CHEMISTRY 3A SPRING 2013

EXAM I

FEBRUARY 28, 2013

Answer Key

NAME _____

SECTION AND/OR TA IF YOU ARE IN THE LABORATORY COURSE: _____

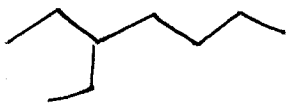
STUDENT ID: _____

- **You will have 2 hours in which to work.**
- **BE NEAT! Non-legible structure drawings will not be graded.**
- **All pages of the exam must be turned in.**
- **No calculators**
- **Molecular models may be used**

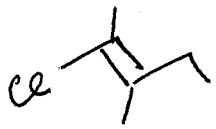
Page	Points (Maximum)	Points (Obtained)
2	37	
3	21	
4	24	
5	24	
6	22	
7	22	
8	16	
9	17	
10	17	
Total	*200*	

1. (18 points) Draw line drawings of the following molecules. Use wedges and dashes to illustrate stereochemistry.

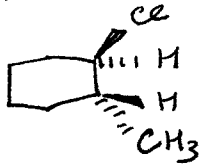
a) 3-ethylheptane



b) (*E*)-2-chloro-3-methyl-2-pentene

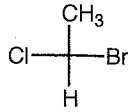


c) (*1R,2R*)-1-chloro-2-methylcyclohexane



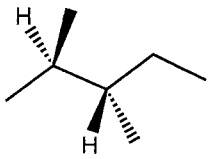
2. (12 points) Write the names of the following molecules, including stereochemistry when necessary.

a.



(R) - 1-bromo-1-chloro ethane

b.



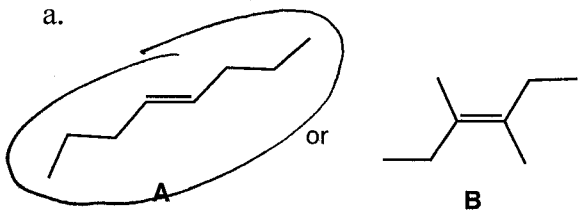
(S) - 2,3-dimethylpentane

3. (28 points) For the following pairs of molecules, identify

(i) the molecule that has the more negative heat of combustion. → less stable

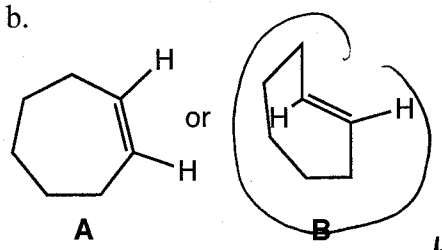
(ii) Explain your answer in one or two sentences.

a.



Explanation: The less substituted alkene is less stable, therefore, has a more negative heat of combustion. The molecules are isomers

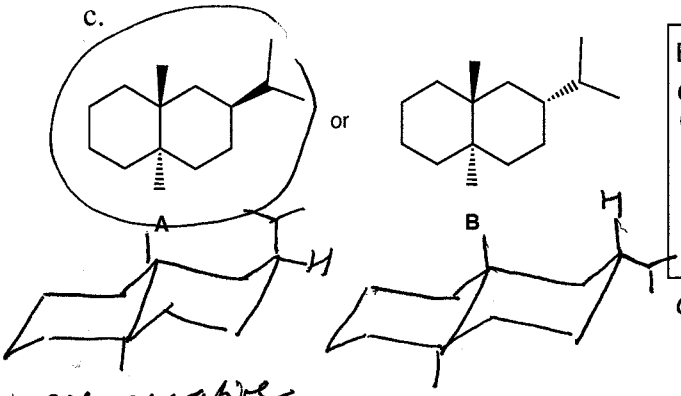
b.



more negative heat of combustion & less stable

Explanation: B less stable because a trans-substituted alkene is very strained in a 7-membered ring.

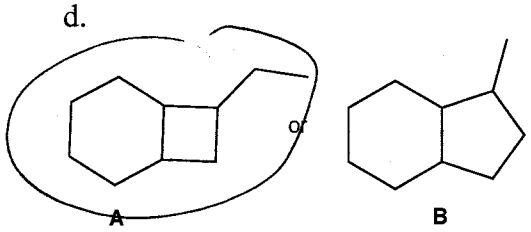
c.



more negative heat of combustion & less stable

Explanation: A is less stable because the iPr group is axial and is destabilized by the 1,3 diaxial interactions (gauche interactions). This group is equatorial in B & only has one gauche interaction with a methyl group. Trans decalin cannot undergo ring flip.

