Spring 5-8-2022

# Ab Initio Study of the Rotation of the C≡C Group in Benzvalyne

Advait Praveen

## Recommended Citation

Praveen, Advait, "Ab Initio Study of the Rotation of the C≡C Group in Benzvalyne" (2022). *Honors Theses*. 2700.
https://egrove.olemiss.edu/hon_thesis/2700

# *AB INITIO* STUDY OF THE ROTATION OF THE C≡C GROUP IN BENZVALYNE

By

Advait Praveen

A thesis submitted to the faculty of The University of Mississippi in partial fulfillment of the requirements of the Sally McDonnell Barksdale Honors College.

Oxford, MS

May 2022

Approved By

Advisor: Professor Steven Davis

Reader: Professor Walter E. Cleland

Reader: Professor Safo Aboaku

# ACKNOWLEDGEMENTS

I would like to thank Dr. Steven Davis for the opportunity to work alongside of him and further my knowledge on research with computational chemistry. This knowledge will be applied towards my future studies and will be instrumental in my professional career. In addition, I would like to thank the Department of Chemistry and Biochemistry as well as the Sally McDonnell Barksdale Honors College for their support. I would also like to thank the Mississippi Center for Supercomputing Research (MCSR) for allowing me the use of their supercomputing time and resources.

# ABSTRACT

ADVAIT PRAVEEN: *Ab Initio* Study of the Rotation of the C≡C Group in Benzvalyne
(Under the direction of Steven Davis

For benzvalyne, we have characterized the minima and transition states of the molecule using the B3LYP, MP2, and M06-2X methods and aug-cc-pVTZ basis set. This was done by calculating the energy of the molecule while rotating the alkyne bond contained within it. After the initial rotation, optimized parameters for the molecule are found. Following this, imaginary frequencies were attempted to be found at the local maximum produced by the graph of the Energy v. rotation angle. Should the negative frequencies be found, the energy of the molecule will be characterized by the CCSD (T) method and aug-cc-pVQZ basis sets. This energy was then corrected using the zero-point correction in order to give us the most accurate ΔE value. This information has not been identified to my previous knowledge, and the ΔE of the molecule was found to be 47.061 kcal*mol$^{-1}$ for B3LYP, 54.218 kcal*mol$^{-1}$ for MP2, 37.498 kcal*mol$^{-1}$ for M06-2X, 52.698 kcal*mol$^{-1}$ for the CCSD (T) calculation in MP2, and 51.993 kcal*mol$^{-1}$ for the CCSD (T) calculation in M06-2X. The CCSD (T) calculations for both MP2 and M06-2X gave nearly identical numbers. In addition, the base MP2 calculation gave a ΔE that was very close to those done by higher quality calculations. The B3LYP calculation as well as the M06-2X calculation seemed to underestimate the value of the ΔE. This could be due to a variety of reasons, but likely stems from the fact that both methods are hybrid and as such, will use both Hartree-Fock methods as well as DFT methods to obtain the estimate of ΔE.

## TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# 1 Introduction

## 1.1 Benzvalyne Structure

The o-benzyne molecule has recently been observed in the Taurus molecular cloud in space [1]. An isomer of o-benzyne is benzvalyne (see Fig 1) which is highly strained due to its tricyclic structure. A recent paper [2] reported the structure, strain energy, and vibrational frequencies of benzvalyne. It was reported that the "gold standard" of computational chemistry, namely the CCSD(T) method, failed to represent benzvalyne as a minimum on the potential energy surface - one imaginary vibrational frequency is present at this level. The perturbative approximation of the triples contribution in the CCSD(T) method was found to be the culprit as the CCSDT-1b and CCSDT-2 methods both gave all real harmonic frequencies.

The vibrational frequency that was represented as imaginary at the CCSD(T) level was a hindered rotation of the C5-C6 group, so we were interested in the potential energy surface of that rotation. Additionally, we were interested in the possibility of the C5-C6 group dissociating from the bicyclobutane moiety due to the strain present in benzvalyne. To this end, we initiated this study of the potential energy surface of the rotation of the C5-C6 moiety of benzvalyne.

