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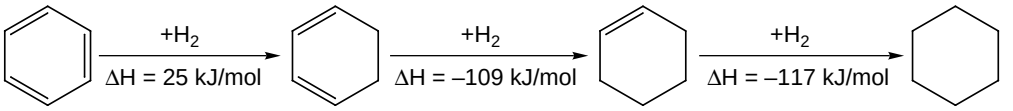
Is Azulene Aromatic?

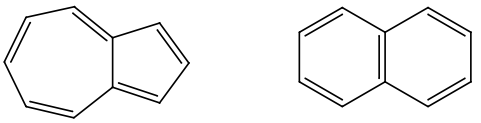
Aromatic molecules are (thermodynamically) more stable than might have been anticipated. The famous case is benzene. Here, the first step in its complete hydrogenation (to cyclohexane) is *endothermic*, while both of the remaining steps are *exothermic*.



The difference in the hydrogenation energy between the first step and either the second or third steps (134 kJ/mol and 142 kJ/mol, respectively) provides a measure of the aromatic stabilization.

Aromatic molecules may also be distinguished in that they incorporate bonds intermediate in length between normal (single and double) linkages. For example, all carbon-carbon bond lengths in benzene are 1.39Å, which is longer than a double bond (1.30 to 1.34Å) but shorter than a single bond (1.48 to 1.55Å).

Is azulene, known for its intense blue color and the basis of numerous dyes, aromatic as is its isomer naphthalene? Both molecules incorporate 10 π electrons in a planar fused-ring skeleton.



azulene naphthalene

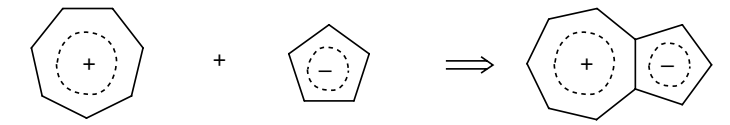
In this activity, you will compare energies, geometries and electrostatic potential maps for azulene and naphthalene in an effort to decide.

1. Build azulene and naphthalene and obtain their equilibrium geometries using the HF/3-21G model. Is azulene more stable (lower in energy), less stable or about as stable as naphthalene? If

it is less stable, is the energy difference between the two isomers much less, much greater or about the same as the "aromatic stabilization" of benzene? On the basis of energy, would you conclude that azulene is or is not aromatic?

Calculate an "average" carbon-carbon bond length in azulene. Is this average similar to the carbon-carbon bond length in benzene? Next, calculate the mean absolute deviation from the average to provide a measure of the uniformity of bond lengths. Is this deviation similar to the corresponding quantity for naphthalene? On the basis of uniformity in bond lengths alone, would you conclude that azulene is or is not aromatic?

It is common to suggest that azulene is made up of the "fusion" of two aromatic ions, both with 6 π electrons, cycloheptatrienyl (tropylium) cation and cyclopentadienyl anion.



cycloheptatrienyl cation | cycloheptadienyl anion | azulene

This being the case, the "cycloheptatrienyl side" of azulene should be "positively charged" (relative to naphthalene) while the "cyclopentadienyl side" should be "negatively charged".

2. Request electrostatic potential maps for naphthalene and azulene, and display them in the same scale and side-by-side on screen.

> Set the "color scale" for both molecules to be the same and centered at "0". For each molecule, select **Properties** from the **Display** menu and *click* on the electrostatic potential map. Inside the **Surface Properties** dialog which results, change the property range to be the same for both molecules (-30 to 30 is a good range).

Do you see evidence of charge separation in azulene? Is it in the expected direction? What effect would you expect charge separation to have on the energy of azulene? Elaborate.