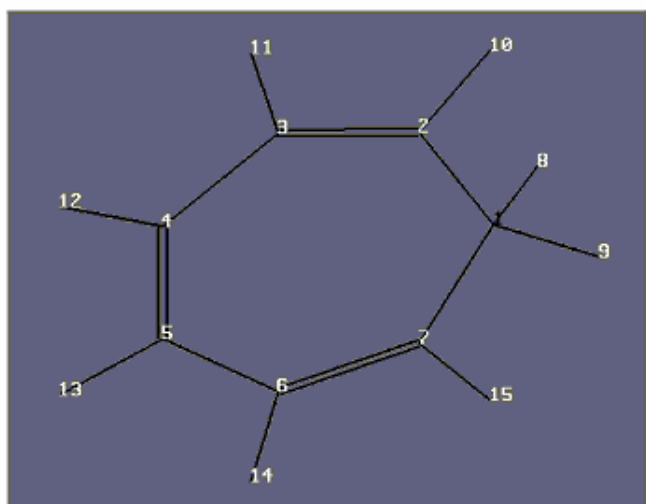
| | | | |
|---|-----------|-----------|-----------|
| C | -0.827680 | 0.760070 | -0.761686 |
| C | 0.439057 | 1.412560 | -0.547085 |
| C | 1.580658 | 0.702328 | -0.209441 |
| C | 1.580658 | -0.702328 | -0.209441 |
| C | 0.439057 | -1.412560 | -0.547085 |
| C | -0.827680 | -0.760070 | -0.761686 |
| C | -1.422559 | 0.000000 | 0.437760 |
| H | 0.489443 | 2.491209 | -0.650879 |
| H | 2.499498 | 1.236346 | 0.000138 |
| H | 2.499498 | -1.236346 | 0.000138 |
| H | 0.489443 | -2.491209 | -0.650879 |
| H | -1.568106 | -1.270505 | -1.365202 |
| H | -2.499498 | 0.000000 | 0.516462 |
| H | -0.869993 | 0.000000 | 1.365202 |
| H | -1.568106 | 1.270505 | -1.365202 |

Int2



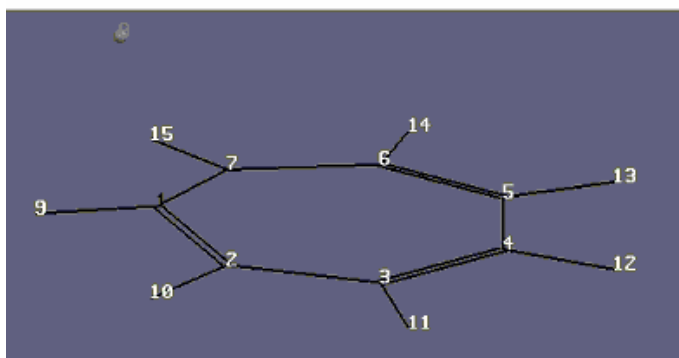
TS3

| | | | |
|---|-----------|-----------|-----------|
| C | 0.807720 | -1.129182 | -0.580554 |
| C | -0.588052 | -1.424574 | -0.497112 |
| C | -1.544398 | -0.521854 | -0.062388 |
| C | -1.302342 | 0.846263 | -0.048934 |
| C | -0.083628 | 1.449618 | -0.511652 |
| C | 1.149783 | 0.884640 | -0.441145 |
| C | 1.477632 | -0.327270 | 0.430630 |
| H | -0.889161 | -2.427216 | -0.790936 |
| H | -2.547894 | -0.877721 | 0.135985 |
| H | -2.123984 | 1.511102 | 0.195596 |
| H | -0.170179 | 2.427216 | -0.976136 |
| H | 1.979609 | 1.319744 | -0.984580 |
| H | 2.547895 | -0.479981 | 0.512054 |
| H | 0.989109 | -0.298621 | 1.400792 |
| H | 1.388428 | -1.541317 | -1.400792 |



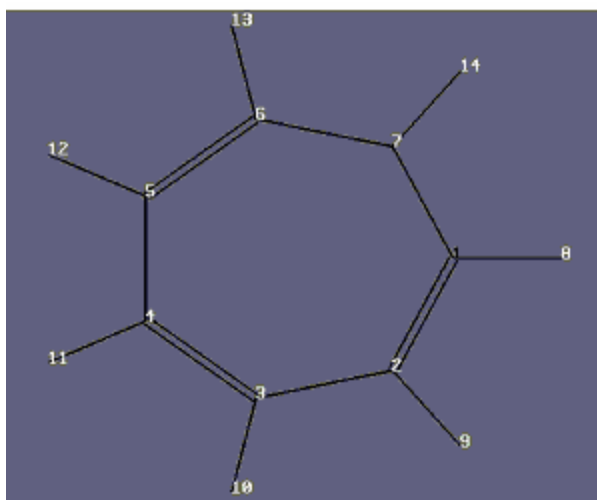
Int3

| | | | |
|---|-----------|-----------|-----------|
| C | 1.700917 | 0.000000 | 0.000000 |
| C | 0.994421 | 1.300814 | 0.000000 |
| C | -0.338541 | 1.590456 | 0.000000 |
| C | -1.433253 | 0.693441 | 0.000000 |
| C | -1.433253 | -0.693441 | 0.000000 |
| C | -0.338541 | -1.590456 | 0.000000 |
| C | 0.994421 | -1.300814 | 0.000000 |
| H | 2.413067 | 0.000000 | 0.845899 |
| H | 2.413067 | 0.000000 | -0.845899 |
| H | 1.667666 | 2.153352 | 0.000000 |
| H | -0.599830 | 2.642946 | 0.000000 |
| H | -2.413066 | 1.159158 | 0.000000 |
| H | -2.413066 | -1.159158 | 0.000000 |
| H | -0.599830 | -2.642946 | 0.000000 |
| H | 1.667666 | -2.153352 | 0.000000 |



TS4

| | | | |
|---|-----------|-----------|-----------|
| C | -1.486111 | 0.000269 | -0.807721 |
| C | -0.858957 | -1.269271 | -0.873722 |
| C | 0.494238 | -1.569363 | -0.823083 |
| C | 1.578114 | -0.694569 | -0.724371 |
| C | 1.578274 | 0.694369 | -0.724425 |
| C | 0.494613 | 1.569432 | -0.823148 |
| C | -0.858651 | 1.269693 | -0.873599 |
| H | -1.970332 | -0.000095 | 0.981951 |
| H | -2.547011 | 0.000418 | -0.981951 |
| H | -1.525337 | -2.110164 | -0.945833 |
| H | 0.744622 | -2.614486 | -0.863835 |
| H | 2.546734 | -1.158862 | -0.665717 |
| H | 2.547011 | 1.158434 | -0.665885 |
| H | 0.745262 | 2.614486 | -0.864003 |
| H | -1.524869 | 2.110759 | -0.945213 |

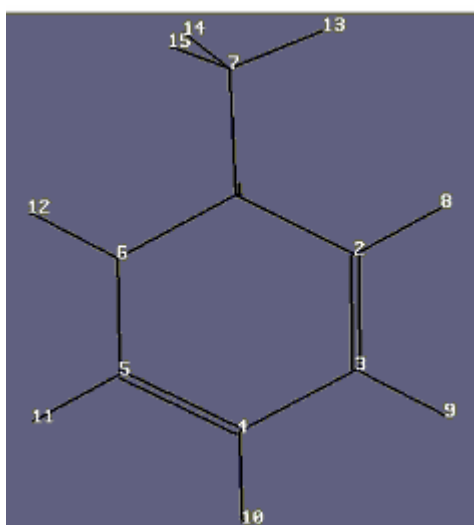


Tr⁺

| | | | |
|---|-----------|-----------|----------|
| C | 1.471476 | 0.000000 | 0.000000 |
| C | 0.867250 | -1.254514 | 0.000000 |
| C | -0.490273 | -1.564386 | 0.000000 |
| C | -1.578933 | -0.696204 | 0.000000 |
| C | -1.578933 | 0.696204 | 0.000000 |
| C | -0.490273 | 1.564385 | 0.000000 |
| C | 0.867250 | 1.254514 | 0.000000 |
| H | 2.556396 | 0.000000 | 0.000000 |
| H | 1.543698 | -2.102740 | 0.000000 |
| H | -0.731737 | -2.622106 | 0.000000 |
| H | -2.556396 | -1.166966 | 0.000000 |
| H | -2.556396 | 1.166966 | 0.000000 |
| H | -0.731737 | 2.622106 | 0.000000 |
| H | 1.543698 | 2.102740 | 0.000000 |

