

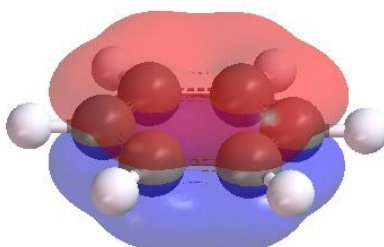


Aromatic stabilization energy

Bởi:

Thanh Truong

Despite being an important concept in organic chemistry, aromaticity is difficult to define precisely and thus quantifying it is also difficult. It is being understood for a ring molecule that has an unusual stability. Such ring structure often is planar and has equivalent C-C bond lengths rather than having alternate single and double bonds as in its Lewis structures. Benzene is the classic example of an aromatic molecule.



There are several ways to estimate the aromatic stabilization energy (ASE)[\[1\]](#).

1. Isodesmic Reaction Approach

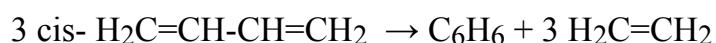
The simplest isodesmic reaction representing ASE in benzene is



Using the experimental heats of formation for these molecules, ASE is estimated to be about -64 kcal/mol. This isodesmic reaction, however, does not preserve the local bonding pattern of carbon atoms in benzene and separate the ring strain energy from ASE. Although can use different reference molecule such as cyclo-hexene as the reference, generally the isodemic reaction approach does not perform well.

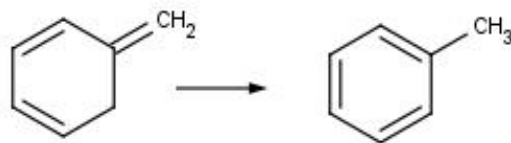
2. Homodesmotic Reaction Approach

Homodesmotic reaction preserves the C(sp²)-C(sp²)-C(sp²) pattern and geometrical arrangement in benzene by using the cis-cyclobutadien as a reference molecule.



3. Isomerization Stabilization Energy (ISE) Approach

This approach represents ASE by an isomerization reaction that converts an isomer to its aromatic analog. This approach cannot be used directly for benzene but it can for toluene. Here we can assume that ASE for toluene and benzene are nearly the same.



A number of studies have been done and estimated the ASE for benzene to be about -28 kcal/mol.

This experiment has two parts. Part A is to verify the accuracy of the above three approaches for estimating ASE for benzene using molecular orbital theory and Part B is to use the ISE approach to estimate ASE for a number of unsaturated cyclic hydrocarbons.

Procedure: Using tools in Avisto. You can download Avisto and its tools at [Astonis](#).

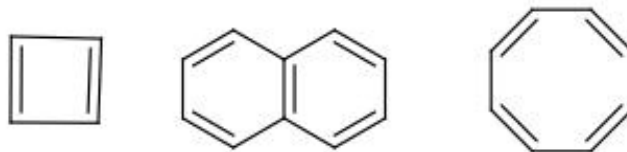
Part A:

1. Use MolDesign to build 3D structures for CH₄, H₃C-CH₃, H₂C=CH₂, cis- H₂C=CH-CH=CH₂ and then use MolLib to send the 3D structure of benzene to your workbench. Make two copies of benzene then use MolDesign to edit one into toluene and the other into its cyclo-hexadiene isomer.
2. Use Basic QChem Edu, Basic QChem, Mopac GUI Cloud or Pro to search for stable structures for these species then record their heats of formation.
3. Calculate the reaction energies that represent ASE from the above three reactions then compare to the literature value of -28 kcal/mol.

Part B:

1. Write the ISE reaction for representing ASE in cyclobutadiene, naphthalene, and cyclo-octatetraene as shown respectively below.

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(note that you need to add a methyl group to these molecules in order to use the ISE approach).

2. Use MolLib to send out 3D structures for the above three molecules then use MolDesign to edit them for adding methyl group and making their isomer analogs.
3. Repeat step 2 in part A then calculate the ASE for these molecules.
4. What can you draw for a conclusion about the relative ASE of these molecules compared to benzene? Does your conclusion support the $(4n + 2)$ rule for aromatic molecules and the $4n$ rule for anti-aromatic molecules where n is the number of pi-electrons?

References

1. S. M. Bachrach, Computational Organic Chemistry, 2007, Willey & Sons.