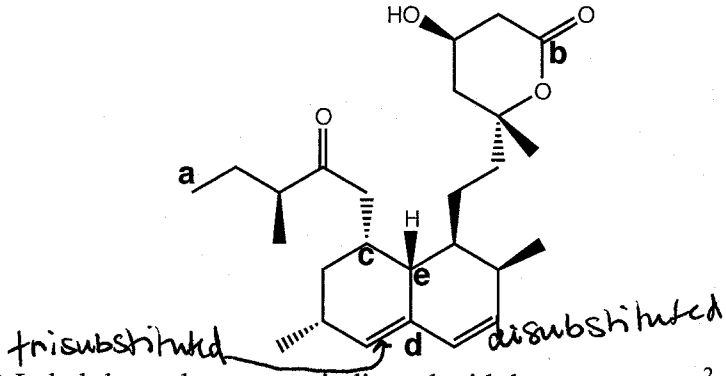
d.



more negative heat of combustion & less stable

Explanation: A is less stable because the 4-membered ring is more strained than the five-membered ring.

4. (24 points) The drug Lovastatin was one of the first statins to be discovered to lower cholesterol levels. It is found in several different organisms, including some mushrooms.



a) Label the carbon atoms indicated with letters as sp, sp^2, or sp^3 hybridized.

a sp^3

b sp^2

c sp^3

d sp^2

e sp^3

b) Are the carbons labeled **a** through **e** chirality centers? If so, determine whether they are *R* or *S*.

a no

b no

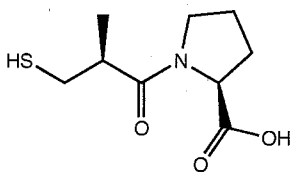
c R

d no

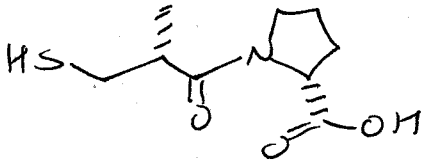
e R

c) Label all alkenes in the structure as mono-, di-, tri-, or tetrasubstituted. You can put your labels on the structure drawn at the beginning of this problem.

5. (24 points) The structure of the non-peptide ACE inhibitor captopril is shown below. The specific rotation of captopril is -130°.



a) Draw the enantiomer of this molecule.



b)You develop a synthesis of captopril and wish to determine the enantiomeric purity of your product mixture. The concentration of your solution of captopril is 0.5 g/mL and the pathlength of your optical rotation measurement is 1 dm. You observe a rotation of 32.5°. Remember that the specific rotation of the enantiomer of captopril you are trying to synthesize is -130°. Calculate the specific rotation of your product mixture. Show your work.

$$[\alpha]_{mixture} = \frac{\alpha}{c \cdot l} = \frac{32.5^\circ}{0.5\,g/mL \cdot 1\,dm} = 65^\circ$$

c)What is the %ee of your product mixture from part b of this question? Show your work.

$$\%ee = \frac{[\alpha]_{mixture}}{[\alpha]_{pure}} = \frac{65^\circ}{130^\circ} \times 100 = 50\%$$

d) In your mixture, what is the percent composition of the enantiomer with the specific rotation of -130°? Show your work.

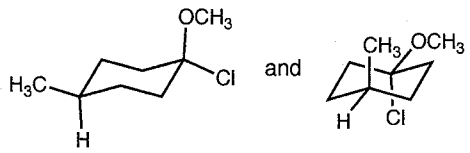
50% (+)-enantiomer 50% of 1:1 mixture of (+) & (-) enantiomers

75% of (+) enantiomer

25% of (-) enantiomer

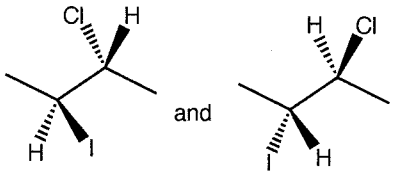
6. (10 points) Identify whether the following pairs of molecules are enantiomers, diastereomers, identical (including conformational isomers), or different molecules.

a.



