



Computational Chemistry Workshops
West Ridge Research Building-UAF Campus
9:00am-4:00pm, Room 009

Electronic Structure - July 19-21, 2016
Molecular Dynamics - July 26-28, 2016

Why are the Azulene and Naphthalene Molecules So Different?

Azulene and Naphthalene: Why are these molecules so different?

Azulene and naphthalene, shown in Figure 1 below, are both aromatic hydrocarbons, have the same molecular formula, $C_{10}H_8$, and are geometric isomers.

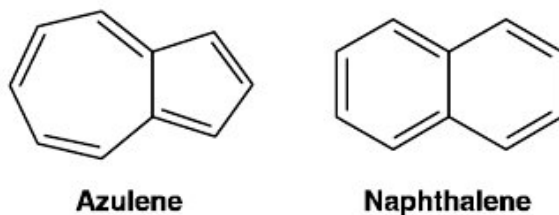


Figure 1: The azulene and naphthalene molecules.

Dipole Moment of Azulene versus Naphthalene

Hydrocarbons are generally considered to be non-polar, or weakly polar, characterized by dipole moments that are typically only a few tenths of a debye. One recognizable exception to this trend is azulene, which has a dipole moment of 0.8 debye.

Optimization of the geometry of azulene, and naphthalene as a reference, followed by the calculation of an electrostatic potential map, yields the following results when they are displayed side by side:

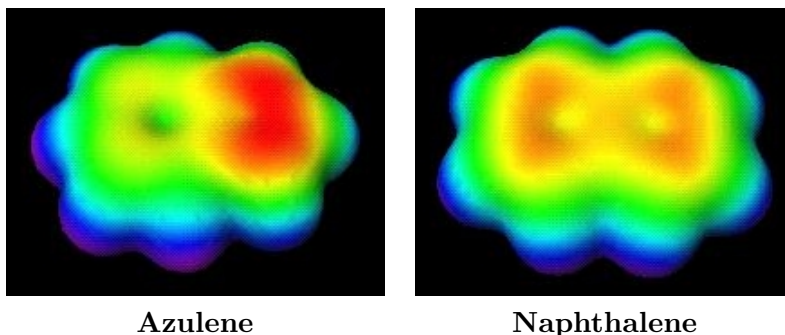


Figure 2: Electrostatic Potential Energy Surfaces

Relative to naphthalene as a standard (blue-green-yellow-red), the seven-membered ring is more positive (blue-green-yellow) while the five-membered ring is more negative (red), and is consistent with the sign of the dipole moment.

The simplest interpretation is that azulene is composed of two aromatic rings, the cycloheptatrienyl (tropylium) cation and the cyclopentadienide anion, each containing 6 π -electrons, and then fused together. There is a significant contribution from the resonance structure shown below, in which the seven-membered ring donates a π -electron into the five-membered ring.

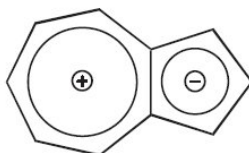
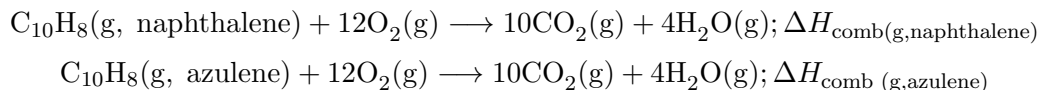


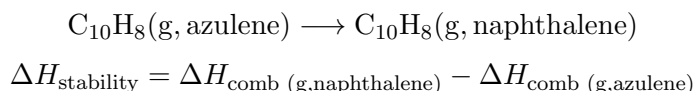
Figure 3: Charge Polarization within the Azulene Molecule

Difference in Stability Between Azulene and Naphthalene

It is important to compare the experimental heats of combustion of azulene and naphthalene, obtained with a bomb calorimeter experiment, and then relate the observed difference to theoretically computed energy difference of the two molecules. Since naphthalene and azulene are isomers, they have the same heat of combustion reaction:



Subtracting the above two equations yields:



Thus, the difference in heats of combustion of these two molecules immediately provides a measure of the difference in their stability. The experiment can be characterized as measuring the difference in resonance stabilization energies of two aromatic molecules: Experimental values for heats of combustion can be readily obtained from the CRC Handbook or the online NIST Chemistry WebBook (<http://webbook.nist.gov>).

