



Computational Chemistry Workshop

Blue Azulene and Colorless Naphthalene: Why?

Angelo R. Rossi
Department of Chemistry
The University of Connecticut
angelo.rossi@uconn.edu

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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.

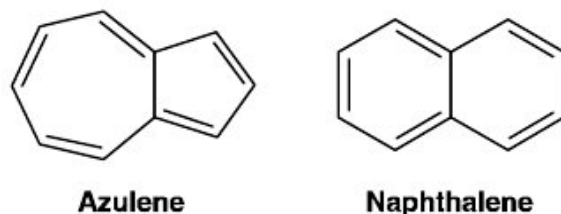


Figure 1: The azulene and naphthalene molecules.

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:

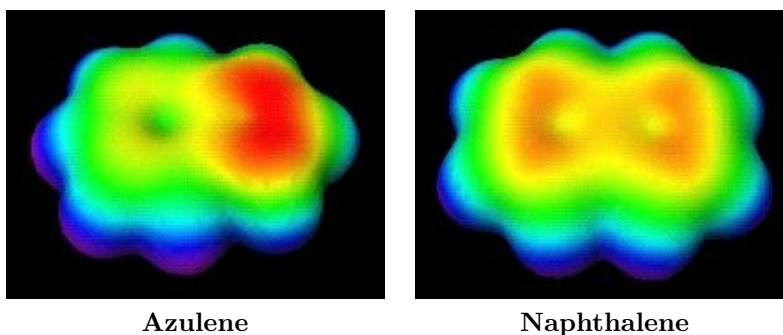


Figure 2: Electrostatic Potential Energy Surfaces

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.

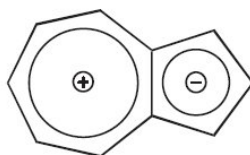


Figure 3: Charge Polarization within the Azulene Molecule

Excited States of Azulene and Naphthalene

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.

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.

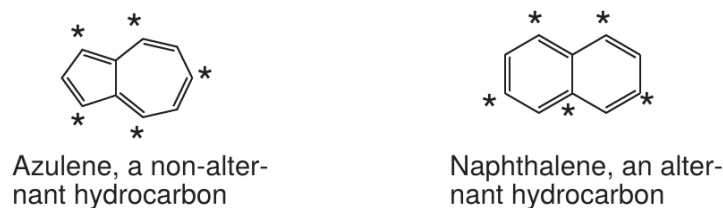


Figure 4: non-alternate hydrocarbon, azulene and alternate hydrocarbon, naphthalene.

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 Hückel molecular orbitals come in pairs arranged symmetrically about a non-bonding 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 molecular orbitals obtained from Hückel theory are shown in [Figure 5](#) below:

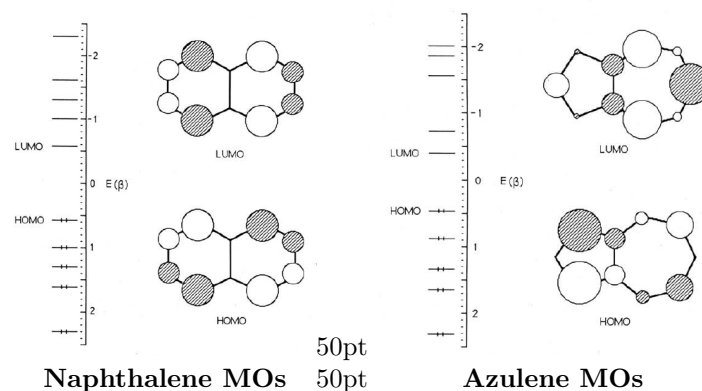


Figure 5: Hückel molecular orbital energies of the HOMO and LUMO of naphthalene and azulene.

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.

Azulene

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 between these electrons, reduces electron repulsion, and yields a corresponding **lower** electronic transition.

Azulene has C_{2v} symmetry. The following include reasons why azulene fluorescence is blue:

1. The $S_0 \rightarrow S_1$ transition occurs at approximately 600 nm because of a small energy gap between the ground and excited states, which absorbs in the red portion of the spectrum.
So, at first glance, absorption should yield a blue color for azulene. Wavelengths in the red color region are absorbed, leaving the remaining wavelengths of light in the complementary blue color region. Meanwhile, fluorescence emission ($S_1 \rightarrow S_0$) should yield wavelengths > 600 nm.
But the absorption $S_0(^1A_1) \rightarrow S_1(^1B_2)$ is very weak, leading to little absorption, as well as essentially little fluorescence.
2. The $S_0(^1A_1) \rightarrow S_2(^2A_1)$ absorption is much stronger, but any $S_2 \rightarrow S_1$ transition via internal conversion, following Kasha's Rule, would again involve a weak fluorescence by emission to the ground state, S_0 .
3. Nevertheless, on placing azulene under UV light, a blue fluorescence is obtained. The allowed $S_2 \rightarrow S_0$ transition, somewhat unusual because of the weakly fluorescent S_1 state as well as poor overlap between S_1 and S_2 states, leads to blue fluorescence light from the higher excited state. This fluorescence is also enhanced by similar geometries between the S_2 and S_0 states, allowing for good Franck-Condon overlap.
4. There is also the possibility of radiationless decay from an $S_1 \rightarrow S_0$ non-adiabatic transition through a conical intersection.