The benzvalyne structure is reported to be a $C_{2v}$ minimum in several levels of theory, including MCSCF, MP2, CCSD, CCSD (T), and CCSDT-2[2]. The alkyne bond contained within the molecule is highly strained, with an angle of 108°. This is extremely significant, as an unstrained alkyne would normally contain an angle of 180°. As such, the strain energy produced by the molecule is considered to be significant, with a majority coming from the alkyne. Figure 2 shows the alkyne bond being rotated 90°. In this experiment, this bond was rotated in orders of 10°, with the maximum energy being found at 90°.

### 1.2 ΔE and Activation Energy

The local extrema were examined for benzvalyne ($C_6H_4$). The alkyne bond present in benzvalyne was rotated, thus affecting the position of other atoms in the molecule through intramolecular forces. After optimizing parameters of these atoms through the use of methods and basis sets, the electronic energy of the transition state is calculated for the stable molecule as well as the rotated molecule. The energy of the initial molecule is subtracted from the highest energy state to obtain the ΔE of the molecule.

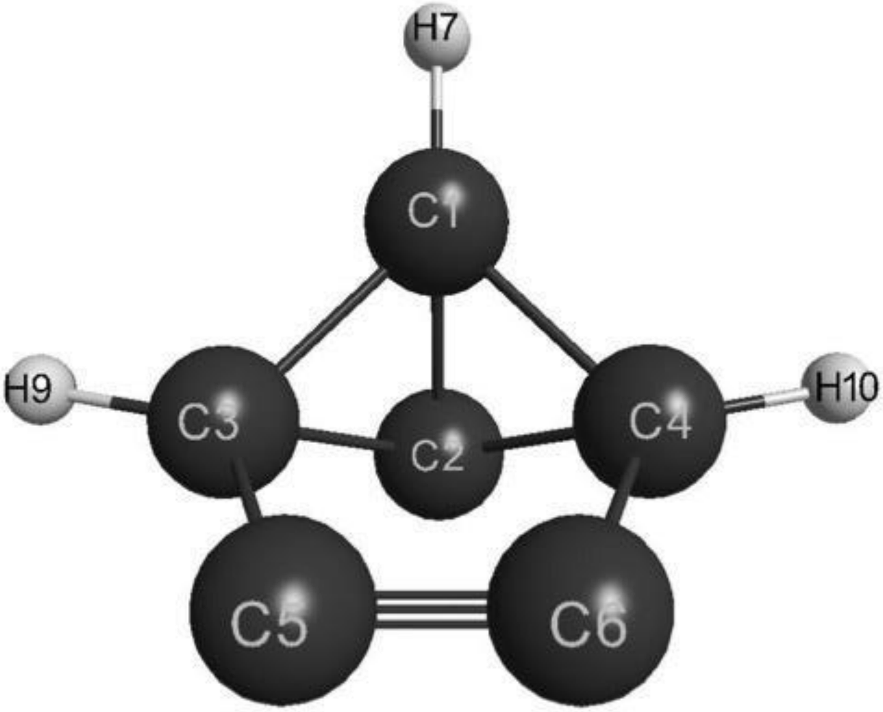

**Figure 1: 0° rotation of the C≡C benzvalyne**

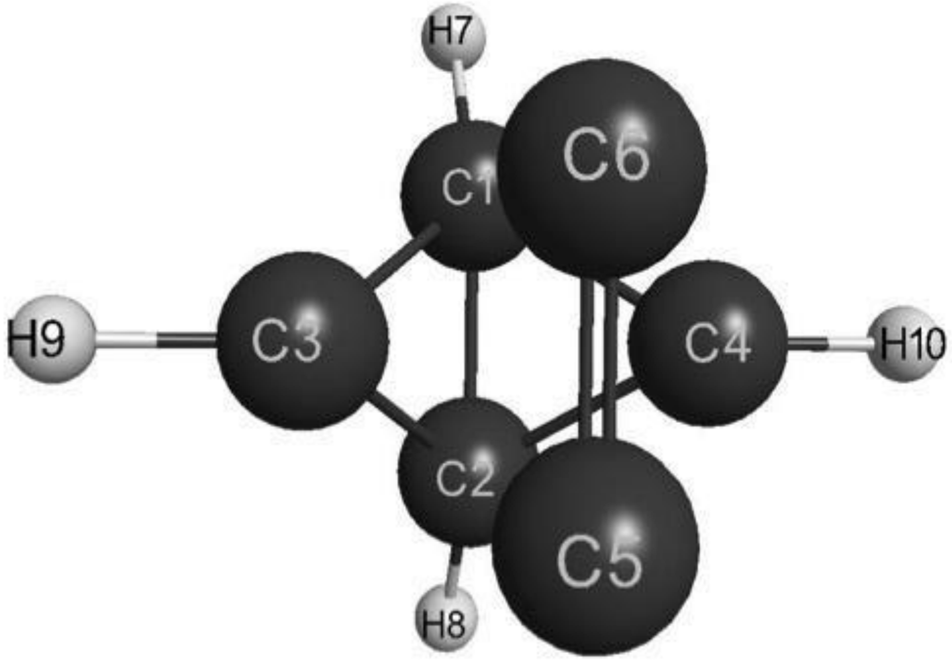

**Figure 2: 90° rotation of the C≡C benzvalyne**

# 2 Computation Details

## 2.1 Methods

Gaussian 16 was used for all the calculations [3]. The following methods were used to calculate the energy of benzvalyne while the $C_5$-$C_6$ group was rotated around the $C_2$ axis of the molecule: B3LYP, MP2, and M06-2X.

The B3LYP method, formally known as the Becke-3 parameter-Lee-Yang-Parr, is known generally as a density functional theory method, or DFT method [6]. These methods became increasingly prevalent due to the relative accuracy of the calculation as well as the substantial increase in computational efficiency. Other methods provide greater accuracy, however, B3LYP consumes resources at a much slower rate [4].

The Møller-Plesset perturbation theory, also known as the MP method, is known as a post Hartree-Fock method [8]. These methods will excite a set number of electrons to a random excited state, and using those molecular orbitals, it will calculate the energy of a molecule. In terms of the MP2 calculation that was used in this experiment, the number of excited electrons was 2 so the reaction is perturbed to the 2nd order and MP2 [8]. In terms of optimizing geometry, MP2 is considered to be a great quality calculation. However, in cases where the Hartree-Fock method provides an inaccurate estimate, the MP2 calculation will provide less accurate values [8].