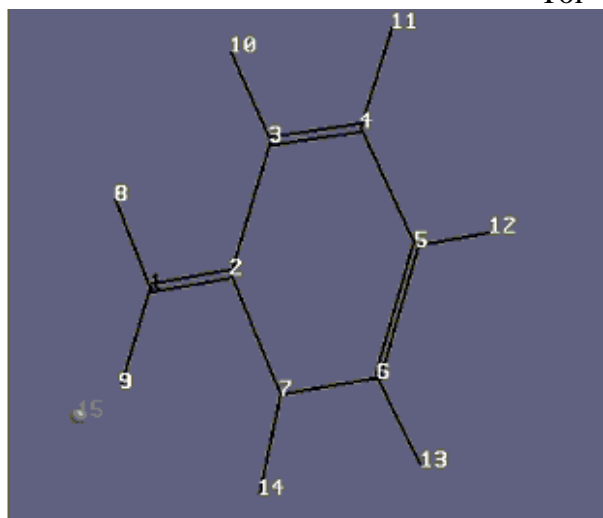
APPENDIX B: Structural Details of Scheme 3.2

Structural details (Cartesian Coordinates) of Scheme 3.2 with HF/6-31G(d, p)



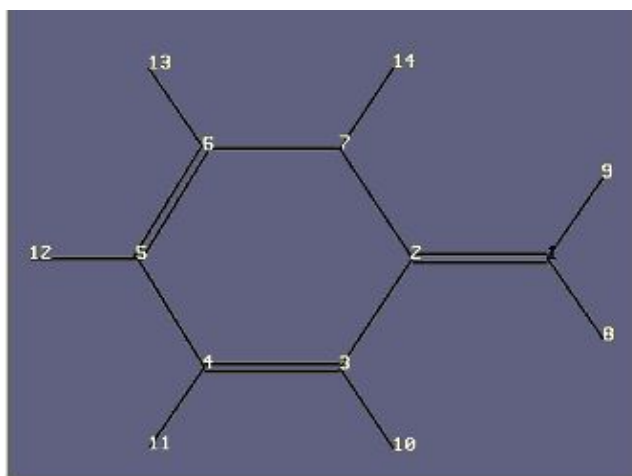
| | | | |
|---|-----------|-----------|-----------|
| C | 0.013789 | 0.959782 | 0.000000 |
| C | -1.229527 | 0.267431 | 0.000000 |
| C | -1.245023 | -1.089746 | 0.000000 |
| C | -0.021873 | -1.826665 | 0.000000 |
| C | 1.222435 | -1.160251 | 0.000000 |
| C | 1.246915 | 0.203053 | 0.000000 |
| C | 0.078522 | 2.446760 | 0.000000 |
| H | -2.142460 | 0.832701 | 0.000000 |
| H | -2.176773 | -1.625027 | 0.000000 |
| H | -0.055993 | -2.900741 | 0.000000 |
| H | 2.134479 | -1.726748 | 0.000000 |
| H | 2.176773 | 0.742326 | 0.000000 |
| H | -0.901401 | 2.900740 | 0.000000 |
| H | 0.631695 | 2.784310 | 0.873398 |
| H | 0.631695 | 2.784310 | -0.873398 |

Tol⁺



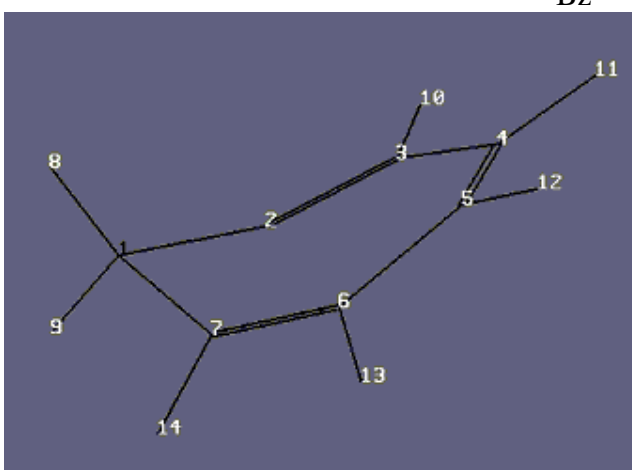
| | | | |
|---|-----------|-----------|-----------|
| C | -2.337024 | 0.017035 | -0.965186 |
| C | -0.963754 | 0.011102 | -0.876512 |
| C | -0.242557 | 1.234612 | -0.803532 |
| C | 1.124929 | 1.226525 | -0.817922 |
| C | 1.825477 | 0.005544 | -0.916011 |
| C | 1.164885 | -1.218385 | -0.965504 |
| C | -0.224996 | -1.243930 | -0.894658 |
| H | -2.888682 | 0.939541 | -0.974421 |
| H | -2.899221 | -0.896895 | -1.032094 |
| H | -0.784959 | 2.161025 | -0.753716 |
| H | 1.672480 | 2.149148 | -0.772547 |
| H | 2.899222 | 0.027150 | -0.962461 |
| H | 1.719546 | -2.133835 | -1.040620 |
| H | -0.765866 | -2.161025 | -1.038959 |
| H | -0.468025 | -1.567273 | 1.040619 |

TS5



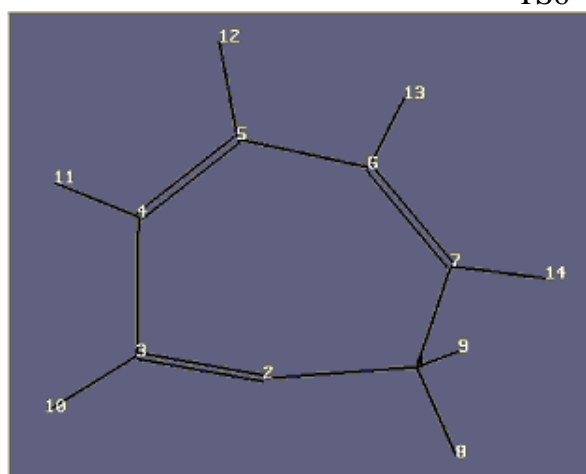
Bz⁺

| | | | |
|---|-----------|-----------|-----------|
| C | 2.315381 | -0.000022 | 0.000409 |
| C | 0.958280 | -0.000021 | -0.000376 |
| C | 0.230696 | -1.238261 | -0.000541 |
| C | -1.131304 | -1.231646 | -0.000040 |
| C | -1.802548 | -0.000055 | 0.000427 |
| C | -1.131323 | 1.231587 | -0.000044 |
| C | 0.230650 | 1.238261 | -0.000400 |
| H | 2.878587 | -0.916741 | 0.000877 |
| H | 2.878499 | 0.916746 | 0.000918 |
| H | 0.776249 | -2.164900 | -0.000367 |
| H | -1.690745 | -2.147237 | 0.000057 |
| H | -2.878587 | -0.000048 | 0.000691 |
| H | -1.690819 | 2.147144 | 0.000125 |
| H | 0.776186 | 2.164901 | -0.000918 |



