Indian Institute of Science Education and Research, Kolkata

Summer Internship Report

Computational studies on the aromaticity, electronic property and reactivity in some selected chemical systems

By,

Karthiayani Vijai

3rd year BS-MS

Department of Chemical Sciences

Indian Institute of Science Education and Research, Kolkata

Under the Supervision of

Prof. Debasis Koley

Department of Chemical Sciences,

Indian Institute of Science Education and Research (IISER) Kolkata

Declaration by the Student

I, Karthiayani Vijai, hereby certify that I have performed all calculations for this work based on my personal study and effort. This report is based on two study papers that I have acknowledged at the end. Along with these, I independently did additional work. Calculations were done independently, and similar results were obtained.

Date: 25/07/2024

………………………………

Place: IISER Kolkata

Karthiayani Vijai

Department of Chemical Sciences

Indian Institute of Science Education and Research Kolkata

Mohanpur, 741246

West Bengal, India

Acknowledgments

I would like to express my sincere gratitude to my mentor, Prof. Debasis Koley, for his invaluable assistance throughout this project. His guidance at every step helped me learn many new things, making his presence during the internship incredibly valuable.

I would also like to thank Miss Leya and other CCMM members for their guidance throughout the project. I am also grateful to IISER Kolkata and CCMM lab for providing the necessary facilities for this work. Additionally, I extend my heartfelt thanks to my friends and parents for their unwavering support and encouragement. Finally, I thank God for His blessings.

Date: 25/07/2024

…………………………………………..

Place: IISER Kolkata

<div align="right">

Karthiayani Vijai

Department of Chemical Sciences

Indian Institute of Science Education and Research Kolkata

Mohanpur, 741246

West Bengal, India

</div>

Table of Contents

Report 1:

A Computational study of the quantitative thermodynamic description of Aromaticity with visualization of Molecular orbitals and Electrostatic potential maps of different aromatic systems

Abstract

Aromatic compounds play a crucial role in organic synthesis and are involved in various reaction types. In this study, we examined different aromatic systems using computational energy calculations to identify aromatic, antiaromatic, and non-aromatic compounds. The energetic cost of disrupting the cyclic conjugated system was found for each compound, and the results were used to categorize the compounds into aromatic, non-aromatic, or antiaromatic systems. Further calculations were performed using higher basis sets to ensure accuracy. Additionally, visualization of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) was done, and the behavior of corresponding electrostatic potential plots was studied. This analysis provided insights into the properties and behavior of aromatic compounds. The computational tools used in this study include Gaussian 16, GaussView 6, and Chemcraft for calculations and visualization.
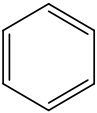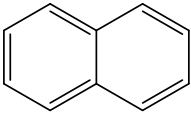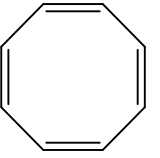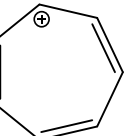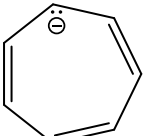
Introduction

Computational chemistry provides critical insights into molecular structures and characteristics. Electronic structure approaches are used by researchers from several chemistry departments to predict molecular structures and physicochemical qualities and explain various chemical processes. Powerful computers now allow for high-level calculations that match with the experimental results. In this study, we studied the aromaticity of aromatic, antiaromatic, and non-aromatic compounds by analyzing the resonance energies of these compounds, which are determined using calculated results from similar isodesmic reactions using HF/3-21G level using AM1 geometry. Further single-point (sp) energy calculations are done in different level of theories such as HF/3-21G*, HF/6-31G*, B3LYP/6-31G*, BP86/6-31G*, MP2/6-31G*, M06-2X/6-31G* for refined energies. Their resonance energies were calculated and compared. From the computed results, HOMO-LUMO energy differences are determined. Additionally, the plotted Electrostatic Potential Map (the property of electrostatic potential mapped upon the electron density) provides an indication of charge distribution in a molecule.

Part 1: Aromatic, Antiaromatic or Nonaromatic

Aromaticity of some structures as shown in scheme 1 are studied.

The resonance energies are calculated using appropriate isodesmic reactions, as shown in the Table 1. Here, we have substituted methyl groups for our aromatic systems. The resonance energies obtained for such isodesmic reactions are the cost of disrupting the cyclic conjugated system. Single-point energy calculations are made at the Hatree-Fock 3-21G* level of theory.