The M06-2X method employed in this study is a density functional that is similar to B3LYP but is a greater quality density functional due to the greater number of parameters involved [7]. This makes it a less efficient, albeit greater quality calculation. It is a hybrid functional that is primarily used in obtaining thermochemical and kinetic values [7].

For this experiment, the values obtained from the MP2 and M06-2X calculation are looked at more favorably than the B3LYP calculation due to the quality of calculations involved.

## 2.2 Basis Sets

Basis sets are defined as a combination of functions intended to reproduce molecular orbitals in computational chemistry. In this experiment, the Dunning's Correlation Consistent basis set cc-pVXZ was used, with X = D, T, Q [9]. The X will change depending on the number of basis functions for each orbital. The D indicates two basis functions for each atomic orbital while T and Q will indicate three and four basis functions respectively [9]. In this experiment, both cc-pVTZ and cc-pVQZ were used. Cc-pVTZ was used to obtain the optimized parameters of benzvalyne while cc-pVQZ was used in the CCSD (T) calculation to obtain the energy of the molecule. In addition, the "aug" prefix was used in conjunction with the basis set to factor angular momentum in the CCSD (T) calculation for a more accurate value [9].

# 3 Experimental

Optimized parameters for benzvalyne as it undergoes the rotation was found using the aforementioned methods and basis sets. Initially, the B3LYP method was used in conjunction with the cc-pVTZ basis set and Cartesian coordinates obtained from the stable molecule. Using these values, we can calculate the optimized position of each atom in the molecule after the alkyne has undergone a 10° rotation. Now, we can input the newly optimized parameters for the 10° rotation into the same calculation while altering the angle to 20°. The optimized parameters for the 10° rotation are now optimized for a 20° rotation. This was then input back into the calculation while the degrees were further increased by 10 to a total of 30°.