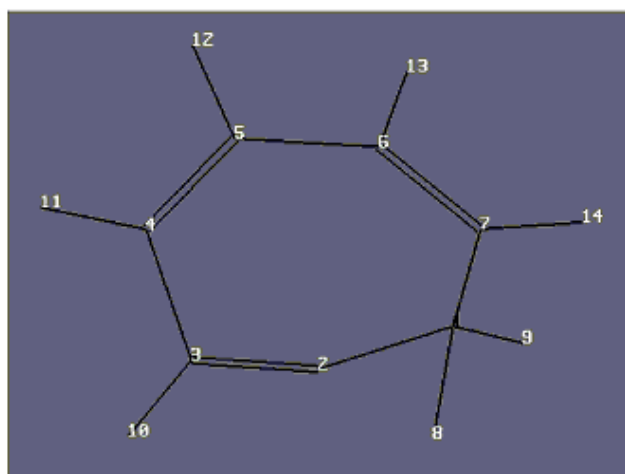
TS6

| | | | |
|---|-----------|-----------|-----------|
| C | -1.766449 | -0.434017 | -0.047443 |
| C | -0.616931 | -1.026519 | -0.580093 |
| C | 0.618803 | -1.416561 | -0.567238 |
| C | 1.685779 | -0.451726 | -0.325106 |
| C | 1.421404 | 0.848259 | -0.171918 |
| C | 0.127777 | 1.450666 | -0.449439 |
| C | -1.105435 | 0.926112 | -0.516264 |
| H | -1.913974 | -0.546567 | 1.017884 |
| H | -2.674190 | -0.534396 | -0.620481 |
| H | 0.816670 | -2.475507 | -0.625699 |
| H | 2.674190 | -0.845994 | -0.188411 |
| H | 2.230718 | 1.523149 | 0.037011 |
| H | 0.184952 | 2.475507 | -0.775655 |
| H | -1.849016 | 1.517206 | -1.017884 |



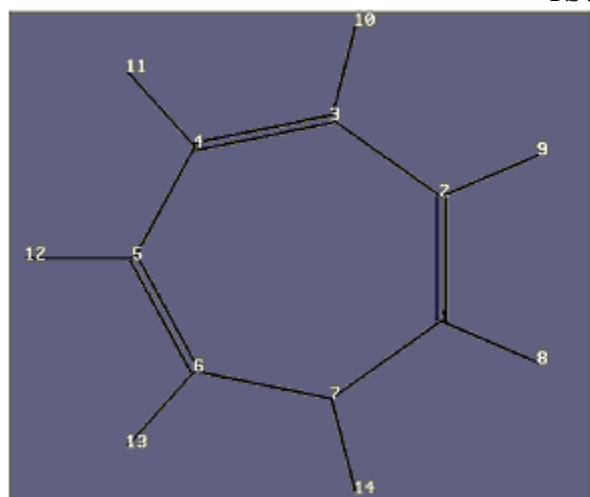
Int4

| | | | |
|---|-----------|-----------|-----------|
| C | 1.061630 | -1.307677 | 0.158574 |
| C | -0.338120 | -1.429186 | -0.189969 |
| C | -1.469409 | -1.112775 | -0.655223 |
| C | -1.601801 | 0.246179 | -0.024863 |
| C | -0.639783 | 1.180117 | -0.008292 |
| C | 0.743408 | 1.095273 | -0.475336 |
| C | 1.525469 | 0.022728 | -0.402792 |
| H | 1.567503 | -2.127955 | -0.352947 |
| H | 1.227894 | -1.434799 | 1.223129 |
| H | -2.222681 | -1.622161 | -1.223130 |
| H | -2.534536 | 0.412371 | 0.483613 |
| H | -0.919691 | 2.127955 | 0.419778 |
| H | 1.170307 | 2.013910 | -0.836924 |
| H | 2.534537 | 0.062072 | -0.771070 |



| | | | |
|---|-----------|-----------|-----------|
| C | 1.318511 | -1.145026 | 0.341006 |
| C | 0.052952 | -1.572962 | 0.090584 |
| C | -1.126292 | -1.315143 | -0.403788 |
| C | -1.594991 | -0.037354 | 0.140360 |
| C | -0.754563 | 1.011654 | 0.182049 |
| C | 0.651705 | 1.112151 | -0.236109 |
| C | 1.619872 | 0.186234 | -0.216036 |
| H | 1.190096 | -2.102381 | -0.506888 |
| H | 1.930828 | -1.612043 | 1.096515 |
| H | -1.674672 | -1.925826 | -1.096514 |
| H | -2.619174 | 0.068722 | 0.447112 |
| H | -1.177688 | 1.948870 | 0.500465 |
| H | 0.942095 | 2.102381 | -0.542790 |
| H | 2.619174 | 0.416735 | -0.534376 |

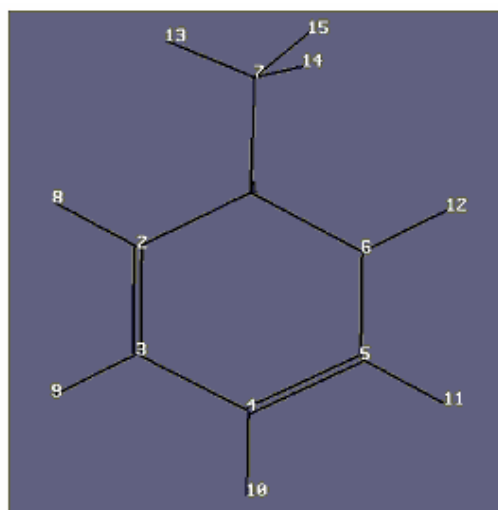
TS7



| | | | |
|---|-----------|-----------|----------|
| C | 1.574247 | -0.694318 | 0.000000 |
| C | 1.574247 | 0.694318 | 0.000000 |
| C | 0.488568 | 1.560118 | 0.000000 |
| C | -0.865252 | 1.251118 | 0.000000 |
| C | -1.467759 | 0.000000 | 0.000000 |
| C | -0.865252 | -1.251118 | 0.000000 |
| C | 0.488568 | -1.560118 | 0.000000 |
| H | 2.543063 | -1.160875 | 0.000000 |
| H | 2.543063 | 1.160875 | 0.000000 |
| H | 0.727846 | 2.608463 | 0.000000 |
| H | -1.535694 | 2.091825 | 0.000000 |
| H | -2.543063 | 0.000000 | 0.000000 |
| H | -1.535694 | -2.091825 | 0.000000 |
| H | 0.727846 | -2.608463 | 0.000000 |

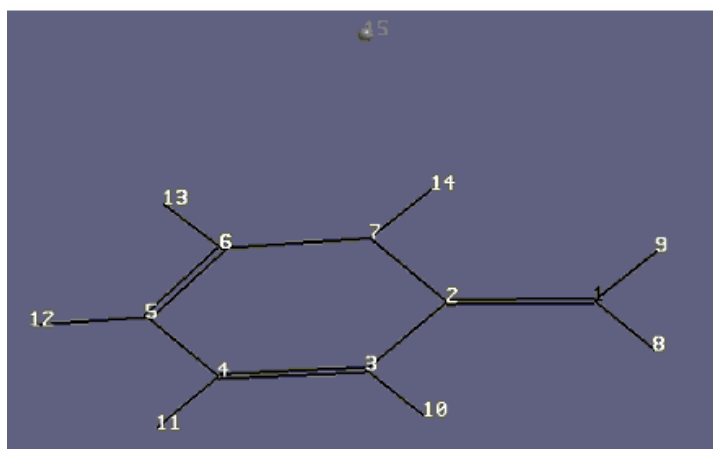
Tr⁺

Structural details (Cartesian Coordinates) of Scheme 3.2 with B3LYP/6-311++G(2d)



