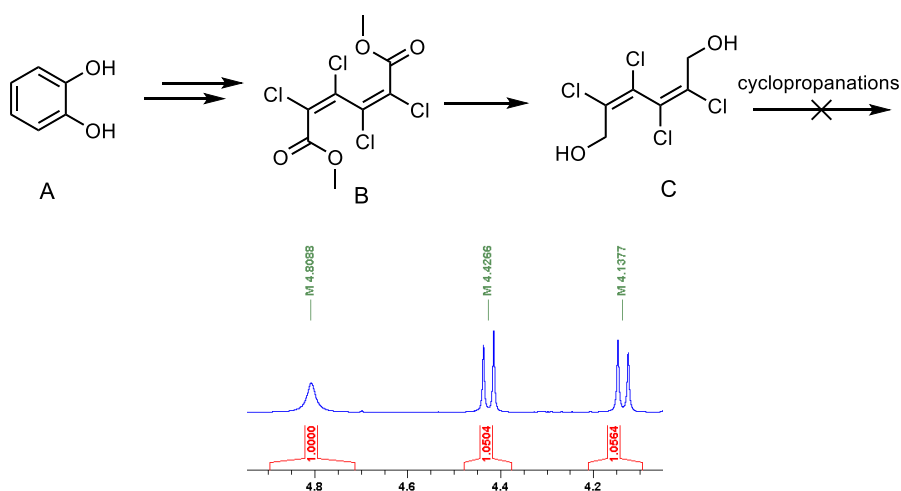
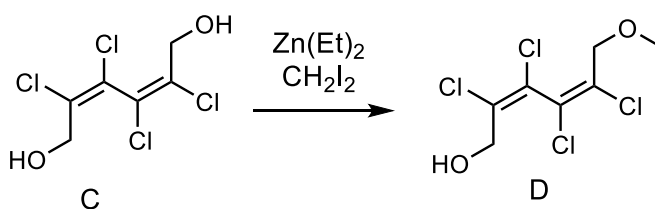


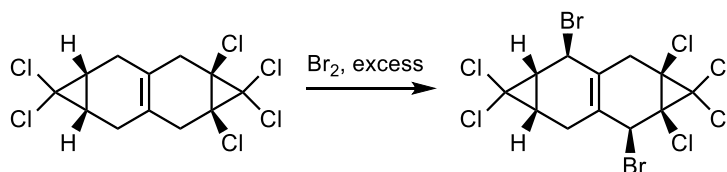
1a) Several routes to various 10-annulenes were sought, one of which involved the chlorination and ring cleavage of catechol **A**. Product **C** was obtained after several steps as an oil and had three protons in the NMR spectrum (shown below). Explain the NMR data. What does this imply about the molecule? Is it possible to obtain the expected spectrum (two singlets) by manipulating the NMR conditions?



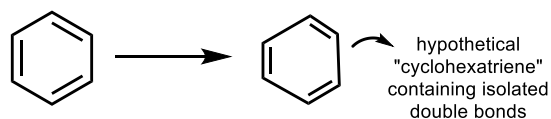
1b) Cyclopropanations of this substrate failed with all attempted methods. However, during investigations an unusual product was obtained when the diene was subjected to Simmons-Smith cyclopropanation conditions. Propose a mechanism for this transformation.



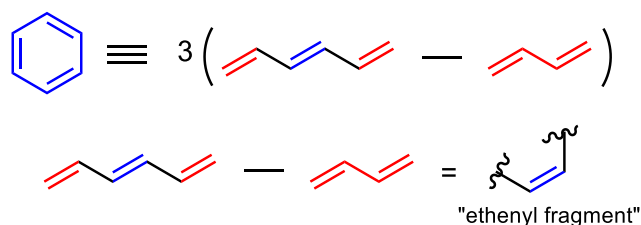
2. Propose a mechanism for the following transformation. What is the symmetry in the molecule (as drawn)? Is it chiral?



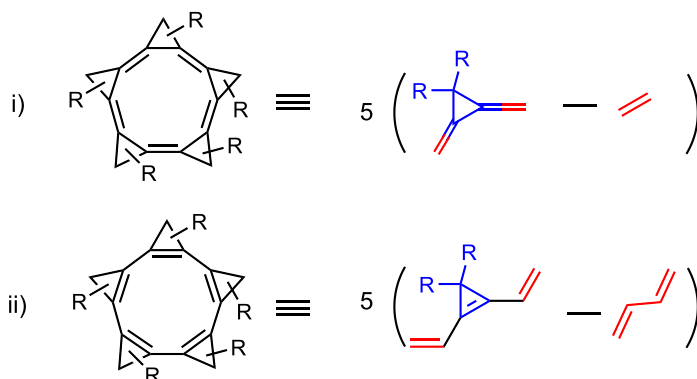
3. Quantifying the aromaticity of a molecule is often quite difficult to do experimentally. Many methods have attempted to do so with mixed results. One such method measures the aromatic stabilization energy (ASE) by comparing a hypothetical non-conjugated molecule with the fully conjugated and apparently aromatic species. This can be done for benzene by comparing the parent structure with the hypothetical non-conjugated cyclohexatriene containing isolated (non-interacting) double bonds.



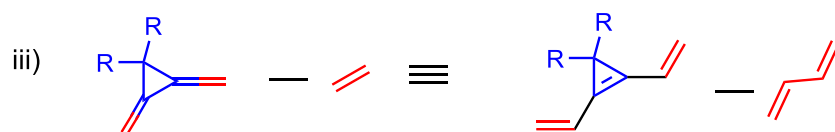
Since this structure is hypothetical it must be investigated computationally. One way to approximate this species is by creating a reaction that compares benzene against individual and isolated alkenes. For benzene we can create isolated ethenyl fragments by subtracting butadiene from hexatriene. The sum of the energies of three ethenyl fragments are then compared with the energy of benzene, the difference between these two values is taken to be the ASE of benzene. If benzene is *lower* in energy than the fragments it is **aromatic** if it is higher in energy it is either non-aromatic or antiaromatic.



There are typically multiple ways to fragment a molecule, especially when two different Kekule structures exist (note that benzene has two *degenerate* Kekule structures). Planar cyclopropanated 10-annulenes are an instructive case:



When $R=F$ the top equation (i) shows that the annulene is *lower* in energy than the fragments on the right (it is **aromatic**). Equation (ii) shows that the annulene is *higher* in energy than the fragments on the right (it is **non-/anti-aromatic**). We can omit the annulene itself and simply compare the fragments to see a similar trend:



In this case (equation iii), the sum of the fragments on the *right* are *lower* in energy than the fragments on the left, suggesting that it is more stable. Draw the fragments depicted by the equations (like the ethenyl fragment for benzene above). What is the origin of the different ASE values from (i/ii)? (look at iii for a hint) What does this imply regarding the aromaticity of the molecule (Which Kekule structure dominates in the overall structure)?