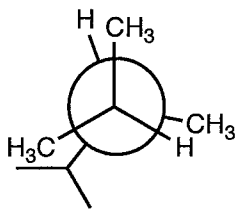
identical

b.

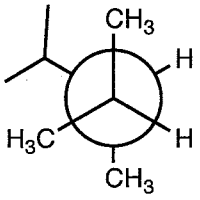


enantiomers

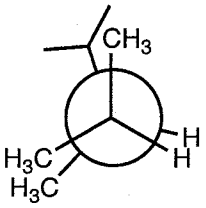
7. (22 points) Consider the conformations shown below and answer the following questions:



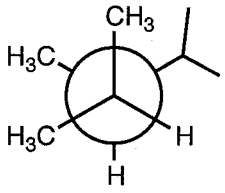
A



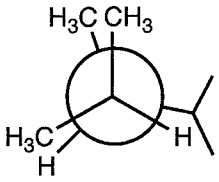
B



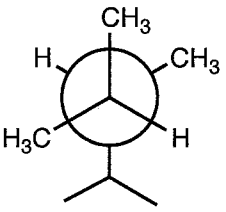
C



D



E

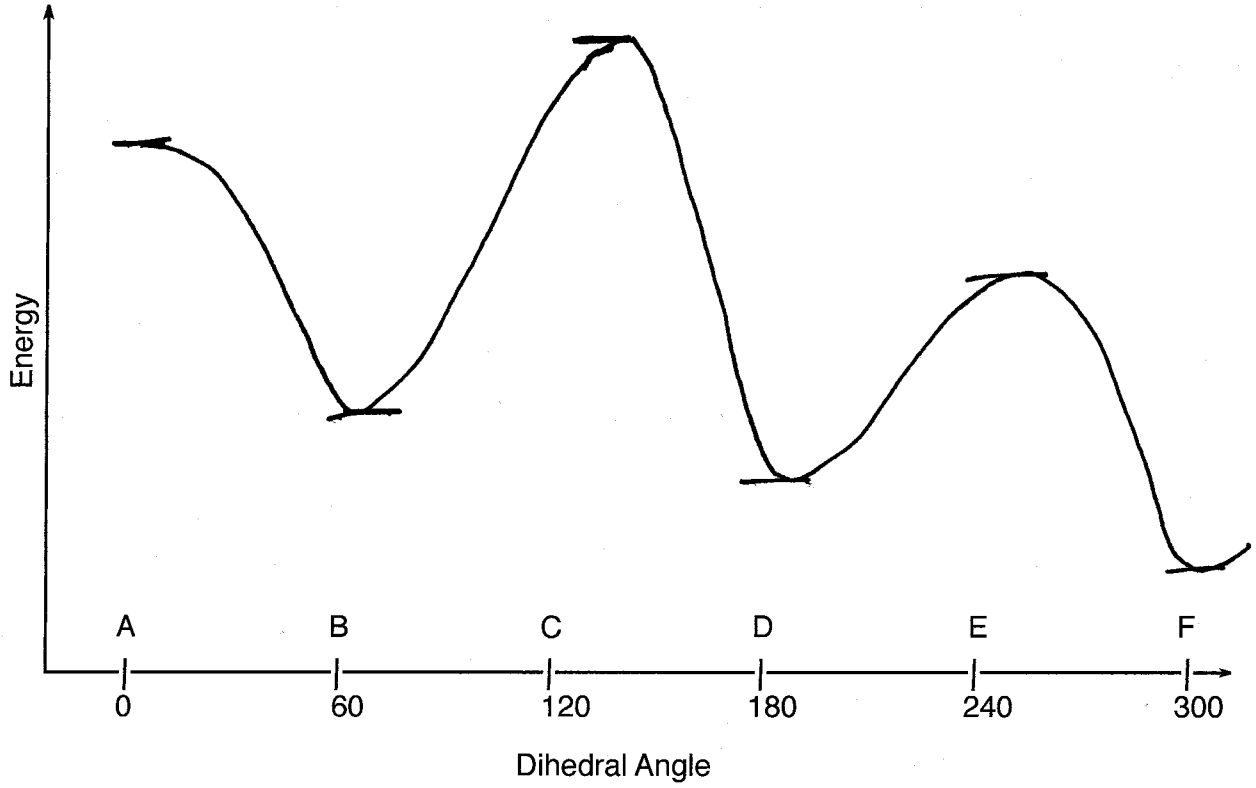


F

a. Which of the six conformations is most stable? F

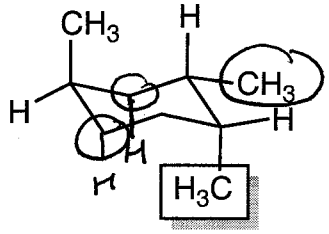
b. Which of the six conformations is least stable? C

c. Fill in the energy versus dihedral angle plot shown below for this molecule. Indicate the relative stabilities of the conformations because you do not know the precise energy differences between the different conformations.



8. (28 points) Most cyclohexanes interconvert rapidly between two chair conformations at room temperature.

a. For the cyclohexane chair conformation shown below, consider the CH_3 group with a square around it. **Circle** all of the groups that have gauche interactions with the CH_3 group with a square around it.