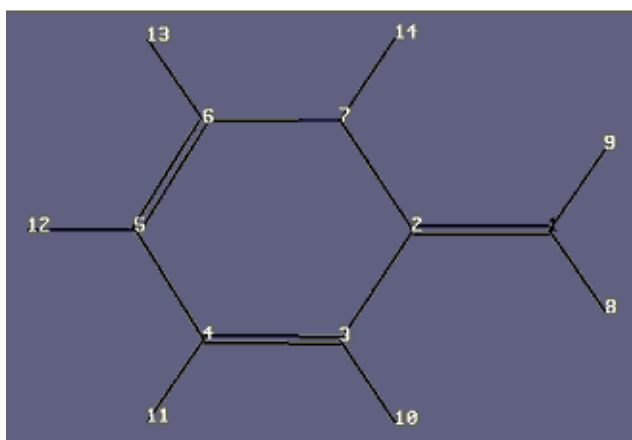
| | | | |
|---|-----------|-----------|-----------|
| C | 0.010135 | 0.970378 | 0.000000 |
| C | -1.231761 | 0.261598 | 0.000000 |
| C | -1.244692 | -1.102986 | 0.000000 |
| C | -0.016104 | -1.820216 | 0.000000 |
| C | 1.225804 | -1.141339 | 0.000000 |
| C | 1.241985 | 0.222462 | 0.000000 |
| C | 0.053372 | 2.442080 | 0.000000 |
| H | -2.156349 | 0.825918 | 0.000000 |
| H | -2.179195 | -1.650164 | 0.000000 |
| H | -0.033867 | -2.904078 | 0.000000 |
| H | 2.147494 | -1.709392 | 0.000000 |
| H | 2.179195 | 0.766955 | 0.000000 |
| H | -0.929577 | 2.904078 | 0.000000 |
| H | 0.623306 | 2.802959 | 0.866998 |
| H | 0.623306 | 2.802959 | -0.866998 |

Tol⁺



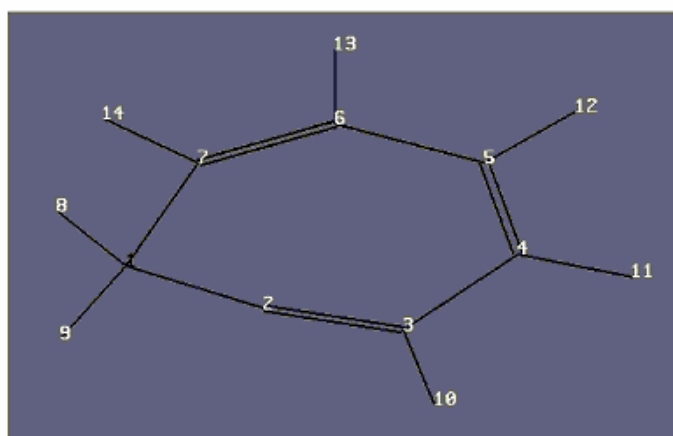
| | | | |
|---|-----------|-----------|-----------|
| C | 2.324749 | -0.022693 | -1.056845 |
| C | 0.963914 | -0.005653 | -0.990771 |
| C | 0.220238 | -1.233790 | -0.898927 |
| C | -1.147622 | -1.207822 | -0.910864 |
| C | -1.817493 | 0.025126 | -1.019993 |
| C | -1.130840 | 1.242194 | -1.088142 |
| C | 0.245782 | 1.245130 | -1.049811 |
| H | 2.882525 | -0.951337 | -1.035935 |
| H | 2.901428 | 0.891140 | -1.137192 |
| H | 0.760173 | -2.171077 | -0.831587 |
| H | -1.718252 | -2.125664 | -0.849759 |
| H | -2.901428 | 0.031286 | -1.053145 |
| H | -1.680971 | 2.171077 | -1.166874 |
| H | 0.804168 | 2.167773 | -1.153512 |
| H | 0.357137 | 1.830352 | 1.166874 |

TS5



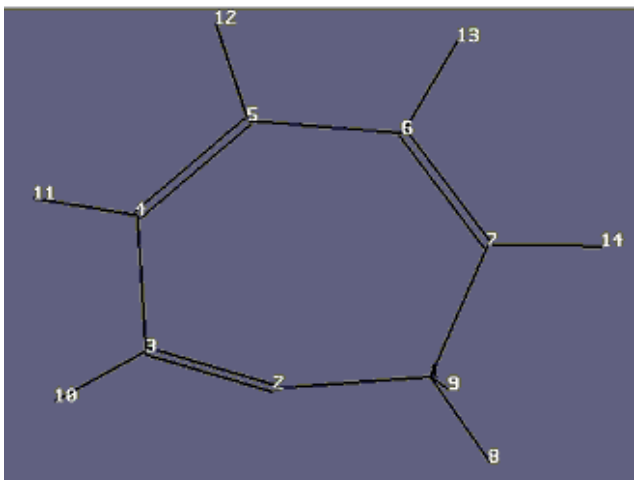
| | | | |
|---|-----------|-----------|-----------|
| C | 2.327096 | 0.000000 | 0.000090 |
| C | 0.963422 | 0.000000 | -0.000128 |
| C | 0.236456 | -1.241481 | -0.000116 |
| C | -1.132293 | -1.230494 | -0.000054 |
| C | -1.810424 | 0.000001 | 0.000001 |
| C | -1.132286 | 1.230500 | -0.000111 |
| C | 0.236456 | 1.241488 | -0.000186 |
| H | 2.895123 | -0.922963 | 0.000300 |
| H | 2.895120 | 0.922967 | 0.000204 |
| H | 0.788095 | -2.174564 | -0.000102 |
| H | -1.694485 | -2.155484 | -0.000039 |
| H | -2.895123 | 0.000008 | 0.000039 |
| H | -1.694488 | 2.155485 | -0.000117 |
| H | 0.788103 | 2.174565 | -0.000301 |

Bz⁺



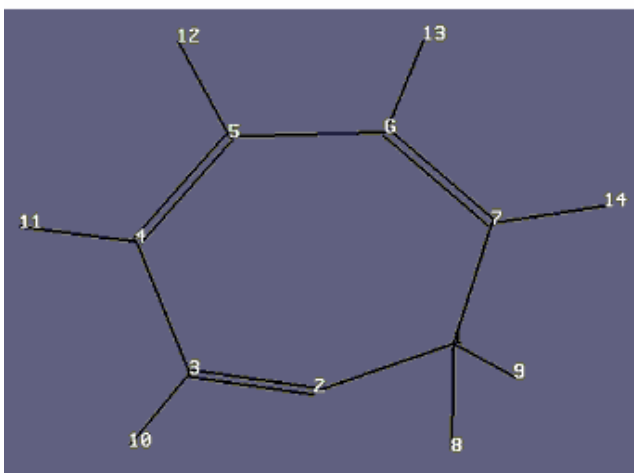
| | | | |
|---|-----------|-----------|-----------|
| C | -1.967792 | -0.546726 | -0.000303 |
| C | -0.728837 | -1.171994 | -0.001733 |
| C | 0.515718 | -1.484278 | -0.018829 |
| C | 1.543415 | -0.436116 | -0.007224 |
| C | 1.240858 | 0.867907 | -0.001219 |
| C | -0.093346 | 1.453770 | -0.010721 |
| C | -1.321389 | 0.923002 | -0.013132 |
| H | -2.566314 | -0.661829 | 0.905530 |
| H | -2.566884 | -0.665967 | -0.905530 |
| H | 0.791896 | -2.538853 | -0.030724 |
| H | 2.566883 | -0.785706 | 0.000729 |
| H | 2.059602 | 1.576722 | 0.007071 |
| H | -0.099462 | 2.538853 | -0.021570 |
| H | -2.175276 | 1.595574 | -0.033932 |

