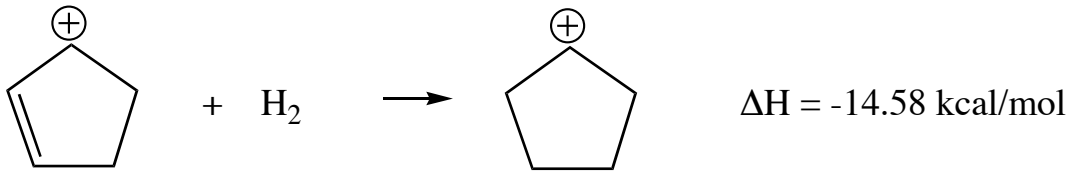
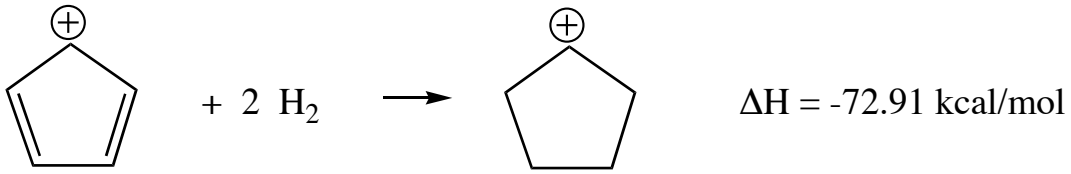
Exercise 111 - Res Energy/MO

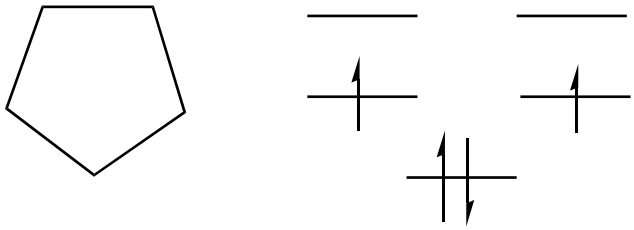
Question
From the following, calculate the resonance energy of the cyclopentadienyl cation.





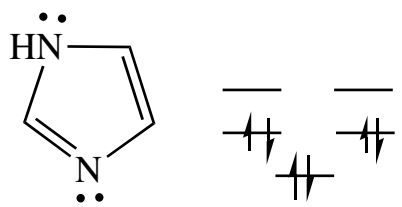
One hydrogenation of the allyl cation liberates -14.58 kcal/mol, so two should liberate -29.16 kcal/mol. Hydrogenation actually gains -72.91 kcal/mol making the cation HIGHER in energy by 43.75 kcal/mol. The resonance energy is NEGATIVE: -43.75 kcal/mol.

Sketch the MO diagram for this species and use it to determine whether this is an aromatic or antiaromatic molecule. Is this consistent with the resonance energy?

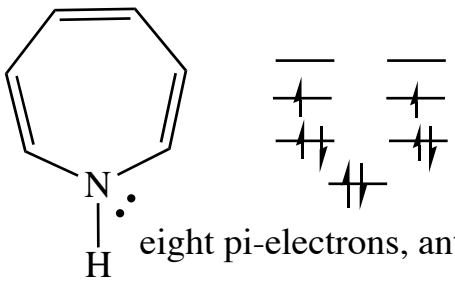


Predicts this cation to be antiaromatic which is consistent with the negative resonance energy.

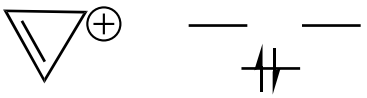
Question
Sketch MO diagrams for the following molecules/ions and use them to predict whether they are aromatic or antiaromatic.



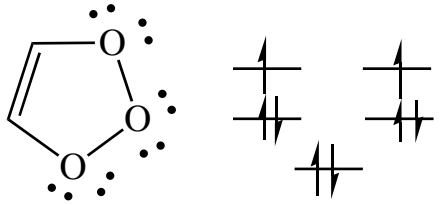
Six pi-electrons, aromatic.



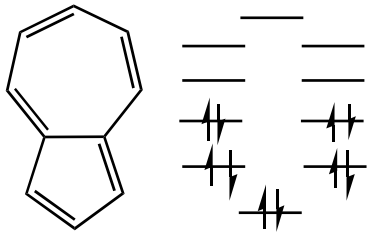
eight pi-electrons, antiaromatic.



Two pi-electrons, aromatic.



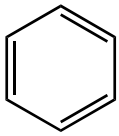
Eight pi electrons, antiaromatic.



Ten pi electrons: aromatic.

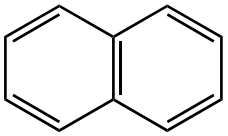
Question Four

i) Shown below are the structures of the first four benzene-based aromatic hydrocarbons and their associated resonance energies. Calculate the REPE (resonance energy per pi electron) for each one. What do you notice?



