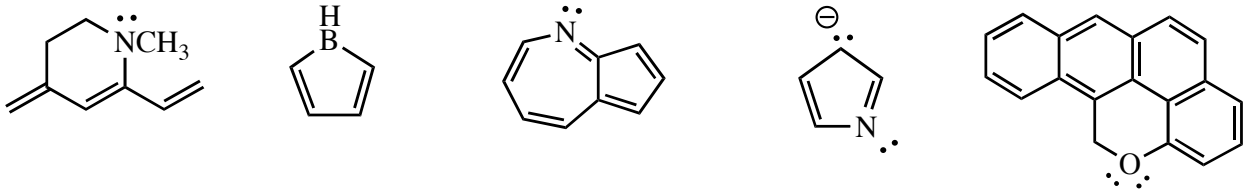
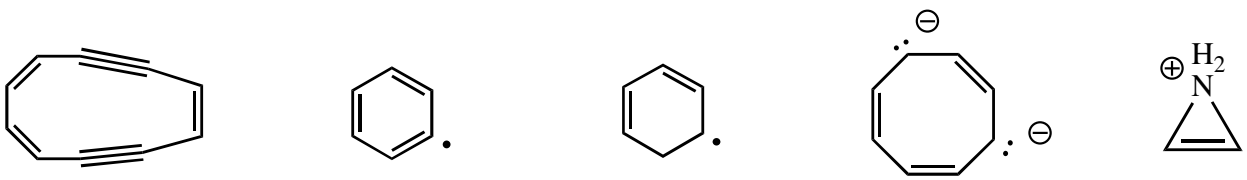
Chem 21 **Homework set 3**

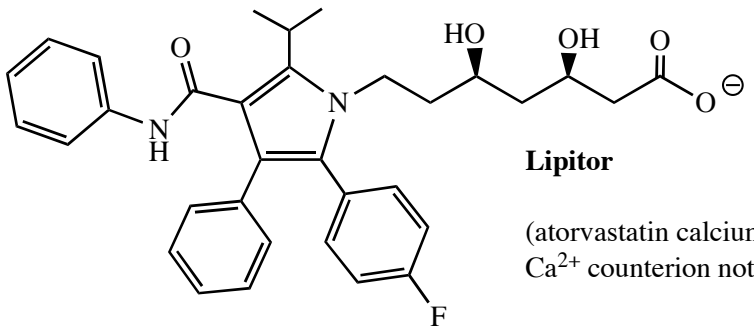
Same as before — lots of practice problems on the first two pages, the last two pages have the ones you need to turn in for credit on Wed 9/30.

End-of-chapter problems from Hornback: Ch16: 15, 16 (this problem shows a reasonable use of the bracket notation for the dianion, but we could instead draw several resonance structures or a representation of the delocalized structure with partial π-bonding and the double negative distributed around the ring), 17 - 22 (best to count around the perimeter here), 27 (note that the resonance stabilization you calculate in this case will be relative to an *isolated* double bond reference), 29 (disregard the SG answer — you can count electrons in the individual cycles, but a more general approach is to count electrons around the perimeter), 30 (same comment), 31.

1. Determine whether each compound below is aromatic, antiaromatic, or non-aromatic. To do this (a) determine whether a conjugated cycle of p-orbitals is present, (b) count π-electrons delocalized around the cycle, (c) apply the appropriate label, and (d) go back and make sure you didn't skip step a! Assume each conjugated π-system is planar.





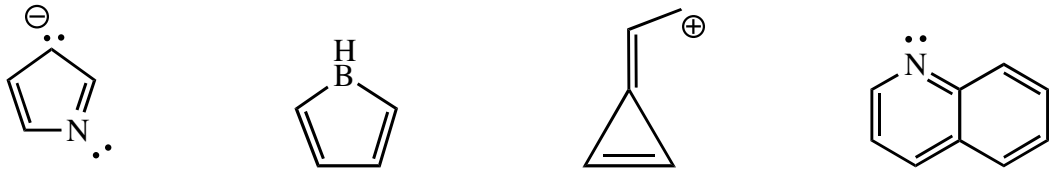


Lipitor

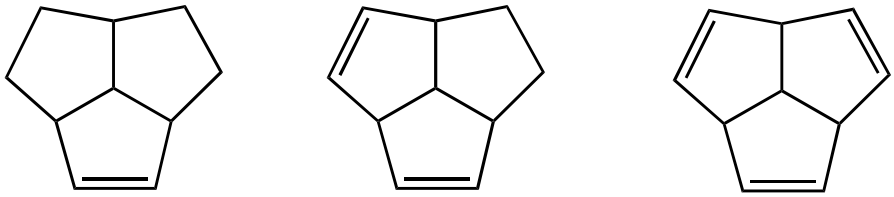
(atorvastatin calcium;
Ca^{2+} counterion not shown)