TS6



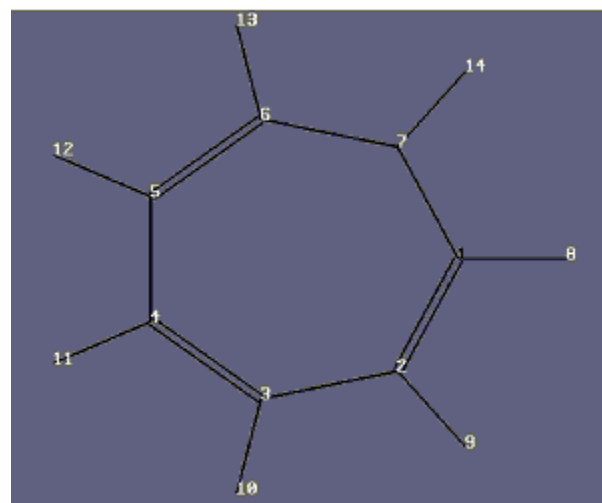
Int4

| | | | |
|---|-----------|-----------|-----------|
| C | 0.996057 | -1.334960 | 0.135814 |
| C | -0.383862 | -1.451783 | -0.223065 |
| C | -1.510006 | -1.078442 | -0.690577 |
| C | -1.589176 | 0.268504 | -0.050913 |
| C | -0.608954 | 1.207830 | -0.042998 |
| C | 0.753952 | 1.085735 | -0.485612 |
| C | 1.502411 | -0.031424 | -0.437795 |
| H | 1.520635 | -2.180201 | -0.337122 |
| H | 1.160697 | -1.460878 | 1.211690 |
| H | -2.315770 | -1.578006 | -1.211689 |
| H | -2.504272 | 0.437293 | 0.510060 |
| H | -0.897465 | 2.180200 | 0.345973 |
| H | 1.235020 | 2.000874 | -0.815302 |
| H | 2.504272 | -0.035700 | -0.851395 |



TS7

| | | | |
|---|-----------|-----------|-----------|
| C | 1.314895 | -1.155743 | 0.305250 |
| C | 0.036696 | -1.594016 | 0.069553 |
| C | -1.151169 | -1.312649 | -0.418640 |
| C | -1.588643 | -0.031839 | 0.110264 |
| C | -0.736944 | 1.032763 | 0.151453 |
| C | 0.650145 | 1.122236 | -0.246110 |
| C | 1.615248 | 0.168300 | -0.239636 |
| H | 1.224159 | -2.121930 | -0.533973 |
| H | 1.941298 | -1.630755 | 1.058185 |
| H | -1.751866 | -1.947777 | -1.058186 |
| H | -2.618971 | 0.086586 | 0.427189 |
| H | -1.181363 | 1.981151 | 0.437150 |
| H | 0.972151 | 2.121930 | -0.521937 |
| H | 2.618971 | 0.390204 | -0.581551 |

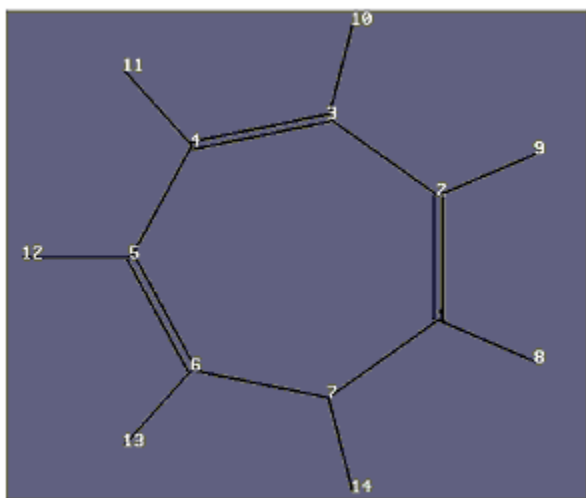


Tr⁺

| | | | |
|---|-----------|-----------|----------|
| C | 1.471476 | 0.000000 | 0.000000 |
| C | 0.867250 | -1.254514 | 0.000000 |
| C | -0.490273 | -1.564386 | 0.000000 |
| C | -1.578933 | -0.696204 | 0.000000 |
| C | -1.578933 | 0.696204 | 0.000000 |
| C | -0.490273 | 1.564385 | 0.000000 |
| C | 0.867250 | 1.254514 | 0.000000 |
| H | 2.556396 | 0.000000 | 0.000000 |
| H | 1.543698 | -2.102740 | 0.000000 |
| H | -0.731737 | -2.622106 | 0.000000 |
| H | -2.556396 | -1.166966 | 0.000000 |
| H | -2.556396 | 1.166966 | 0.000000 |
| H | -0.731737 | 2.622106 | 0.000000 |
| H | 1.543698 | 2.102740 | 0.000000 |

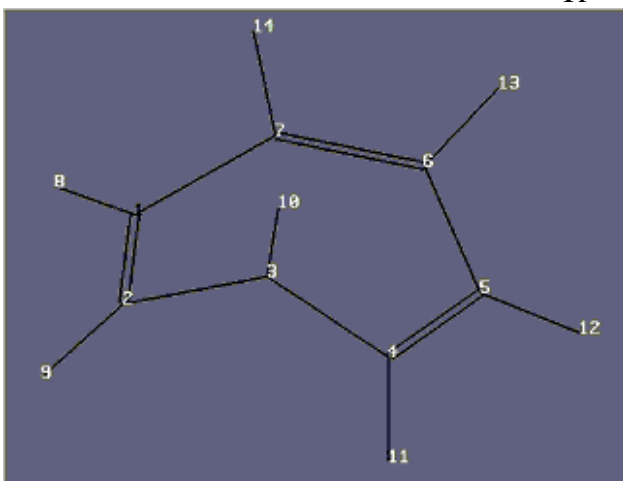
APPENDIX C: Structural Details of Scheme 3.3

Structural details (Cartesian Coordinates) of Scheme 3.3 with HF/6-31G(d, p)



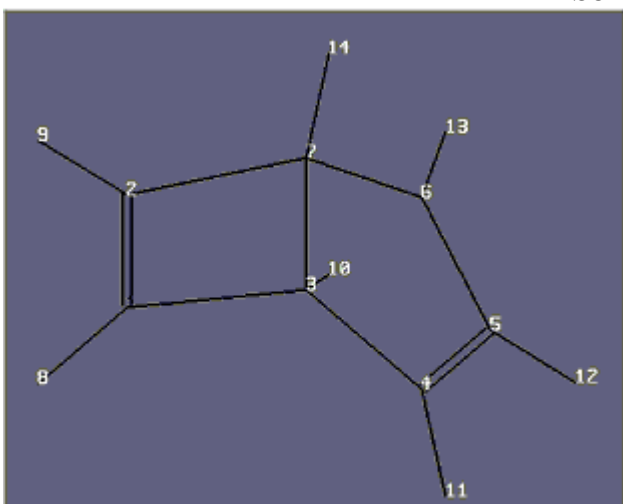
| | | | |
|---|-----------|-----------|----------|
| C | 1.574247 | -0.694318 | 0.000000 |
| C | 1.574247 | 0.694318 | 0.000000 |
| C | 0.488568 | 1.560118 | 0.000000 |
| C | -0.865252 | 1.251118 | 0.000000 |
| C | -1.467759 | 0.000000 | 0.000000 |
| C | -0.865252 | -1.251118 | 0.000000 |
| C | 0.488568 | -1.560118 | 0.000000 |
| H | 2.543063 | -1.160875 | 0.000000 |
| H | 2.543063 | 1.160875 | 0.000000 |
| H | 0.727846 | 2.608463 | 0.000000 |
| H | -1.535694 | 2.091825 | 0.000000 |
| H | -2.543063 | 0.000000 | 0.000000 |
| H | -1.535694 | -2.091825 | 0.000000 |
| H | 0.727846 | -2.608463 | 0.000000 |