Using this type of calculation, the optimized parameters for benzvalyne were found up to 180° in intervals of 10°. In addition to B3LYP, the MP2 and M06-2X methods were also used in conjunction with the cc-pVTZ basis set to calculate optimized parameters for the molecule up to 180°.

These optimized parameters were used with the above methods and basis sets in the calculation of energy of the molecule at that given rotation. This means that the energy of the molecule at specific rotations can be found using the above calculation. A graph of the energy of benzvalyne against the degrees of alkyne bond rotation was produced in order to observe the changes in energy as the rotation increases.

After optimizing the displacement and position of atoms in benzvalyne, the frequency was calculated at the highest energetic point shown in the graph using the same methods and basis sets. An imaginary frequency should be present at this point. This is due to the frequency calculation equation, shown below:

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

In this calculation, the k value is the second derivative of the function. The second derivative will tell us how the slope of the frequency will change with time. A negative second derivate under the radical indicates an imaginary frequency, due to *i* being an imaginary value. Should the molecule happen to possess this trait, it confirms the existence of a local maximum at that point. In addition to confirming the local maximum, this frequency calculation also gave us the zero-point correction that is needed to calibrate the energy obtained.

If the molecule is confirmed to have an imaginary frequency at the maximum found using initial methods, transition state calculations was performed to optimize the geometry to the maximum on the potential energy surface (zero first derivatives and one negative second derivative) at the MP2 and M06-2X levels of theory. A CCSD(T) calculation was performed using aug-cc-pVQZ basis set. This calculation was done at the MP2 and M06-2X optimized geometries. We were not successful at finding a transition state at the B3LYP level. In addition, this method was run for both the 0° and the 90° rotations of the molecule. Doing so would allow us to obtain the energies of the molecule in its stable state and its highest energy state. Unlike the previous calculations, a CCSD(T) calculation is of the highest quality and will give us numbers that are the most accurate to literature data. This calculation was done only after confirming the imaginary frequencies in order to avoid terminations in the project that could result from a real frequency.

After finding the energy value given by the CCSD (T) calculation, we must then correct this energy by adding the zero-point correction obtained earlier to the value. Following this, the energies of the 0° and the 90° rotation molecule are subtracted from one another to give us the value of ΔE. The energetic values obtained from every method and basis set are displayed in Table 1.

# 4 Results

Shown below, Table 1 displays the ΔE obtained from the methods and basis sets listed above. The energies of the molecule after having undergone a 90° rotation are shown along with the energy of the stable molecule. Initial values were found in units of Hartree/Particles and were converted to kcal*mol$^{-1}$. After having found the energies of the molecule, it is important to correct for the zero-point energy. The zero-point correction was found to be 0.068675 Hartree/Particles. When converted to kcal*mol, this value is around 43.094 kcal/mol. After correcting for the zero-point energy, the energetic values of the stable molecule are deducted from those of the transition state, thus allowing us to find the ΔE. The values found were

47.061 kcal*mol$^{-1}$ for B3LYP, 54.218 kcal*mol$^{-1}$ for MP2, 37.498 kcal*mol$^{-1}$ for M06-2X, 52.698 kcal*mol$^{-1}$ for CCSD (T) calculation in MP2, and 51.993 kcal*mol$^{-1}$ for CCSD (T) calculation in M06-2X. In terms of the methods, B3LYP and M06-2X underestimated the value of ΔE, with M06-2X underestimating the value by about 15 kcal*mol. The standard MP2 calculation gave an extremely close estimate to the values found in the much higher quality

CCSD (T) calculations. The barrier heights for the CCSD (T) calculation have a difference of 0.705 kcal*mol, or 1.35%, with the MP2 estimation being higher. In addition, the greater quality of the basis sets present in the CCSD (T) calculation aided in the precision of the values.