The calculated values will be approximate because an approximate model is used to describe the interactions between the positively charged nuclei and electrons of which the molecule is comprised. Theoretical calculations provide a values of $\Delta H_{\text{stability}} = -147$ kJ/mol, compared to -148 kJ/mol for the experimentally determined value. A qualitative explanation for the greater stability of naphthalene over azulene can also be explained in terms of resonance stabilization as will be shown below, since only two resonance structures can be written for azulene (**1**) compared to three for naphthalene (**2**).

Blue Azulene and colorless Naphthalene: Why?

Azulene and naphthalene both have the same chemical molecular formula, $C_{10}H_8$, and also the same number of conjugated double bonds, and yet naphthalene is colorless while azulene is azure or blue.

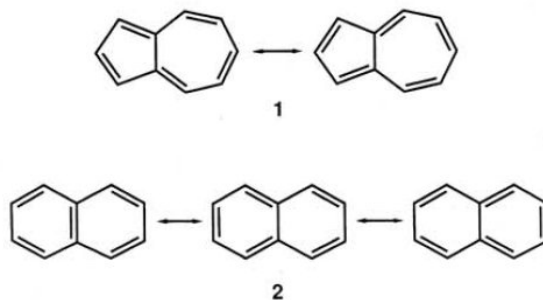


Figure 4: The naphthalene molecule has three resonance structures while azulene molecule has only two.

A fundamental difference between naphthalene and azulene is that the former is an alternant hydrocarbon while the latter is non-alternant hydrocarbon, as shown in Figure 5.

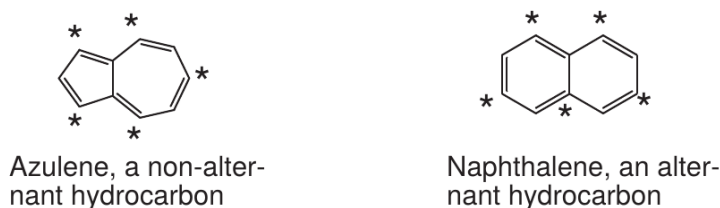


Figure 5: non-alternate hydrocarbon, azulene and alternate hydrocarbon, naphthalene.

The carbon atoms of an alternant hydrocarbon can be divided into two sets, called *starred* and *unstarred*, neither of which contains two adjacent atoms. This is not the case for azulene which has two odd-membered rings. Alternant hydrocarbons have the interesting property that their Huckel molecular orbitals come in pairs arranged symmetrically about a nonbonding energy level. For a *mirror-related pair of orbitals*, the signs of the MO coefficients are switched, but the charge distribution of all atomic orbital coefficients is identical, leading to electrons occupying similar regions of space. The Huckel molecular orbitals obtained from Huckel theory is shown in Figure 6 below: In contrast, non-alternant hydrocarbons do not have *mirror-related* molecular orbitals, and their charge distribution is non-uniform. In azulene there is a significant buildup of electronic charge in the five-membered ring at the expense of the seven-membered ring as seen in Figure 3 above which leads to a large dipole moment.

The most striking characteristic of azulene and its derivatives is their beautiful blue color which is quite rare in hydrocarbons.

A qualitative understanding of the colors of organic compounds can be derived from *one-electron* molecular orbital theory. The narrower the gap between the HOMO and LUMO of a molecule, the less the energy required for an electronic transition, and thus the longer the wavelength of the light that excites the transition. On this basis alone, however, one might predict that azulene should be colorless like naphthalene.

To understand the striking color in azulene, one must take into account the mutual repulsion between electrons, as well as the form of the HOMO and LUMO. Since azulene is a non-alternant hydrocarbon, the HOMO and LUMO are not *mirror-related*. Thus, the atomic orbital coefficients in these two orbitals differ greatly at many of the carbon atoms. As a result, promotion of an electron from the HOMO to the LUMO increases the average separation

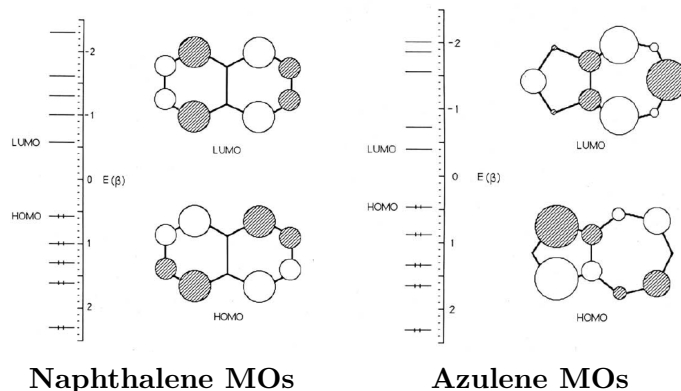


Figure 6: Hückel molecular orbital energies of the HOMO and LUMO of naphthalene and azulene.

between these electrons, reduces electron repulsion, and yields a corresponding **lower** electronic transition. In contrast, for the alternant hydrocarbon, naphthalene, the $\text{HOMO} \rightarrow \text{LUMO}$ transition does not essentially change the electronic charge distribution, because of the mirror relationship of the two orbitals. This leads to larger electron-electron repulsion with a concomitant increase in HOMO/LUMO energy along with a **larger** electronic transition energy.

