

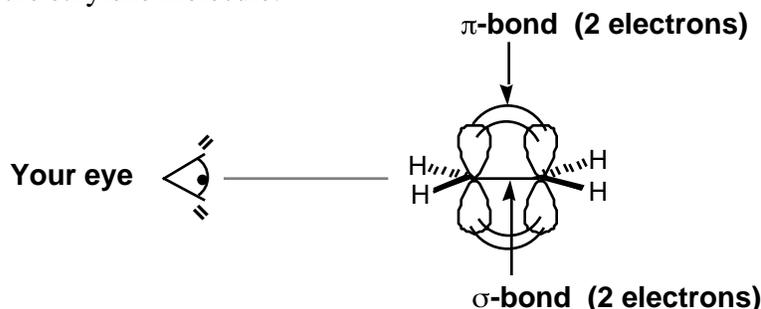
Problem Set #9

Chemistry 3230

March 23, 2001

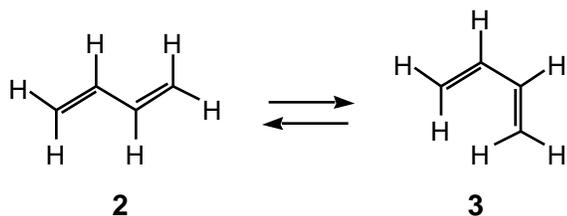
- The difference in energy between the axial and equatorial conformers ($\Delta G = G_{\text{AX}} - G_{\text{EQ}}$) for a mono-substituted cyclohexane is often referred to as the "A value" (A is for axial) for the substituent. For example, as we saw in class, the A value for a $-\text{CH}_3$ group is 1.7 kcal/mol. The A value for a trimethylsilyl group ($-\text{SiMe}_3$) is 2.5 kcal/mol.
 - Calculate the percent of equatorial conformer of trimethylsilyl cyclohexane at equilibrium at 25 °C.
 - Calculate the percent of equatorial conformer of *tert*-butyl cyclohexane at equilibrium at 25 °C. (The A value for the *tert*-butyl group is about 5 kcal/mol.)
 - Silicon is just below carbon on the periodic table. Why is the A value for the $-\text{SiMe}_3$ group so much smaller than for the $-\text{CMe}_3$ group?

- Here is a view of the ethylene molecule:



- Draw a Newman projection down the $\text{C}=\text{C}$ of ethylene. Draw in the $2p$ orbitals on each carbon that go into making the π -bond.
 - In your picture, what is the dihedral angle between the axis of the $2p$ orbital on the front carbon and the axis of the $2p$ orbital on the back carbon?
 - Imagine making a 180° rotation about the $\text{C}=\text{C}$. Draw a Newman projection of the midway structure (90° rotated). Include the $2p$ orbitals on the front and back carbons. What is the dihedral angle between the two $2p$ orbitals? Is there any π -bond possible at this point?
 - Construct an energy vs dihedral angle diagram for the 180° rotation about the $\text{C}=\text{C}$. Indicate the position of the transition state and the barrier to rotation. This barrier turns out to be about 65 kcal/mol (compare to the measly 3 kcal/mol barrier for rotation about the ethane $\text{C}-\text{C}$).
- Which isomer of 2-butene, the *cis* or the *trans*, do you expect to give off more heat when completely burned? Which isomer do you expect to be more thermodynamically stable? Make a careful diagram summarizing the energetics of the combustion process.

4. The difference in energy between the *cis* and *trans* isomers of 2-butene is 0.7 kcal/mol (I don't mean to imply here which one is the more stable; I leave you to guess that). Once thermodynamic equilibrium has been established, what will be the ratio of *cis* to *trans* isomers in a 2-butene sample?
5. A flask of *cis*-2-butene and a flask of *trans*-2-butene are each stored for a year. Analysis reveals that the *cis* sample remains uncontaminated by the *trans* isomer and vice versa. Draw a careful energy diagram to explain why the system does not seem to be reaching equilibrium.



6. The two most stable conformers of 1,3-butadiene are shown above. The barrier for rotation about the central single bond is about 5 kcal/mol in the direction **2** → **3**. First build a model of 1,3-butadiene, then address the following questions:
 - (a) Why do the two most stable conformers have all four carbons in the same plane?
 - (b) Why is the barrier to rotation around the central C–C single bond a bit higher than for a “normal” C–C single bond as, for example, in ethane?
 - (c) Which is the more stable conformer, **2** or **3**? Why?
 - (d) How does the barrier for conversion of **3** → **2** higher compare to the barrier for conversion of **2** → **3** (higher, lower, the same)?