Tr⁺



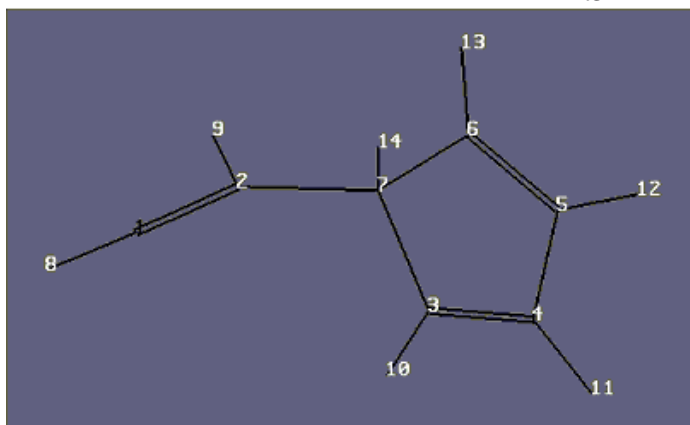
| | | | |
|---|-----------|-----------|-----------|
| C | -1.607277 | 0.678154 | -0.828181 |
| C | -1.738722 | -0.593080 | -0.514565 |
| C | -0.508606 | -0.708355 | 0.303625 |
| C | 0.655452 | -1.156530 | -0.424294 |
| C | 1.511671 | -0.158980 | -0.716169 |
| C | 0.973250 | 1.105845 | -0.350767 |
| C | -0.393114 | 1.275722 | -0.157776 |
| H | -2.281726 | 1.317664 | -1.368580 |
| H | -2.456887 | -1.342551 | -0.783166 |
| H | -0.499339 | -0.543082 | 1.368580 |
| H | 0.694108 | -2.154592 | -0.828187 |
| H | 2.456887 | -0.277867 | -1.211316 |
| H | 1.626782 | 1.929105 | -0.112929 |
| H | -0.641234 | 2.154592 | 0.420413 |

TS8



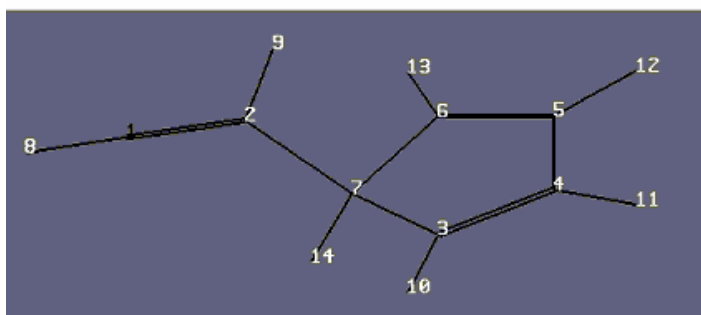
| | | | |
|---|-----------|-----------|-----------|
| C | 1.798221 | 0.657453 | -0.726115 |
| C | 1.798137 | -0.657726 | -0.726046 |
| C | 0.602659 | 0.770658 | 0.239855 |
| C | -0.696744 | 1.119459 | -0.375400 |
| C | -1.445576 | -0.000016 | -0.680718 |
| C | -0.696934 | -1.119557 | -0.375399 |
| C | 0.602572 | -0.770904 | 0.239825 |
| H | 2.408002 | 1.418367 | -1.172090 |
| H | 2.407837 | -1.418739 | -1.172023 |
| H | 0.792064 | 1.292049 | 1.172090 |
| H | -1.004479 | 2.128068 | -0.594046 |
| H | -2.408001 | -0.000081 | -1.153163 |
| H | -1.004841 | -2.128068 | -0.594228 |
| H | 0.792112 | -1.292361 | 1.171992 |

Int5



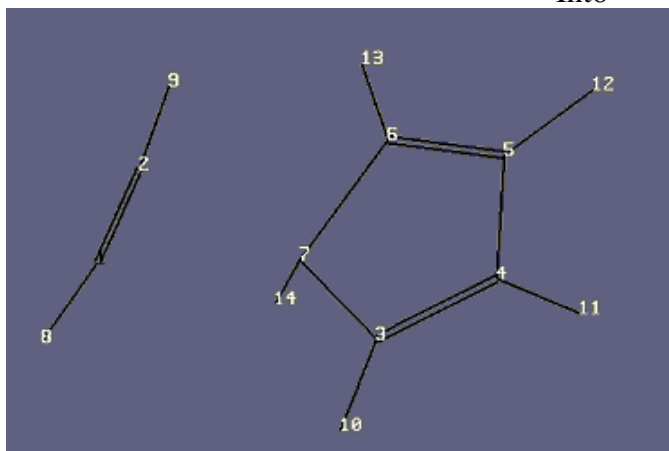
| | | | |
|---|-----------|-----------|-----------|
| C | 2.263057 | 0.308749 | -0.669926 |
| C | 1.190978 | -0.349589 | -0.596205 |
| C | -0.757890 | 1.226333 | -0.172098 |
| C | -1.981981 | 1.026245 | -0.637580 |
| C | -2.263139 | -0.426211 | -0.698197 |
| C | -1.208622 | -1.102160 | -0.267922 |
| C | -0.139803 | -0.117853 | 0.153760 |
| H | 3.192871 | 0.826666 | -0.780127 |
| H | 1.315143 | -1.248356 | -1.210471 |
| H | -0.270335 | 2.165394 | 0.006252 |
| H | -2.681891 | 1.789741 | -0.917722 |
| H | -3.192871 | -0.847940 | -1.027895 |
| H | -1.106660 | -2.165393 | -0.165080 |
| H | 0.098313 | -0.213458 | 1.210472 |

TS9



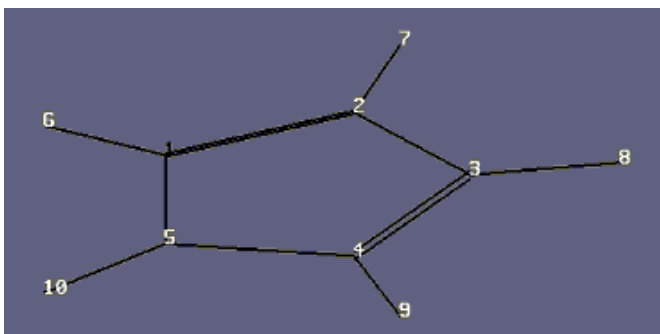
| | | | |
|---|-----------|-----------|-----------|
| C | -2.139952 | -0.001205 | -0.138155 |
| C | -0.919218 | -0.000019 | -0.471736 |
| C | 1.149166 | 1.188220 | 0.187648 |
| C | 2.327816 | 0.738545 | -0.226612 |
| C | 2.327966 | -0.738331 | -0.226559 |
| C | 1.149413 | -1.188180 | 0.187764 |
| C | 0.269814 | -0.000057 | 0.512282 |
| H | -3.169245 | 0.005318 | 0.152826 |
| H | -0.701341 | -0.000206 | -1.535082 |
| H | 0.839043 | 2.206666 | 0.314548 |
| H | 3.168986 | 1.343235 | -0.506370 |
| H | 3.169245 | -1.342875 | -0.506303 |
| H | 0.839432 | -2.206666 | 0.314693 |
| H | -0.088372 | -0.000056 | 1.535082 |