Scheme 1: Conjugated Cyclic Hydrocarbons and Hydrocarbon Ions
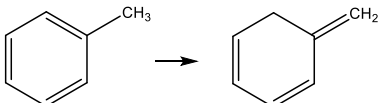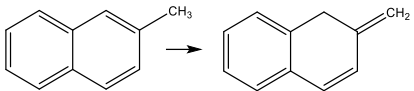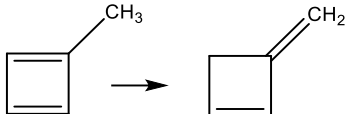
Structure						
Compound	**U**	**V**	**W**	**X**	**Y**	**Z**
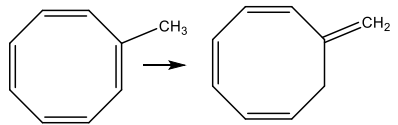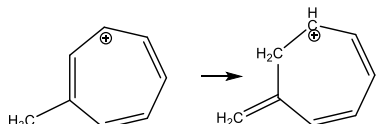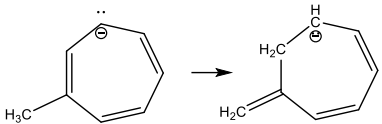
Compound	Resonance structures (A→B)	Energy of A	Energy of B	ΔE/(au)	ΔEsp/ (kcal/mol)
U		-268.24	-268.19	0.058	36.5
V		-420.04	-419.99	0.04	23.6
W		-191.59	-191.66	-0.06	-41.2
X		-344.63	-344.63	0.00085	0.5
Y		-306.22	-306.17	0.050	31.4
Z		-306.35	-306.37	-0.023	-14.5

Table 1. Resonance Energy for Hydrocarbons and Hydrocarbon Ions

From Table 1, we can determine the resonance energies following the isodesmic reactions. When the ΔE_{sp} is positive, negative, and nearly zero then the respective compounds are classified as aromatic, anti-aromatic, and non-aromatic.

Discussion:

Through computational analysis, we identified aromatic, antiaromatic, and non-aromatic compounds. During my study, I noticed that the initial guess geometry of the molecule, drawn in GaussView as input, significantly affected the results. Slight differences in calculated energy were observed based on the placement of hydrogen atoms, necessitating careful construction of structures.

Moreover, for the same initial guess geometry, repeated calculations yielded consistent results. Larger structures required more computation time, but since the molecules studied were relatively small, the overall time was reasonable. For charged species, adjustments were made in the Gaussian input file to account for spin and multiplicity, as failure to do so resulted in segmentation errors during program execution.

In the case of aromatic compounds, positive values (indicating highly exothermic reactions) confirmed that disrupting the conjugation in the aromatic ring does not lead to a more energetically favorable product, thereby affirming the stability of aromatic compounds. On the other hand, for antiaromatic compounds, conjugation does not contribute to stability, so breaking up the conjugation results in a more stable product. In the case of non-aromatic compounds, the presence or absence of conjugation has minimal impact on stability.

For a compound to be aromatic, it must be cyclic, planar, fully conjugated, and have 4n+2 π electrons (Huckel's rule). Antiaromatic compounds should also be cyclic, planar, and fully conjugated systems but with 4n π electrons. Whereas nonaromatic compounds may lack cyclic structure, planarity, or conjugation. Similar observations were found on analyzing the molecular structures under study, which were in good agreement with the computational results.
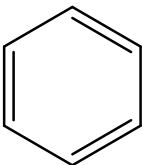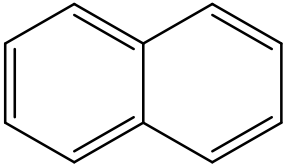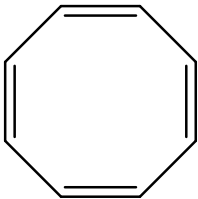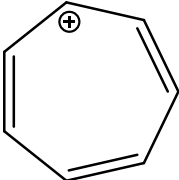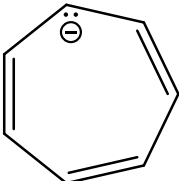
Compound	Structure	Number of π-electrons	Geometry	Resonance Energy/ (kcal/mol)	Aromaticity
U		6	Planar	36.5	Aromatic
V		10	Planar	23.6	Aromatic
W		4	Planar	-41.2	Antiaromatic
X		8	Nonplanar	0.54	Nonaromatic
Y		6	Planar	31.4	Aromatic
Z		8	Planar	-14.5	Antiaromatic