**Table 1: Energy and Methods**

| | B3LYP | MP2 | M06-2X | CCSD (T) with MP2 | CCSD (T) with M06-2X |
|---|---|---|---|---|---|
| E at 90° rotation (Hartree) | -230.744 | -230.169 | -230.673 | -230.308 | -230.307 |
| E at 0° rotation (Hartree) | -230.819 | -230.255 | -230.733 | -230.392 | -230.391 |
| ΔE (kcal/mol) | 47.061 | 54.218 | 37.498 | 52.698 | 51.993 |

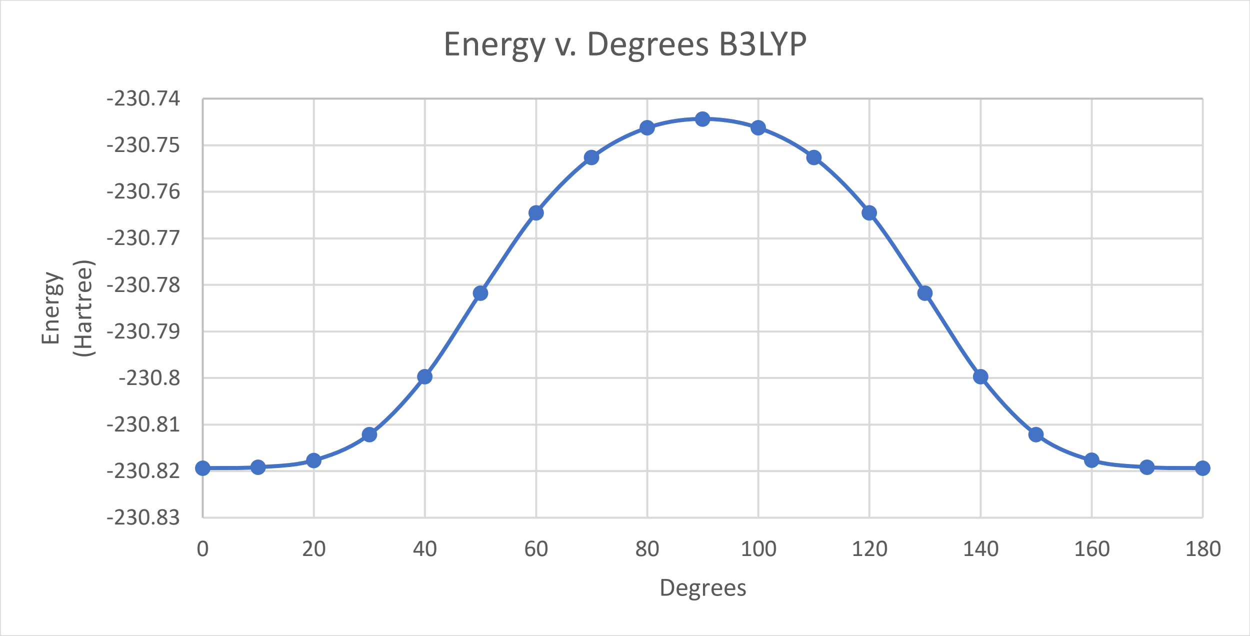

**Figure 3: The graph of energy vs. degrees rotated for the B3LYP method and cc-pVTZ basis sets for benzvalyne. As shown above, the maximum is observed to be at the 90° rotation, however, when frequencies were calculated, an imaginary frequency was not found.**