Int6



| | | | |
|---|-----------|-----------|-----------|
| C | 2.051416 | 0.175710 | -0.020430 |
| C | 1.540656 | -0.540094 | 0.802774 |
| C | -0.577186 | 1.166759 | -0.024971 |
| C | -1.761285 | 0.687779 | 0.336708 |
| C | -1.800464 | -0.781492 | 0.120893 |
| C | -0.638201 | -1.198655 | -0.360133 |
| C | 0.221217 | 0.030419 | -0.563713 |
| H | 2.660197 | 0.791254 | -0.638630 |
| H | 1.151266 | -1.157459 | 1.575787 |
| H | -0.240362 | 2.183586 | -0.007533 |
| H | -2.585938 | 1.261999 | 0.712341 |
| H | -2.660197 | -1.396119 | 0.305261 |
| H | -0.348184 | -2.183586 | -0.666287 |
| H | 0.590906 | 0.118688 | -1.575787 |

TS10



| | | | |
|---|----------|-----------|-----------|
| C | 0.000000 | 0.706473 | -1.189594 |
| C | 0.000000 | 1.143110 | 0.154220 |
| C | 0.000000 | 0.000000 | 0.984741 |
| C | 0.000000 | -1.143110 | 0.154220 |
| C | 0.000000 | -0.706473 | -1.189594 |
| H | 0.000000 | 1.336939 | -2.057373 |
| H | 0.000000 | 2.163282 | 0.485628 |
| H | 0.000000 | 0.000000 | 2.057372 |
| H | 0.000000 | -2.163282 | 0.485628 |
| H | 0.000000 | -1.336939 | -2.057373 |

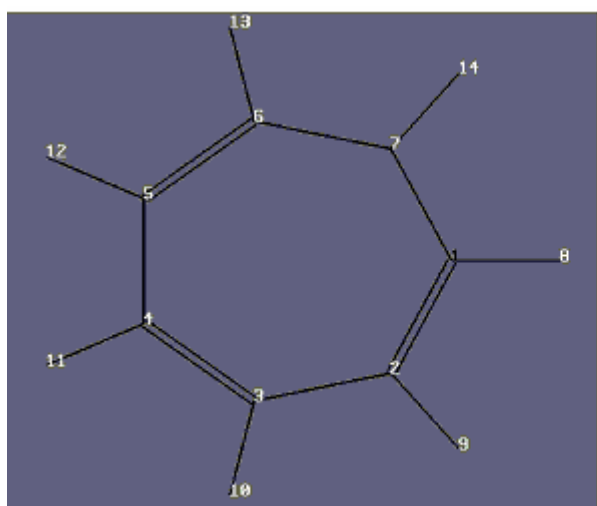
$C_5H_5^+$



| | | | |
|---|-----------|-----------|----------|
| H | 0.000394 | -1.649919 | 0.000000 |
| C | 0.000192 | -0.593042 | 0.000000 |
| C | 0.000192 | 0.593032 | 0.000000 |
| H | -0.000394 | 1.649919 | 0.000000 |

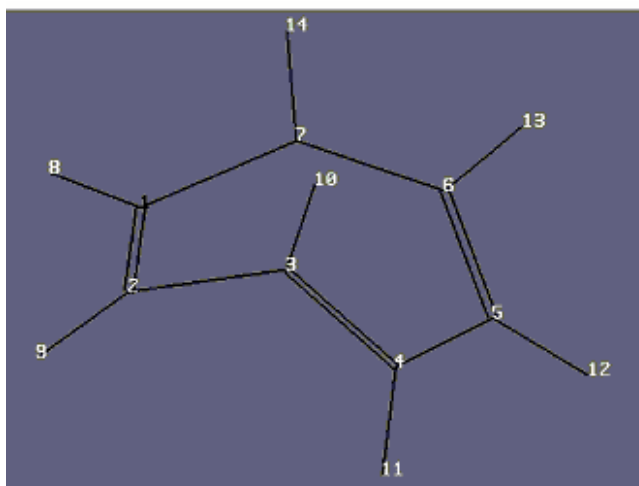
C_2H_2

Structural details (Cartesian Coordinates) of Scheme 3.3 with B3LYP/6-311++G(2d)



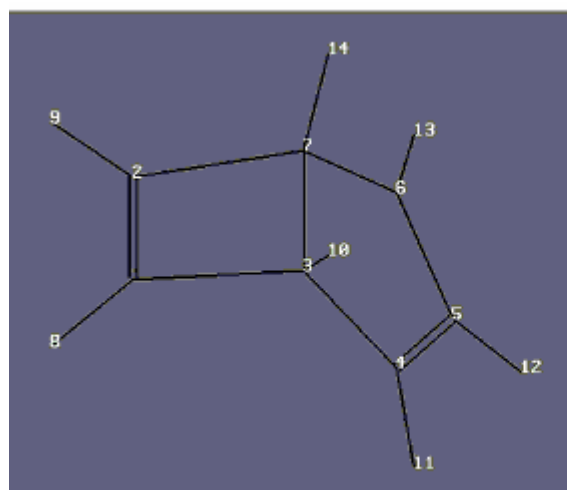
| | | | |
|---|-----------|-----------|----------|
| C | 1.471476 | 0.000000 | 0.000000 |
| C | 0.867250 | -1.254514 | 0.000000 |
| C | -0.490273 | -1.564386 | 0.000000 |
| C | -1.578933 | -0.696204 | 0.000000 |
| C | -1.578933 | 0.696204 | 0.000000 |
| C | -0.490273 | 1.564385 | 0.000000 |
| C | 0.867250 | 1.254514 | 0.000000 |
| H | 2.556396 | 0.000000 | 0.000000 |
| H | 1.543698 | -2.102740 | 0.000000 |
| H | -0.731737 | -2.622106 | 0.000000 |
| H | -2.556396 | -1.166966 | 0.000000 |
| H | -2.556396 | 1.166966 | 0.000000 |
| H | -0.731737 | 2.622106 | 0.000000 |
| H | 1.543698 | 2.102740 | 0.000000 |

Tr^+



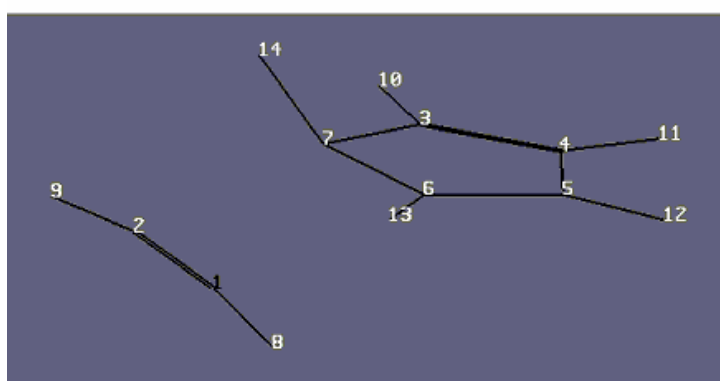
TS8

| | | | |
|---|-----------|-----------|-----------|
| C | -1.580521 | 0.707334 | -0.840815 |
| C | -1.746230 | -0.585824 | -0.581533 |
| C | -0.536068 | -0.750553 | 0.255319 |
| C | 0.606417 | -1.199264 | -0.458166 |
| C | 1.531494 | -0.217299 | -0.714506 |
| C | 1.033589 | 1.060949 | -0.420549 |
| C | -0.341520 | 1.261823 | -0.192923 |
| H | -2.275974 | 1.391892 | -1.315608 |
| H | -2.491240 | -1.304705 | -0.891910 |
| H | -0.527258 | -0.513426 | 1.315608 |
| H | 0.603094 | -2.166739 | -0.954571 |
| H | 2.491240 | -0.390417 | -1.185614 |
| H | 1.702821 | 1.908881 | -0.306310 |
| H | -0.558399 | 2.166740 | 0.377140 |