2. For each compound below, state the number of π-electrons in the conjugated cycle, if any, and state whether the compound is aromatic, antiaromatic, or non-aromatic. Show how the π-electrons are delocalized by *drawing all the important resonance structures* for each.

(a) (b) (c) (d)

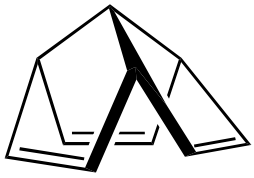


3. The structures and enthalpies of hydrogenation of three tricyclic alkenes are given below. All three produce the same tricyclic alkane.



$\Delta H°_{hydrog}$ = – 27.5 – 55.0 – 78.0 kcal/mol

Although the π-bonds of the diene and triene are not conjugated in the classical sense, their geometries allow the possibility of a *weak* interaction between the π-bonds. These π-bonds are said to be *homoconjugated*. The geometry is shown more clearly for triquinacene (the third compound) at right. (A model will provide a more realistic structure.)



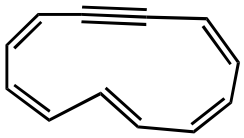
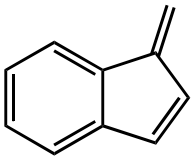
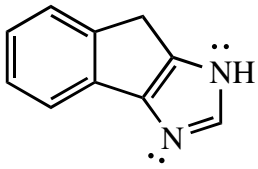
(a) Based on the enthalpies of hydrogenation, calculate the stabilization or destabilization associated with the two homoconjugated π-bonds in the second structure, if any.

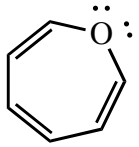
(b) Calculate the stabilization or destabilization associated with the three homoconjugated π-bonds in the third structure, if any. If this compound is more stable than expected, it would be called *homoaromatic*; if less stable, it would be *homoantiaromatic*. But beware: don't just count electrons, make a decision, and then force your calculation to support you preconception. Some of these systems can give you unexpected results. What do the *numbers* tell you?

(c) Draw a diagram showing the relevant actual and calculated enthalpy changes.

Chem 21
Fall 2009 *Name* _____
HW set 3
25 points; due Wed, Sept 30

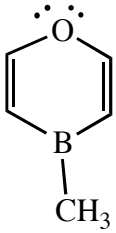
1. Same instructions as for problem 1 on the non-graded part.

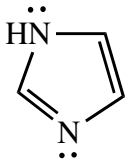


2. Same instructions as for problem 2 on the non-graded part.

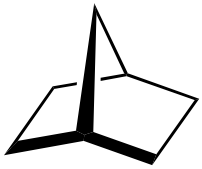
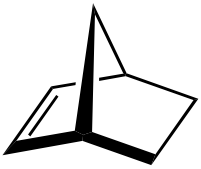
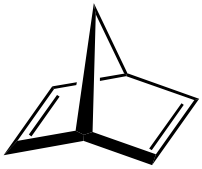
(a)



(b)



3. The enthalpies of hydrogenation of "norbornene" (bicyclo[2.2.1]hept-2-ene, 2nd structure below) and "norbornadiene" (bicyclo[2.2.1]hepta-2,5-diene, 3rd structure below) are given below. The hydrogenation product is "norbornane" (bicyclo[2.2.1]heptane, 1st structure below).

$\Delta H°_{hydrog}$ = **– 29.0** **– 60.0 kcal/mol**

(a) Make a model of the diene (3rd), then redraw the structure in the space below to show how the p-orbitals that make up the π-bonds are oriented in space.

(b) Does your diagram show a possible interaction between the π-bonds? If so, where?

(c) Of course, we can't tell from such a drawing whether that interaction is significant or not. That's where thermochemistry comes in. Use the enthalpies of hydrogenation to calculate the stabilization or destabilization associated with those two homoconjugated π-bonds in the third structure, if any.

(d) Draw a diagram showing the relevant actual and calculated enthalpy changes.