

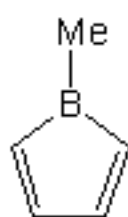
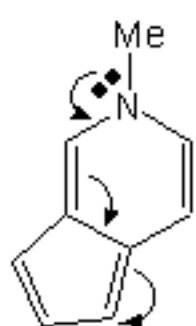
# Organic Chemistry c3444y

## Problem Set 1 - Answer Key

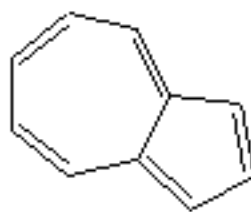
### 1. *Aromatic!!*

If we just count pi electrons, we will count 16, which is a non-Huckel number, and we would conclude that the compound should be antiaromatic. But we must remember the structure of alkynes: They are composed of two pi bonds, which are orthogonal to each other. In this case, only one of those pi bonds will be aligned or oriented properly for overlap with the other double bonds. The other is orthogonal, and therefore, cannot interact. So we only count 2 electrons for the alkyne. This gives 14 overall, which is a Huckel number.

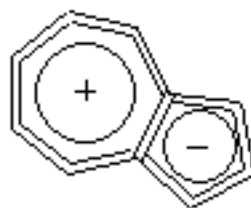
2.



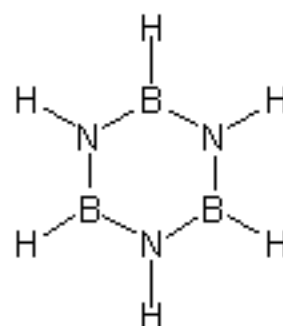
Antiaromatic.  
The B is  $sp^2$ -hybridized. Thus, there is an empty p orbital that interacts with the carbon p orbitals, and there are 4 pi electrons.



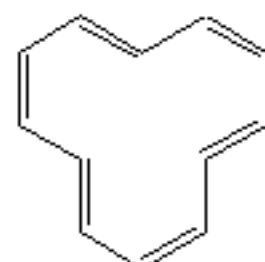
Should have significant aromatic character.



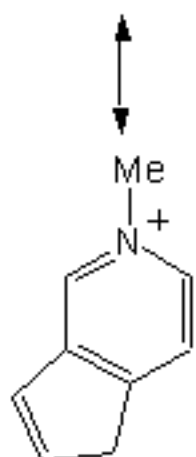
*We discussed this one in class.*



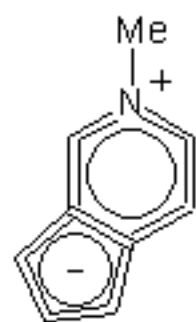
Aromatic!!  
If all B's and N's are  $sp^2$ -hybridized, then there is complete conjugation around the ring. The three lone pairs on the N's adds up to 6 pi electrons.



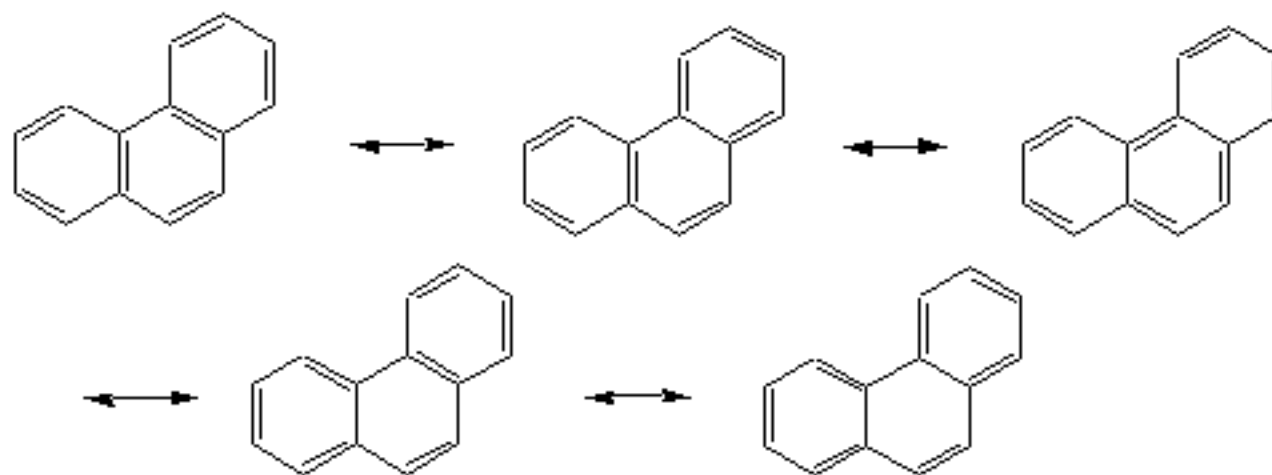
12 pi electrons (non-Huckel number), but large enough ring to have conformational flexibility. Therefore, we would expect this compound to be non-aromatic, just like cyclooctatetraene.