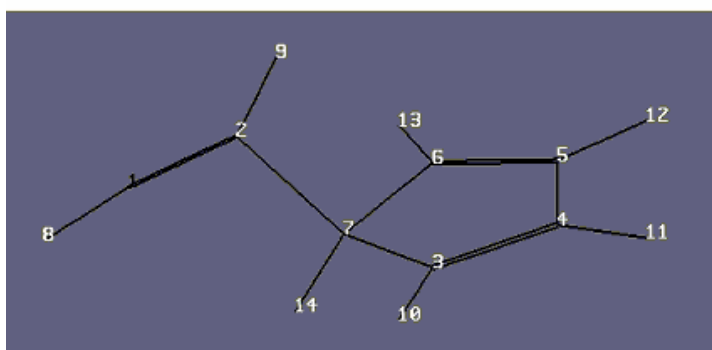
Int5

| | | | |
|---|-----------|-----------|-----------|
| C | -1.798110 | -0.658514 | -0.725365 |
| C | -1.798113 | 0.658427 | -0.725639 |
| C | -0.578753 | -0.772436 | 0.250488 |
| C | 0.695971 | -1.128124 | -0.365099 |
| C | 1.439364 | -0.000005 | -0.685116 |
| C | 0.696028 | 1.128077 | -0.364950 |
| C | -0.578958 | 0.772406 | 0.250369 |
| H | -2.402649 | -1.442905 | -1.158926 |
| H | -2.402726 | 1.442613 | -1.159502 |
| H | -0.817489 | -1.301068 | 1.176887 |
| H | 0.997884 | -2.144504 | -0.595957 |
| H | 2.402726 | -0.000115 | -1.176887 |
| H | 0.997997 | 2.144503 | -0.595496 |
| H | -0.817685 | 1.301325 | 1.176601 |



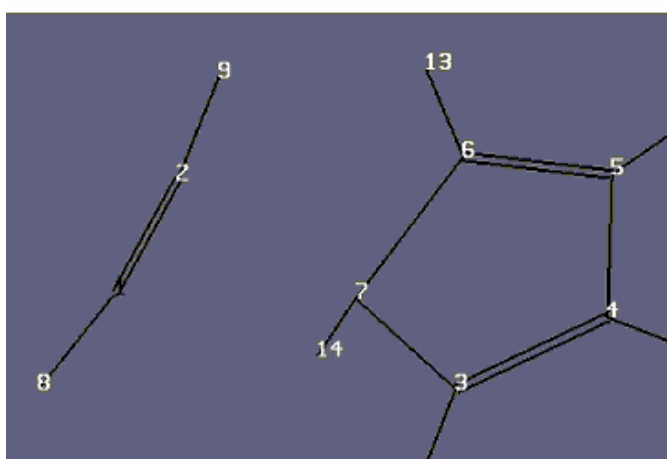
TS9

| | | | |
|---|-----------|-----------|-----------|
| C | 1.502354 | -0.548535 | 0.775547 |
| C | 2.048269 | 0.165178 | -0.045273 |
| C | -0.631170 | -1.206899 | -0.371820 |
| C | -1.817142 | -0.794420 | 0.089372 |
| C | -1.795859 | 0.665293 | 0.304992 |
| C | -0.595285 | 1.164379 | -0.030663 |
| C | 0.216177 | 0.041515 | -0.549479 |
| H | 1.128081 | -1.159032 | 1.573573 |
| H | 2.682554 | 0.783825 | -0.650417 |
| H | -0.321640 | -2.193340 | -0.682040 |
| H | -2.682553 | -1.422994 | 0.248269 |
| H | -2.641877 | 1.239346 | 0.657632 |
| H | -0.270247 | 2.193340 | -0.000626 |
| H | 0.587198 | 0.128256 | -1.573573 |



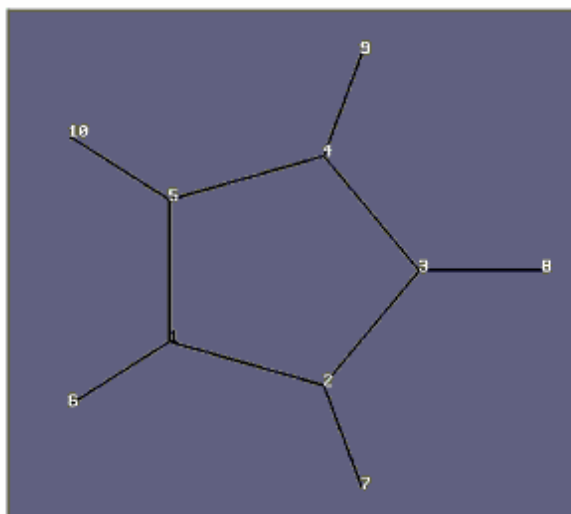
| | | | |
|---|-----------|-----------|-----------|
| C | -2.145858 | -0.000303 | -0.115190 |
| C | -1.119834 | -0.000224 | 0.584239 |
| C | 0.864846 | -1.201567 | -0.314037 |
| C | 2.074558 | -0.735824 | 0.031116 |
| C | 2.074619 | 0.735611 | 0.031154 |
| C | 0.864849 | 1.201494 | -0.313692 |
| C | 0.003718 | 0.000069 | -0.600323 |
| H | -2.942240 | 0.001463 | -0.838728 |
| H | -0.780498 | -0.000689 | 1.607635 |
| H | 0.536109 | -2.223431 | -0.424741 |
| H | 2.942100 | -1.344010 | 0.250064 |
| H | 2.942240 | 1.343729 | 0.249991 |
| H | 0.536269 | 2.223431 | -0.424189 |
| H | -0.423615 | 0.000146 | -1.607635 |

Int6



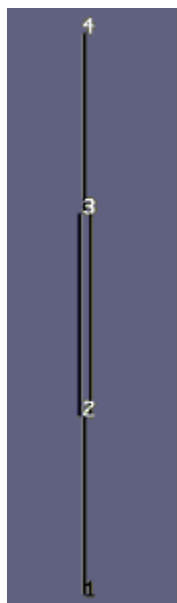
| | | | |
|---|-----------|-----------|-----------|
| C | 2.048218 | 0.164995 | -0.045468 |
| C | 1.503055 | -0.548789 | 0.775755 |
| C | -0.595489 | 1.164267 | -0.030370 |
| C | -1.795926 | 0.664822 | 0.305311 |
| C | -1.816885 | -0.794903 | 0.089435 |
| C | -0.630827 | -1.206957 | -0.371837 |
| C | 0.215990 | 0.041690 | -0.549457 |
| H | 2.682123 | 0.785020 | -0.649604 |
| H | 1.128789 | -1.159740 | 1.573431 |
| H | -0.270616 | 2.193269 | 0.000075 |
| H | -2.642058 | 1.238631 | 0.658084 |
| H | -2.682123 | -1.423710 | 0.248348 |
| H | -0.320982 | -2.193269 | -0.682158 |
| H | 0.587176 | 0.128649 | -1.573431 |

TS10



| | | | |
|---|----------|-----------|-----------|
| C | 0.000000 | 0.710086 | -1.196049 |
| C | 0.000000 | 1.148989 | 0.154696 |
| C | 0.000000 | 0.000000 | 0.989528 |
| C | 0.000000 | -1.148989 | 0.154696 |
| C | 0.000000 | -0.710086 | -1.196049 |
| H | 0.000000 | 1.345692 | -2.070833 |
| H | 0.000000 | 2.177377 | 0.488855 |
| H | 0.000000 | 0.000000 | 2.070833 |
| H | 0.000000 | -2.177377 | 0.488855 |
| H | 0.000000 | -1.345692 | -2.070833 |

$C_5H_5^+$



| | | | |
|---|-----------|-----------|----------|
| H | -0.000464 | 1.662357 | 0.000000 |
| C | 0.000119 | 0.597428 | 0.000000 |
| C | 0.000119 | -0.597521 | 0.000000 |
| H | 0.000464 | -1.662357 | 0.000000 |



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