b. Explain what a gauche interaction is and why it destabilizes alkane and cycloalkane conformations.

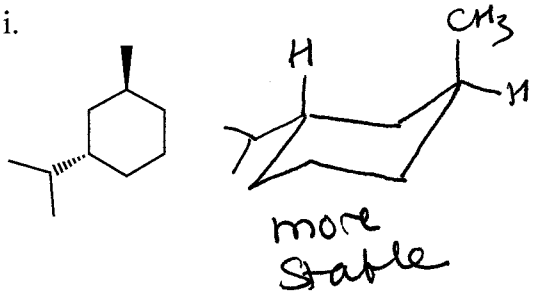
An interaction is called gauche when two groups are next to each other in a staggered Newman projection. They destabilize alkane & cycloalkane conformations because gauche interactions are steric interactions

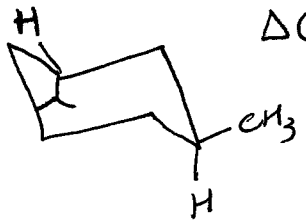
c. For each molecule below 1) draw both chair conformations of the cyclohexane ring, 2) indicate which is more stable, and 3) calculate the free energy difference between the two structures.

You may refer to the following table of "A" values, which are the ΔG° values for the conversion of the cyclohexane conformer with the indicated **R** group equatorial to the conformer with the **R** group axial.

R	ΔG° (kcal/mol)	R	ΔG° (kcal/mol)
CH_3	1.74	F	0.25
$(CH_3)_2CH$	2.20	OCH_3	0.75

i.

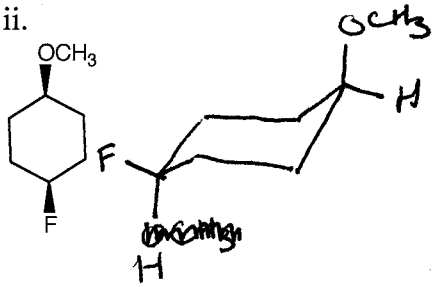


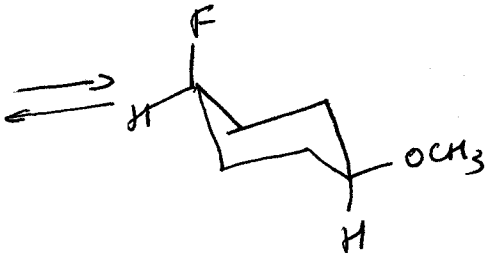


$\Delta G^\circ = 2.20 - 1.74$

$= 0.46$ kcal/mol

ii.