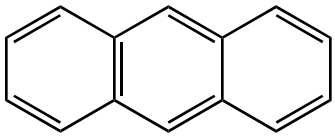
Benzene

36 kcal/mol



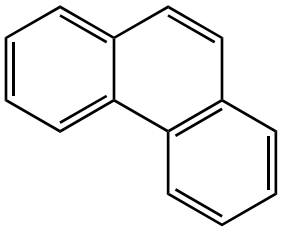
Naphthalene

61 kcal/mol



Anthracene

84 kcal/mol

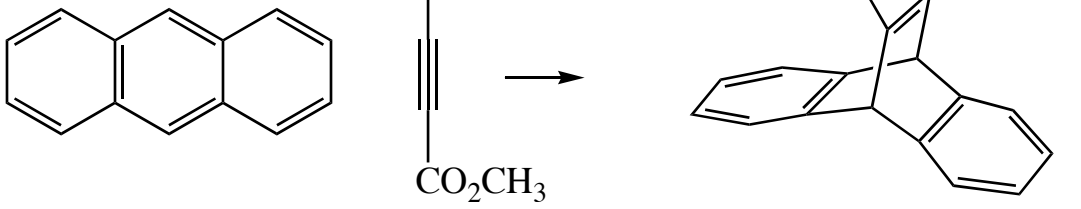


Phenanthrene

92 kcal/mol

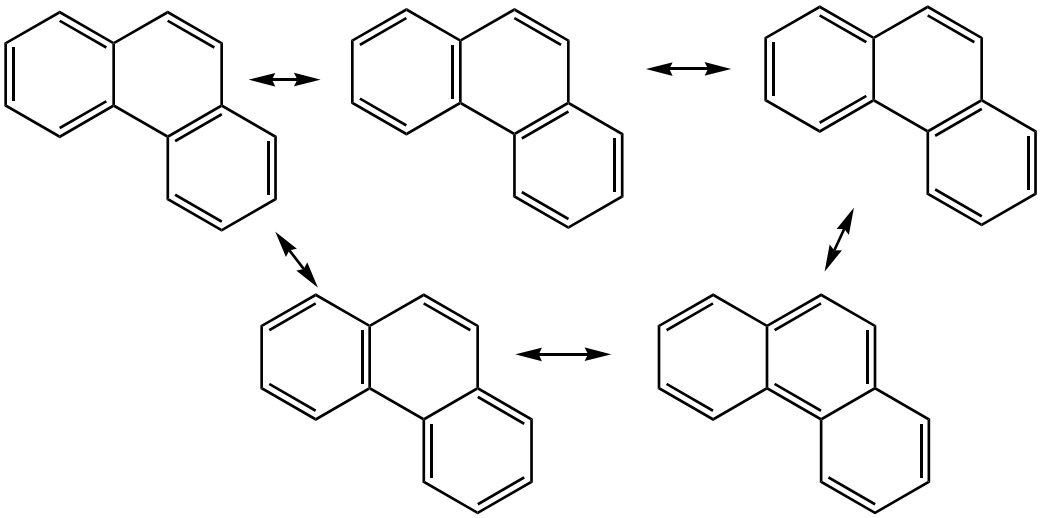
The no. of pi electrons are 6, 10, 14 and 14 respectively.
The REPEs are 6.0, 6.1, 6.0 and 6.6. Note that they are very similar for the first three and somewhat higher for phenanthrene.

ii) Benzene and naphthalene do not undergo addition reactions. Anthracene, however, will react as a Diels-Alder diene:

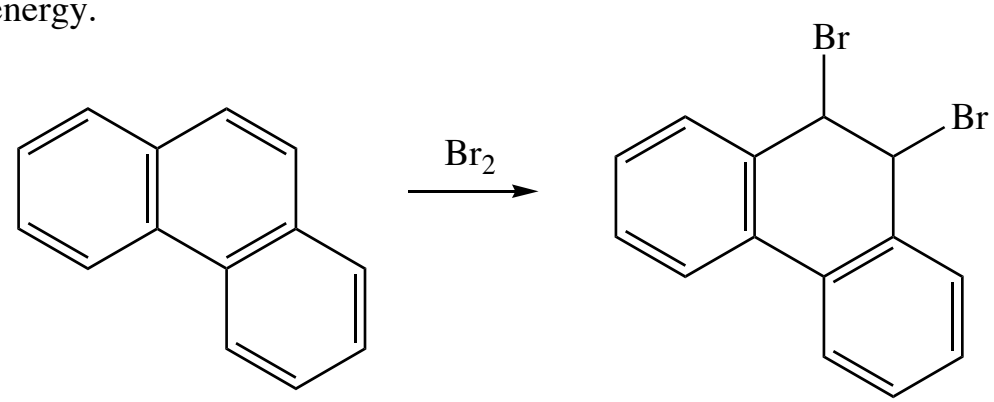


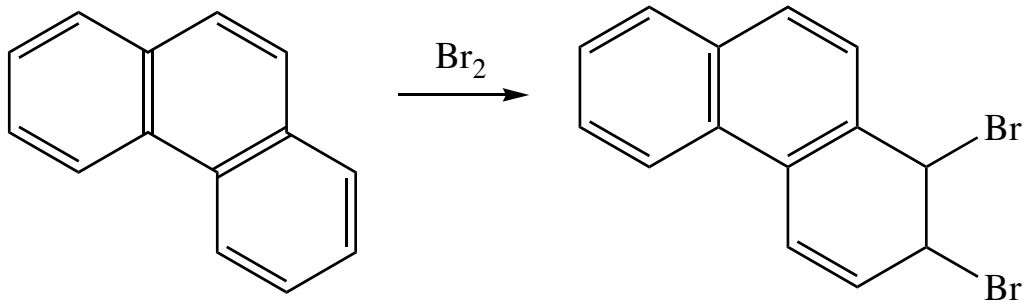
Diels-Alder reactions are normally favourable because of pi to sigma bond conversions. Diels-Alder reaction with benzene costs 36 kcal/mol of energy, though, which will cancel this out making the reaction unfavourable. With naphthalene, a Diels-Alder reaction will take out one of the two rings but leave an intact benzene ring in the product. The net loss is 24 kcal/mol. In anthracene, two benzene rings remain in the product so the net loss of resonance energy is only 84 - 72 = 12 kcal/mol.

iii) Phenanthrene has five Kekulé resonance structures. One of the bonds of phenanthrene reacts with bromine to give an ***addition reaction*** just like an alkene. Which bond? Explain.



Reaction at this bond costs 92 - 72 (two benzenes) = 20 kcal/mol in resonance energy.





Reaction in the other ring costs 92 - 61 or 31 kcal/mol.