Table 2. Aromaticity in Conjugated Cyclic Hydrocarbons and Hydrocarbon Ions

Part 2: Comparison of resonance energy with various Computational Models

The resonance energies were calculated similarly but in different basis sets. The following are the results:

Structure	HF/3-21G*	HF/6-31G*	B3LYP/6-31G*	bp86/6-31g*	M062X/6-31g*	MP2/6-31g*	Aromaticity
U	36.52	35.04	35.83	35.28	36.03	35.04	aromatic
V	23.58	23.31	24.63	24.40	23.88	23.31	aromatic
W	-41.23	-39.60	-36.27	-35.34	-35.86	-39.60	antiaromatic
X	0.54	1.54	-0.73	-1.45	-0.33	1.54	nonaromatic
Y	31.39	30.69	31.89	30.27	31.24	30.69	aromatic
Z	-14.49	-11.05	-14.17	-14.96	-14.79	-11.05	antiaromatic

Table 3: Resonance Energy of aromatic structures in different computational models

Discussion:

The above table shows that the energy values obtained are not excessively sensitive to the size of the basis set used. All other Hartree-Fock methods, as anticipated, need significantly more computational time, hence the HF 3-21G(*) is the most efficient.

Part 3: HOMO and LUMO of aromatic systems

From analyzing the results after the computation of the single point energy of the molecules, we get to obtain the HOMO and LUMO orbital energies.
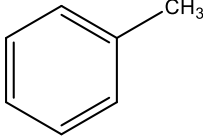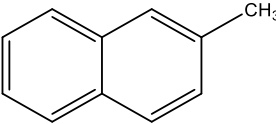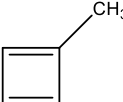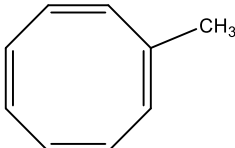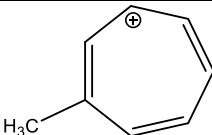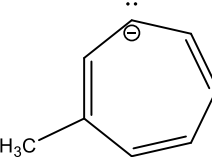
Structure	HOMO Energy	LUMO Energy	HOMO-LUMO gap (au)
Toluene structure with CH_3	-0.326	0.152	0.479
Methylnaphthalene structure with CH_3	-0.289	0.105	0.394
Methylcyclobutadiene structure with CH_3	-0.276	0.115	0.392
Methylcyclooctatetraene structure with CH_3	-0.303	0.119	0.422
Methyltropylium cation with H_3C	-0.557	-0.143	0.415
Methylcycloheptatrienyl anion with H_3C	0.0148	0.303	0.288

Table 4. HOMO-LUMO of aromatic systems

Marked in red are abnormal energy signs for HOMO and LUMO

The HOMO energy is usually negative because it is attached to the nucleus, and the electrons are in a lower state than free electrons in vacuum. Energies of molecular orbitals are often reported relative to the vacuum level. The LUMO energy is often less negative than the HOMO energy and can be even positive, but this depends on the method and basis set used. A positive LUMO energy indicates that an electron would have to gain energy to go into this orbital. The HOMO and LUMO of different aromatic systems are shown below.

Representation of HOMO and LUMO of different cyclic hydrocarbon systems

E

LUMO (0.152412 au) ----------████----------

↑↓

HOMO (-0.326317 au) ----------████----------

E

LUMO (0.104643 au) ----------████----------

↑↓

HOMO (-0.289941 au) ----------████----------

E

LUMO (0.115174 au) ----------████----------

↑↓

HOMO (-0.276698 au) ----------████----------

E

LUMO (0.119194 au) ----------████----------

↑↓

HOMO (-0.303185 au) ----------████----------

LUMO (-0.142608 au)

HOMO (-0.557315 au)

E

LUMO (0.302773 au)

HOMO (0.014772 au)