It is interesting that azulene fluorescence is also blue instead of red. The $S_0 \rightarrow S_1$ transition occurs at approximately 600 nm, so at first glance fluorescence emission at 600 nm - 700 nm might be expected. nevertheless, on placing azulene under UV light, a blue fluorescence is obtained, instead of red. The extremely unusual combination of a small $S_0 - S_1$ gap, large $S_1 - S_2$ energy gap, forbidden $S_1 \rightarrow S_0$ and $S_2 \rightarrow S_1$ transitions, together with the allowed $S_2 \rightarrow S_0$ transition, leads to blue fluorescence light. There is also the possibility of radiationless decay from an S_1/S_0 conical intersection.

The HOMO and LUMOs, together with a qualitative state diagram for azulene is given in Figure 7.

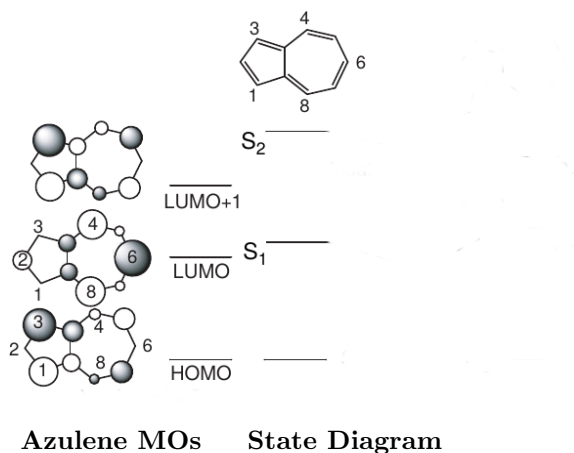
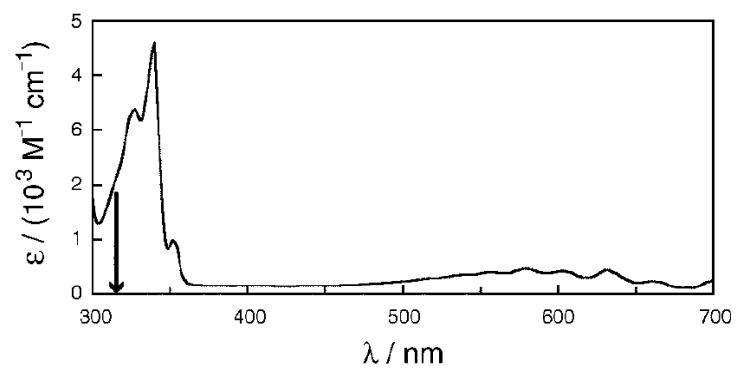


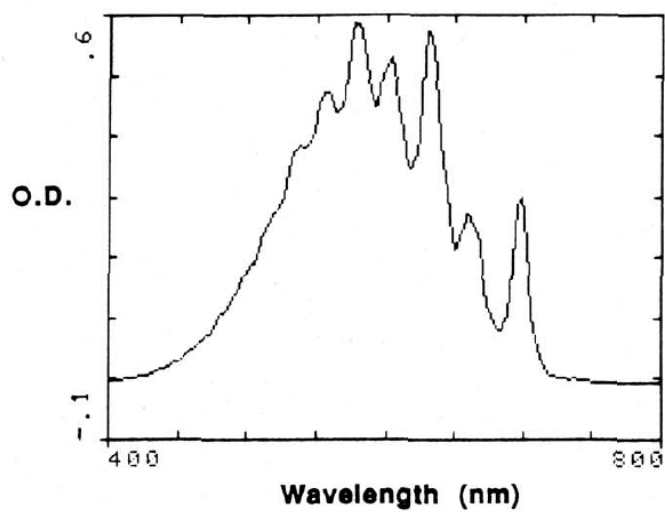
Figure 7: Azulene Molecular Orbitals and State Diagram Showing the S_1 and S_2 Excited States.

Exercise

Using the GAMESS program, perform MCSCF calculations to obtain the geometries and excited states of naphthalene and azulene.



heptane solvent



cyclohexane solvent

Figure 8: Absorption spectra of azulene at room temperature