The HOMO and LUMOs, together with a qualitative state diagram for azulene are given in [Figure 6](#)

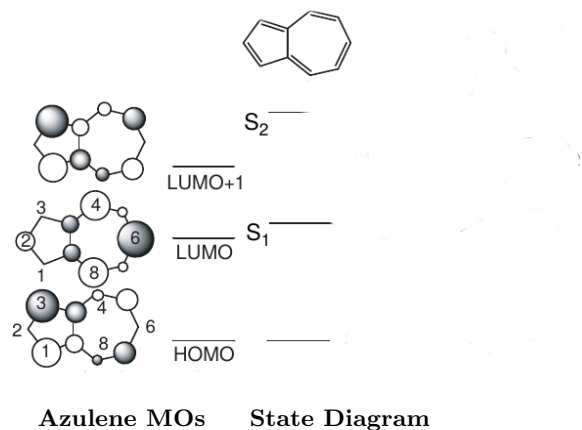


Figure 6: Azulene Molecular Orbitals and State Diagram Showing the S_0 , S_1 , and S_2 States.

Naphthalene

In contrast, for the alternant hydrocarbon, naphthalene, the HOMO \rightarrow 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.

Exercises

1. Perform calculations to obtain optimized geometries of naphthalene and azulene.
2. Use the results step 1 to calculate low-lying excited states of naphthalene and azulene. Use Group Theory and symmetry concepts to verify the calculated oscillator strengths.
3. Calculate electron density shifts for both molecules in going from the ground state to the excited states.
4. Visualize the molecular orbitals for both naphthalene and azulene, and then rationalize the experimental UV spectra of both molecules.
5. Using substituents such as $-\text{CH}_3$ and $-\text{F}$ in appropriate positions on azulene, determine how the excitation and fluorescent spectra can be modified.

Appendix

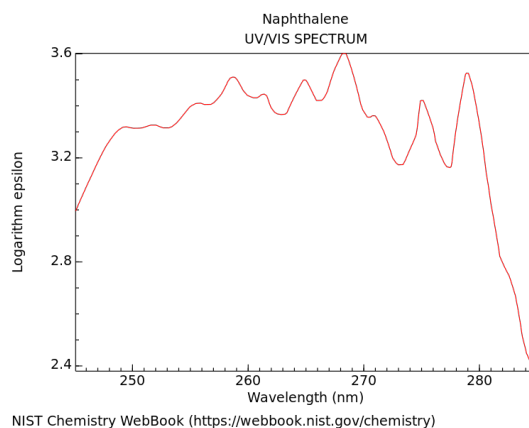


Figure 7: Ferguson, J.; Reeves, L.W.; Schneider, W.G., Vapor absorption spectra and oscillator strengths of naphthalene, anthracene, and pyrene, Can. J. Chem., 1957, 35, 1117-1123.

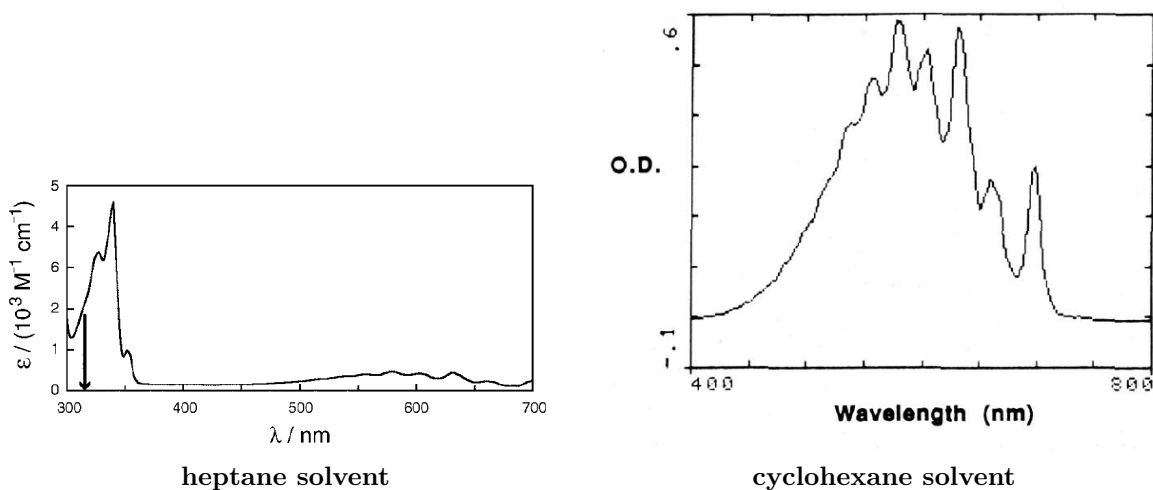


Figure 8: Absorption spectra of azulene at room temperature

Experimental and Calculated Results, in eV Relative to the Ground State, for Low-lying Excited States of Azulene:

	Experiment	Calculated (Relaxed)	Calculated (Vertical)
S_0	0	0	0
S_1	1.78	1.66	1.96
S_2	3.56	3.67	3.81