E
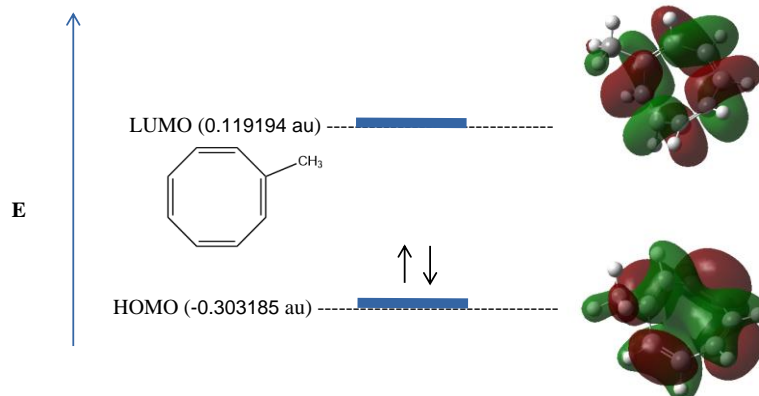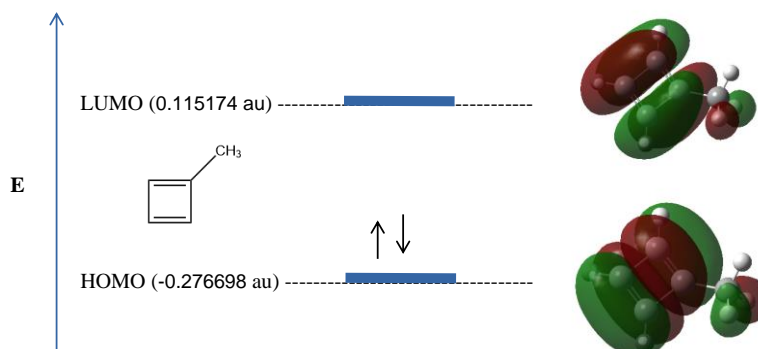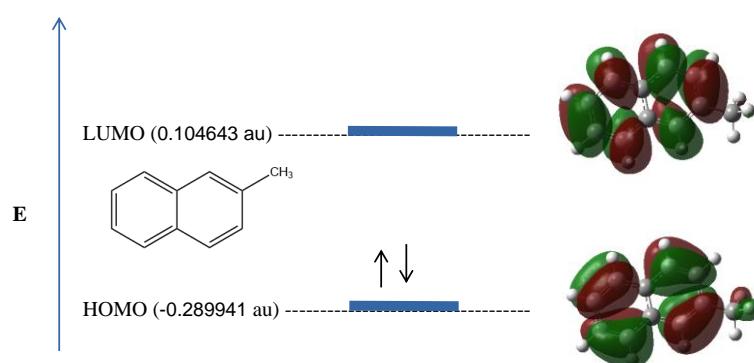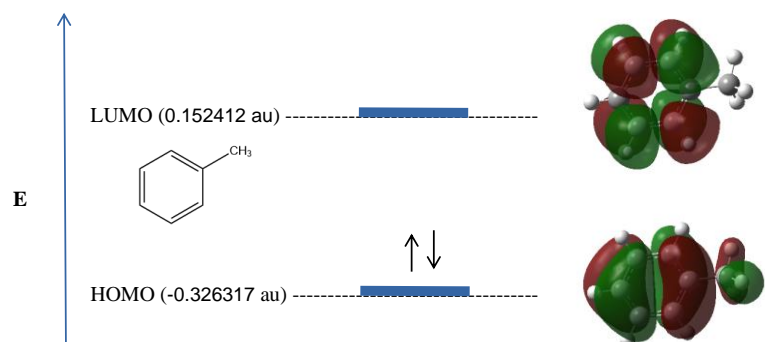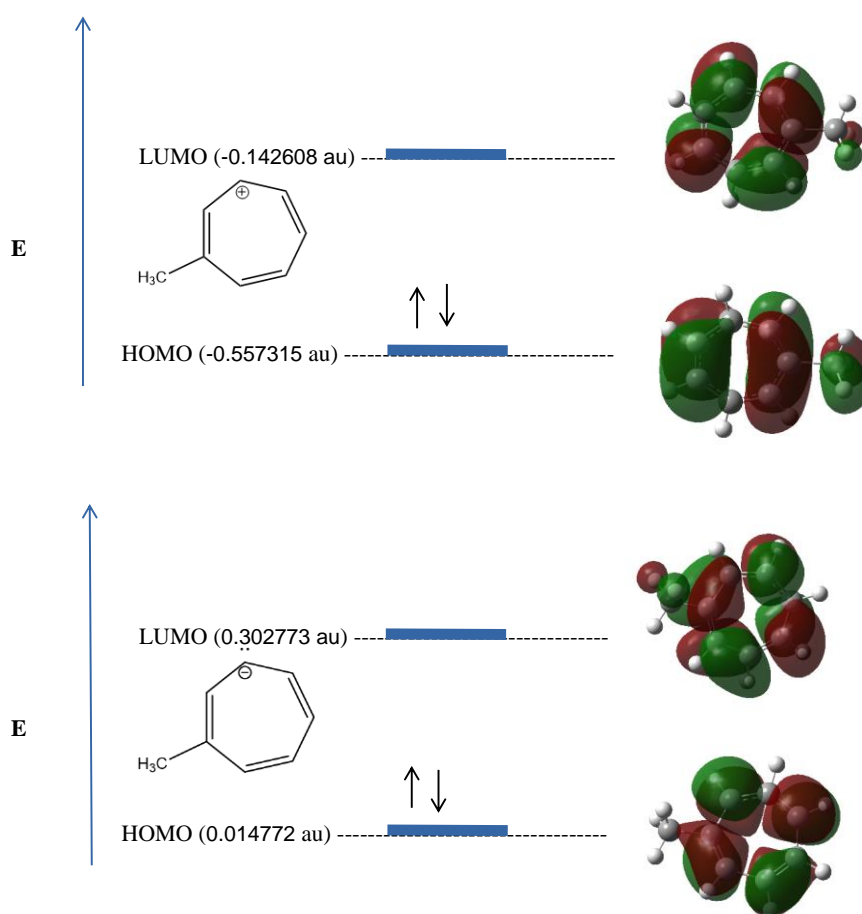
Part 4: Electrostatic Potential Map of aromatic systems