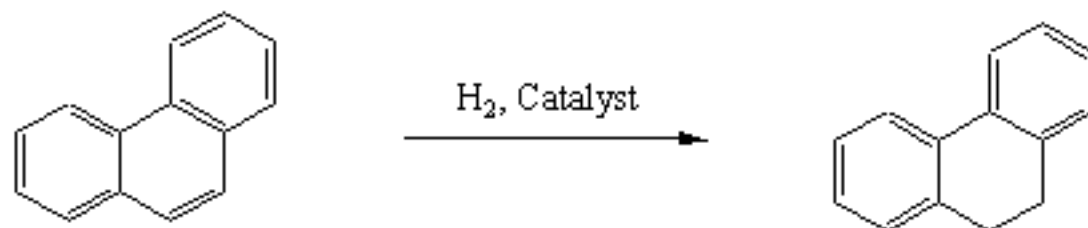
Should have significant aromatic character.



3.

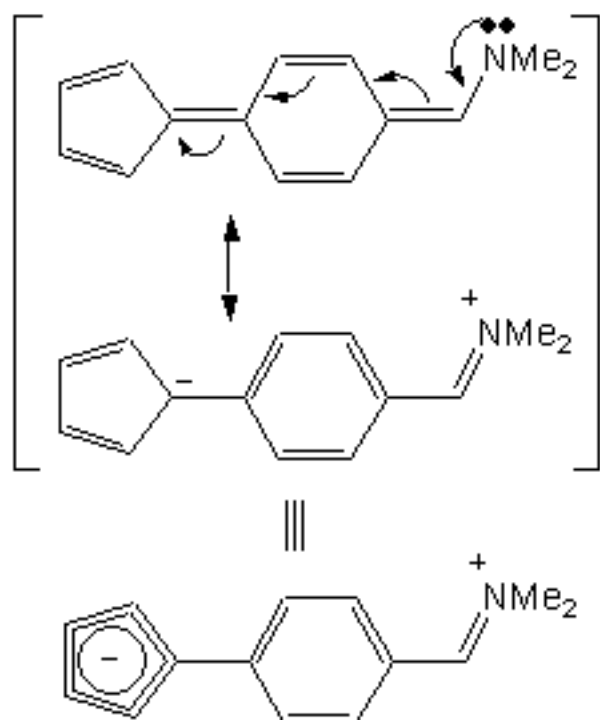


*The rings on the ends are aromatic in 4/5 or 80% of the resonance structures. The ring in the middle is aromatic in 2/5 or 40% of the resonance structures. Overall, this is more "aromaticity per ring" than anthracene where we concluded that each ring is aromatic in 50% of its resonance structures.*