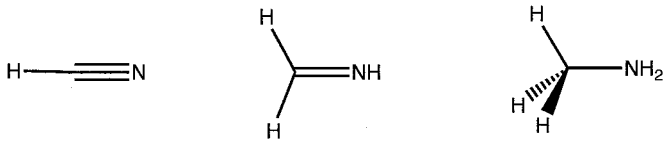


$\Delta G^\circ = 0.25 - 0.75$

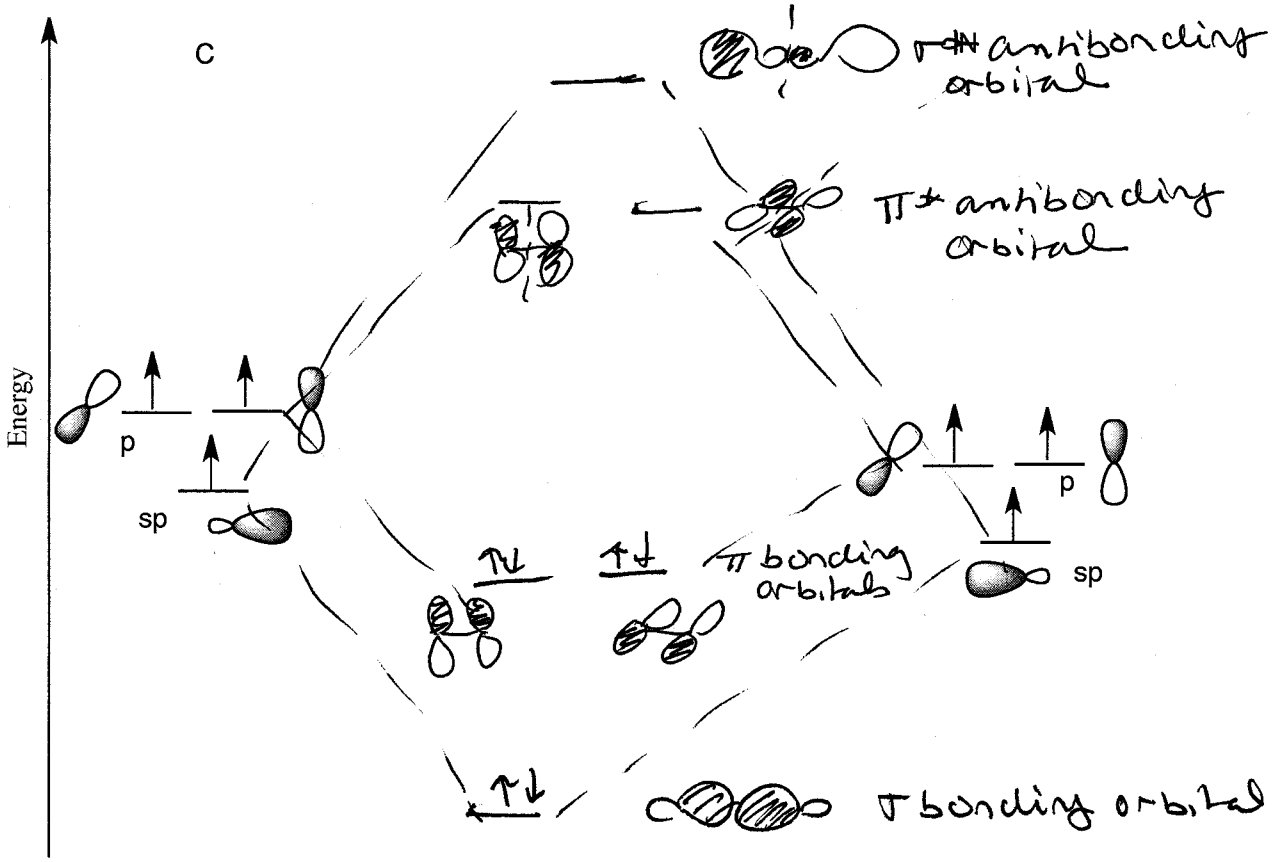
$\Delta G^\circ = -0.50$ kcal/mol

more stable

9. (34 points) Compare the 3 compounds below that contain nitrogen.



a) Fill in the MO diagram of the CN triple bond in HCN shown below. Show the formation of all three bonds of the triple bond on the same diagram. Include:
i) pictures of the molecular orbitals
ii) labels for all orbitals



b) Do you expect the pi bond of $H_2C{=}NH$ to be stronger or weaker than the sigma bond formed between C and N in CH_3NH_2? Explain your answer.