 Overlaying the electrostatic potential onto electron density plots gives rise to Electrostatic Potential Maps. This allows us to study about the charge distribution in compounds.
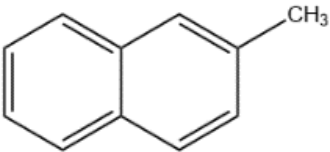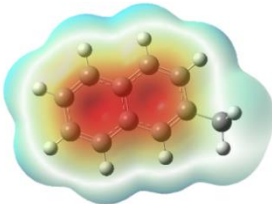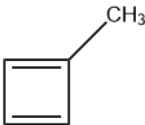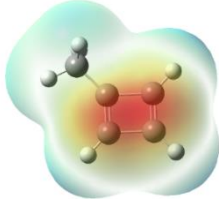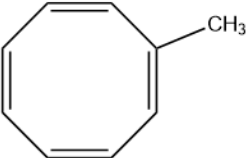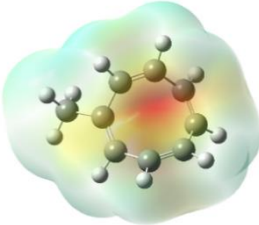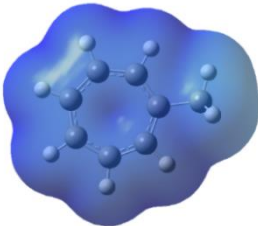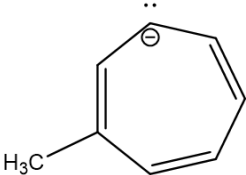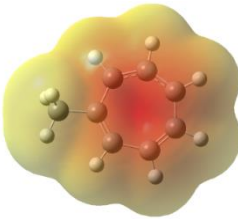
Table 5. Electrostatic Potential Map of conjugated cyclic hydrocarbons

Report 2:

A Computational Analysis of Lewis Acids and Bases: Optimizing Electronic Properties and Reactivity

Abstract

The fundamental concept of Lewis acids and bases is an important topic in advanced inorganic chemistry. This study optimized Lewis acids and bases using single-point energy (SP) calculations performed with the Hartree-Fock (HF) method and the 3-21G basis set. Here for the Lewis acids, we determined some key parameters, including the energy of the Lowest Unoccupied Molecular Orbital (E_{LUMO}), the energy of the Highest Occupied Molecular Orbital (E_{HOMO}), hardness, proton affinity, and the partial charge on the donor atom. And for the Lewis bases, we calculated E_{LUMO}, E_{HOMO}, hardness, ver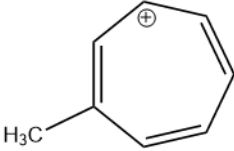tical electron attachment energy, reorganization energy, and the partial charge on the acceptor atom. These computational evaluations give us a good understanding of the electrical characteristics and reactivities of Lewis acids and bases.

