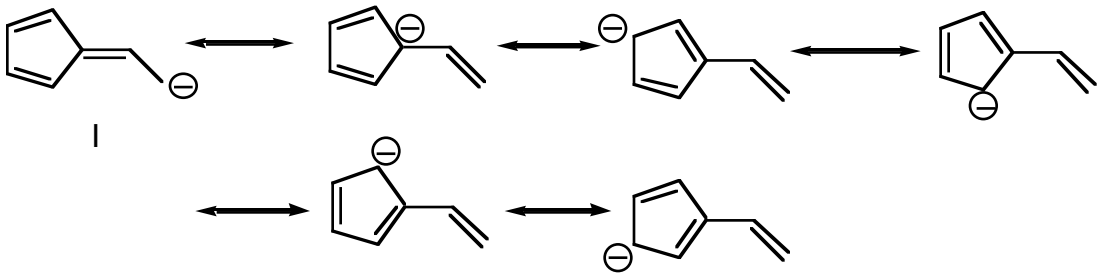
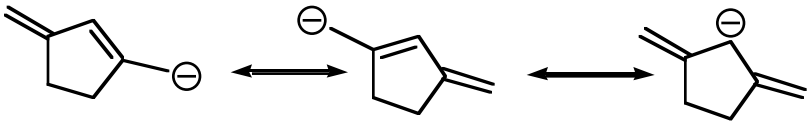
Problem Set #1 Answer Key

1. [14]-Annulene is aromatic. In [14]-Annulene, the aromatic ring current produces different effects inside and outside the ring. The 4 protons on the inside are shielded (chemical shift is at upfield, 0 ppm) while the 10 protons on the outside are deshieled (chemical shift is at downfield 7.6 ppm). Therefore the ratio of the two resonances is 4/10=2/5.
2. The top compound is more acidic since its conjugate base I is more stable. The anion I can delocalize its negative charge to the cyclopentadiene, whose anion is aromatic.
   It can also be explained in another way: the anion I has more resonance structures.
3. The compound III is covalent while the compound has much ionic

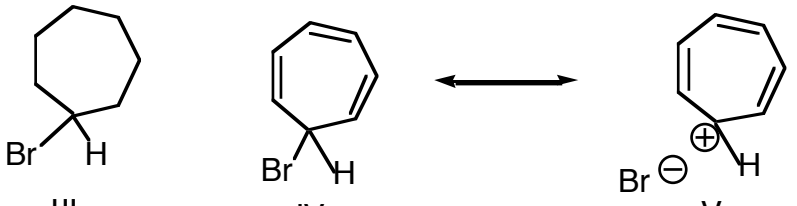


I



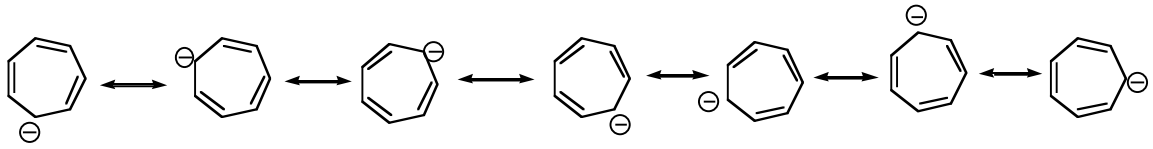
II

character because it has a stable resonance structure V, which has an aromatic cation.

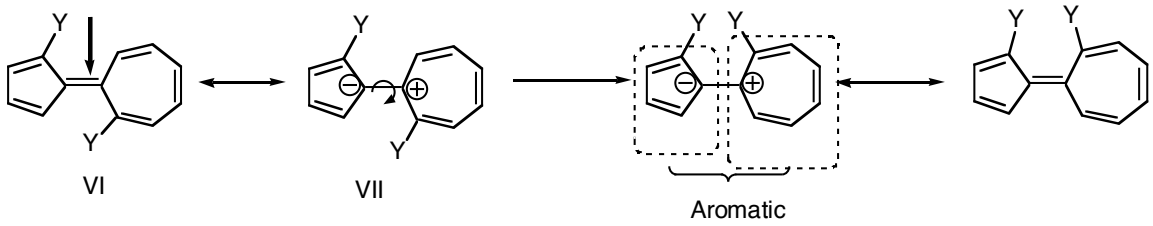


III IV V

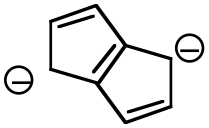
4. 8 π electrons make the anion anti-aromatic, so it is not stable though it has 7 resonance forms.



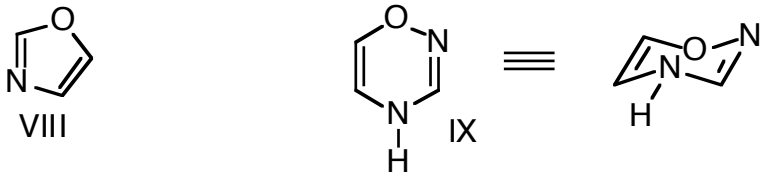
5. The double bond can not rotate as the single bond does since the rotation breaks the π bond. But the double bond indicated in compound VI has much character of single bond since the resonance structure VII is stablized by aromaticity. So the right equilibrium does occur through the rotation.



6. It aromatic because it has 10 π electrons totally or 6 π electrons on each ring.
7. The compound VIII is aromatic because it has 6 π electrons.



The compound IX is non-aromatic because the oxygen and the single bonded nitrogen are sp3-hybridized and their lone electron pairs are not



conjugated with the double bonds. This non-planar structure can avoid the anti-aromatic ring with 8 π electrons.

8. Both of the nitrogen atoms are sp2 hybridized. In pyrrole, the lone pair of electrons on nitrogen is in p-orbital and conjugated with double bonds to make an aromatic ring. But in pyridine, the lone pair of electrons on nitrogen is in sp2-orbital and outside the aromatic ring. The protonation on pyrrole nitrogen destroys the aromaticity while that on pyridine nitrogen does not. So the nitrogen in pyridine is more basic.

9. In the Diels-alder product of anthracene, two benzene rings are left. But the aromaticity will be totally lost if the Diels-alder reaction occurs on benzene.