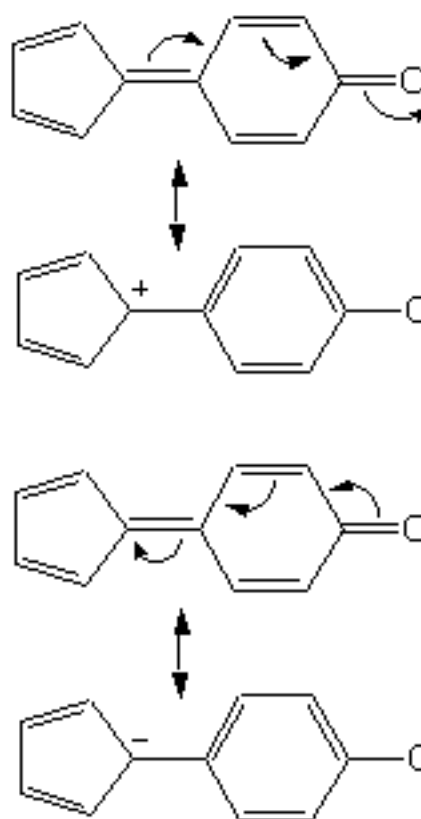


In doing this reduction, we've gone from a phenanthrene to two separate benzene rings, and we've lost  $92 - (36 \times 2) = 20 \text{ kcal/mol}$  of resonance energy. Reduction of any other of the double bonds of phenanthrene would lead to a much greater loss of resonance energy. Try it!

5.



Relatively more stable.  
We would expect a strong contribution from this resonance structure, in which both rings are aromatic with no significant problems.

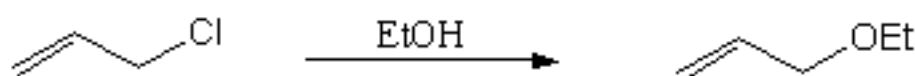


This resonance structure creates an antiaromatic ring, and thus is not a strong contributor.

If we try this, we not only have a put a + charge on O, but we have also deprived it of its full octet. Thus, this resonance structure would not be a strong contributor.

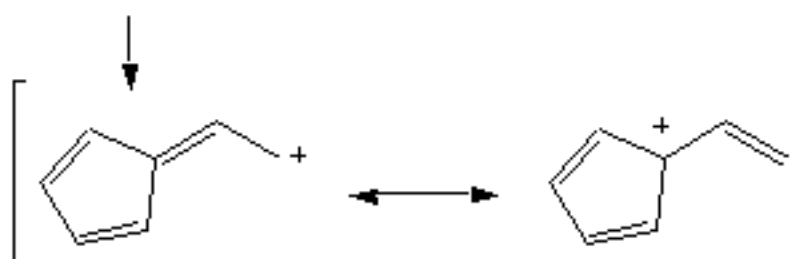
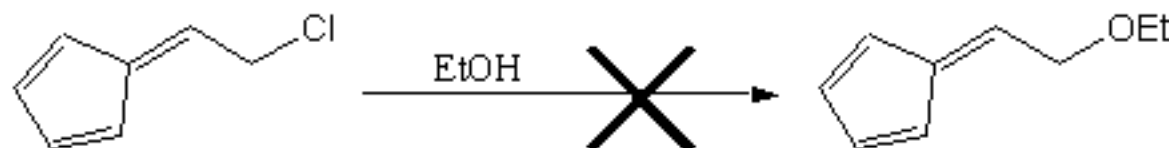
Overall, to the extent that the O is electron withdrawing, this molecule would be expected to have some antiaromatic character and would be relatively less stable.

6. i.



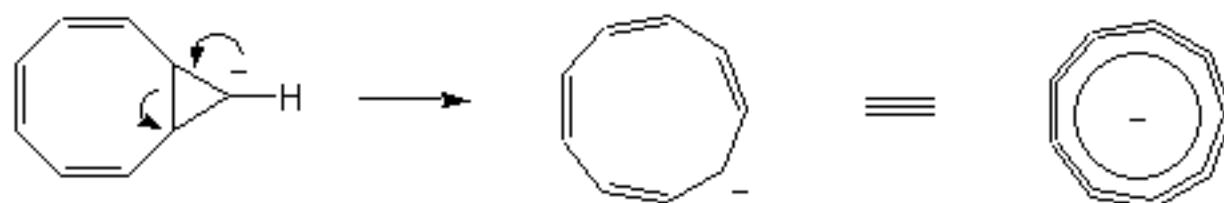
Simple  $S_N2$ . The intermediate cation is allylic.

ii.



In this case, the hypothetical cation intermediate is antiaromatic. Therefore it will not form.  $S_N2$  reactions only occur when the cation is easily formed (tertiary, allylic, e.g.). Here it would be especially unstable, and therefore does not form.

7.



10  $\pi$  electrons - Aromatic!