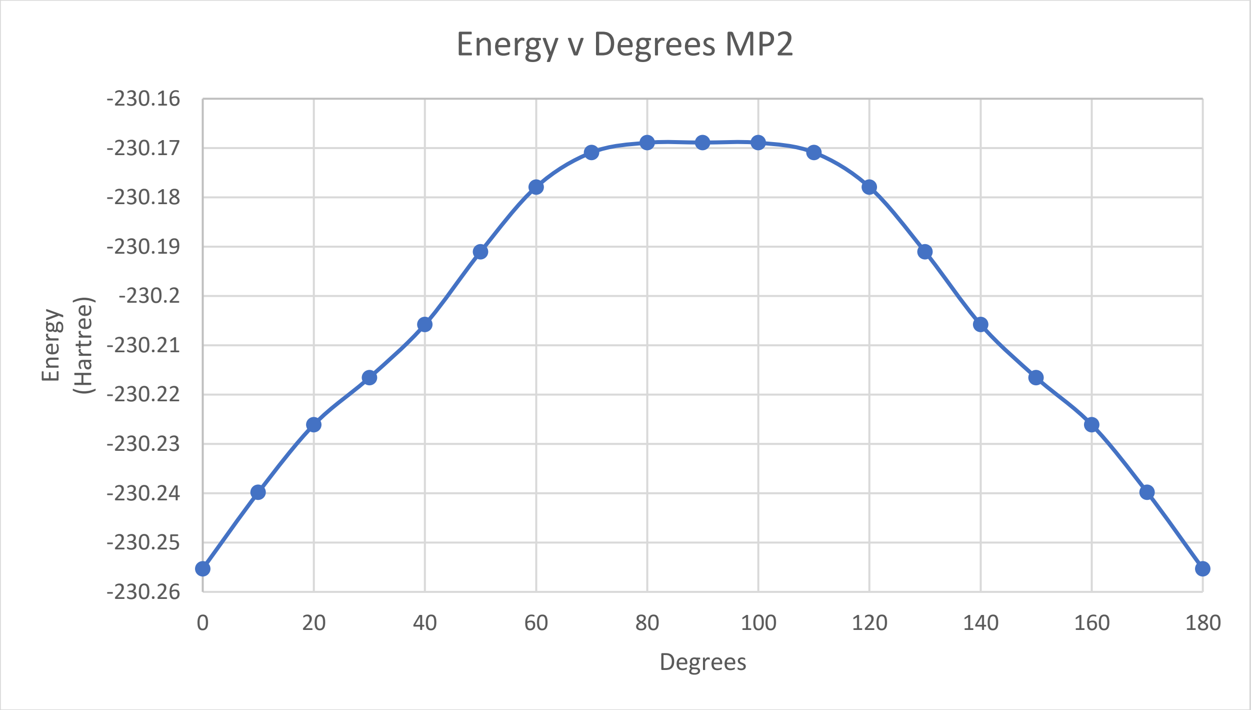

**Figure 4: The graph of energy vs. degrees rotated for the MP2 method and cc-pVTZ basis sets for benzvalyne. As shown above, the maximum is observed to be around the 90° rotation, and an imaginary frequency was found.**