Theory

Lewis acids are electron pair acceptors which have a tendency to accept electrons, while Lewis bases are electron pair donors. Their behavior and interaction can be studied using methods in computational chemistry to learn about their properties and reactivities.

In this study optimization and single-point energy (SP) calculations were done using the HF method with the 3-21G basis set. For Lewis acids E_{HOMO}, E_{LUMO}, hardness, proton affinity, and the partial charge on the donor atom were determined. These factors contribute to a better understanding of acids' electron-accepting capacity and stability.

For Lewis bases E_{HOMO}, E_{LUMO}, hardness, vertical electron attachment energy, reorganization energy, and the partial charge on the acceptor atom were found. These calculations allow us to study the electron-donating capacity and the stability of the bases. The HF/3-21G basis set ensures a balance between computational efficiency and accuracy, providing reliable data for analysing the electronic properties of Lewis acids and bases.

Proper understanding of these fundamental properties is vital for predicting and rationalizing their behaviour in chemical reactions.

Results and Discussion

Table 1. Calculated Properties of the Lewis Bases:

Lewis base	E_{HOMO} (eV)	E_{LUMO} (eV)	Hardness (eV)	PA (kcal/mol)	Q_{DA}
NF$_3$	-15.01	6.02	10.51	127.19	+0.653
PH$_3$	-10.35	4.93	7.64	184.27	+0.089
NH$_3$	-10.58	7.49	9.04	226.94	-0.876
pyridine	-9.68	3.54	6.61	241.22	-0.669
3,5-Dimethylpyridine	-9.13	3.56	6.34	246.06	-0.681
N(CH$_3$)$_3$	-9.08	6.92	7.99	248.03	-0.681
2,6-Dimethylpyridine	-9.06	3.73	6.39	249.56	-0.744

PA(Proton Affinity) is the change in energy calculated for the reaction $BH^+(g) \rightarrow B(g) + H^+(g)$

Q_{DA} is the partial charge on the donor atom

Table 2. Calculated Properties of the Idealized Pyramidal Boron and Aluminum Hydrides and Halides:

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	Hardness (eV)	ΔE$_{EA}$ (kcal/mol)	ΔE$_{reorg}$ (kcal/mol)	Q$_{AA}$
BH$_3$	-12.86	1.15	7.01	8.29	25.79	0.029
BF$_3$	-16.96	0.47	8.72	-5.65	46.19	1.191
AlH$_3$	-11.04	-0.21	5.42	-13.91	20.10	0.711
BCl$_3$	-12.85	-1.39	5.73	-63.76	40.70	0.311
AlCl$_3$	-12.78	-2.28	5.25	-68.45	21.09	1.392

ΔE$_{EA}$ (Vertical electron attachment energy) is the energy that occurs when an electron is added to a neutral MX_3 molecule at the idealized pyramidal geometry.

The reorganization energy necessary to change the geometry of the acid from triagonal planar to the idealized pyramidal structure.

Q$_{AA}$ is the partial charge on the acceptor atom.

Conclusion

This study successfully optimized and characterized Lewis acids and bases using computational chemistry methods. The results that were calculated match with the results in the studied paper (Anderson, 2000) . By doing single-point energy calculations with the HF/3-21G basis set, we were able to determine key electronic parameters such as E_{LUMO}, E_{HOMO}, hardness, proton affinity, and partial charges. These findings help us to study and understand the fundamental properties and activities of Lewis acids and bases, and these results can be used as a foundation to deal with more advanced topics in chemistry.

References

- Gavin, T. (**2005**). Quantitative thermodynamic descriptions of aromaticity: A computational exercise for the organic chemistry laboratory. *Journal of Chemical Education, 82*(6), 953.

- Anderson, W.P. (**2000**). A Lewis Acid-Base Computational Chemistry Exercise for Advanced Inorganic Chemistry. *Journal of Chemical Education, 77*, 209-209.

- Kikuchi, S. (**1997**). A History of the Structural Theory of Benzene - The Aromatic Sextet Rule and Huckel's Rule. *Journal of Chemical Education, 74*, 194-201.