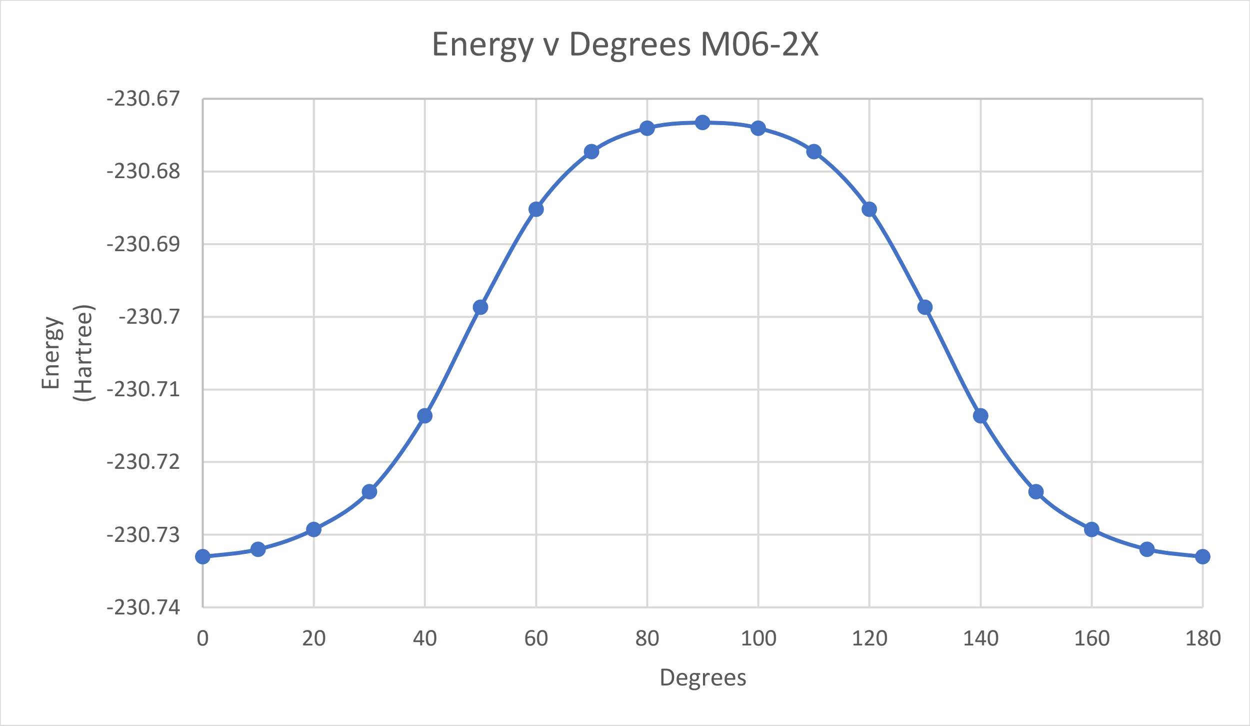

**Figure 5: The graph of energy vs. degrees rotated for the M06-2X method and cc-pVTZ basis sets for benzvalyne. As shown above, the maximum is observed to be around the 90° rotation and an imaginary frequency was found.**

# 5 Conclusion

This study characterized both the transition states as well as local extrema of benzvalyne ($C_6H_4$). This molecule is said to have a $C_{2v}$ symmetry and was further optimized to obtain more accurate parameters. The ΔE of the molecule was found using the B3LYP, MP2, M062X, and CCSD (T) methods and aug-cc-pVXZ basis sets. In addition to optimizing parameters, we found imaginary frequencies at the local maxima as well as the zero-point correction energy. Upon computation, the CCSD (T) values were found to be extremely precise, with a percent difference of 1.35%. In addition, the standard MP2 value was very close, suggesting the efficiency of the method. B3LYP and M06-2X were both underestimating the values and had percent differences of 10.63% and 33.05% respectively. M06-2X was the least precise of the methods but succeeds in reproducing the energy trends of benzvalyne.

# References

[1] J. Cernicharo, M. Agúndez, R. I. Kaiser, C. Cabezas, B. Tercero, N. Marcelino, J. R. Pardo, and P. de Vicente, "Discovery of benzyne, o-$C_6H_4$, in TMC-1 with the QUIJOTE line survey," Astron. Astrophys. 652, L9 (2021).

[2] Kimberley N. Poland, Brent R. Westbrook, David H. Magers, Ryan C. Fortenberry, and Steven R. Davis, "Benzvalyne: Real or Imaginary," J. Chem. Phys. 156, 024302 (2022).

[3] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[4] *DFT*, https://www.cup.uni-muenchen.de/ch/compchem/energy/dft1.html.

[5] *Chapter 9: Density Functional Theory ... - Uni-Stuttgart.de*. https://www2.icp.uni-stuttgart.de/~icp/mediawiki/images/b/b8/DFT.pdf.

[6] Jessop. "B3LYP Explained." *Chemistry Stack Exchange*, 1 July 1964, https://chemistry.stackexchange.com/questions/61366/b3lyp-explained#:~:text=B3lyp%20is%20a%20functional%2C%20that,with%20heavier%20atoms%20is%20questionable.

[7] Wang, Ying, et al. "Revised M06 Density Functional for Main-Group and Transition-Metal Chemistry." *PNAS*, https://www.pnas.org/doi/10.1073/pnas.1810421115.

[8] Cremer, Dieter. *Mllerplesset Perturbation Theory: From Small Molecule Methods to* ... https://sites.smu.edu/dedman/catco/publications/pdf/320.MP_review.pdf.

[9] Shrill, C. David. *Basis Sets in Quantum Chemistry* . http://vergil.chemistry.gatech.edu/courses/chem6485/pdf/basis-sets.pdf.