The π bond of $H_2C{=}NH$ is weaker than the sigma bond formed between C and N in CH_3NH_2. The overlap between the side-by-side orbitals in the π bond is not as good as the overlap between the sp^3 orbitals that point directly at each other along the C-N bond in CH_3NH_2

c) Compare the bond strengths of the C-H bond in HCN, $H_2C{=}NH$, and H_3CNH_2. Which bond do you expect to be strongest and why?

The C-H bond in HC≡N is stronger than in $H_2C{=}NH$ than in H_3CNH_2. The sp orbital on C in HC≡N is shorter & wider than the sp^3 orbital on C in H_3CNH_3. Therefore, the overlap between the 1s orbital on H & the sp orbital on C is better than between the 1s of H & the sp^3 of C. Therefore the C-H bond in HC≡N is stronger than in $H_3C{-}NH_2$.

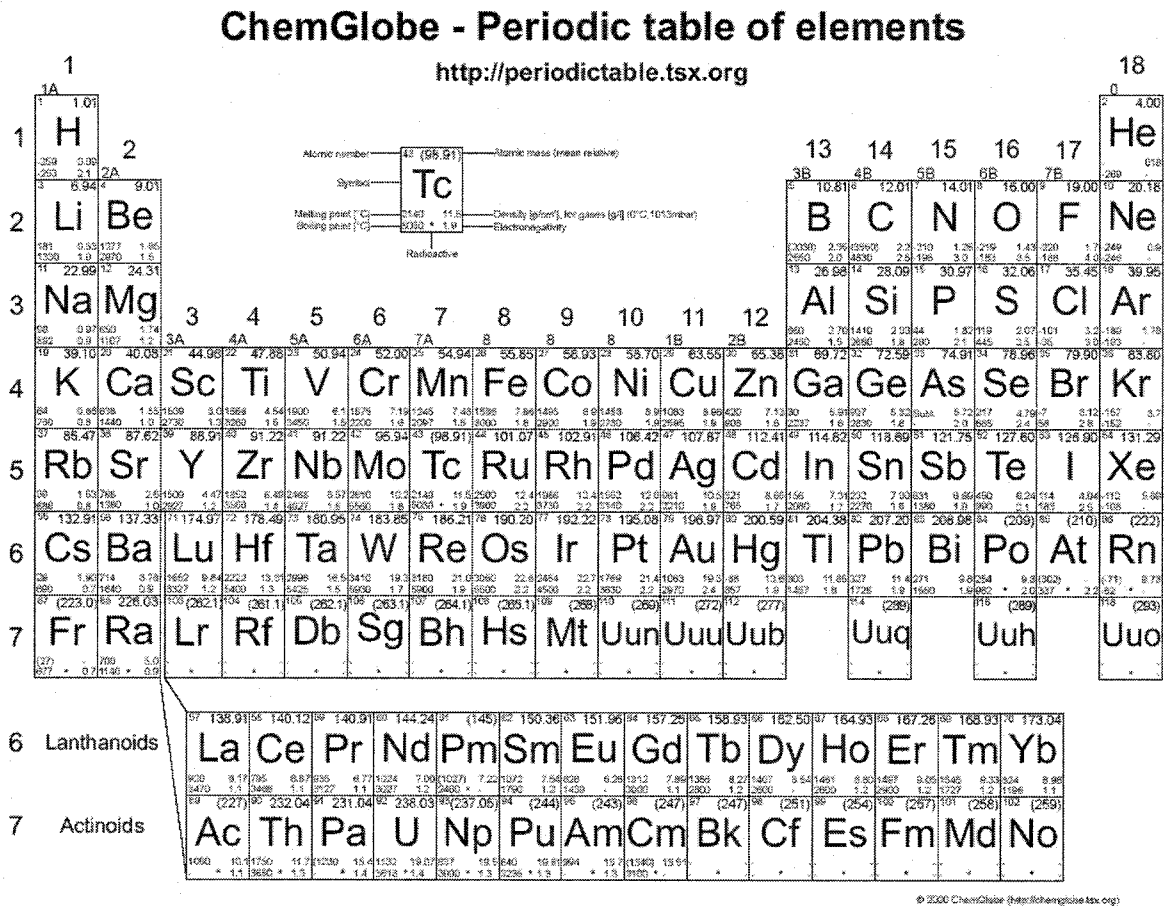
d) In lecture, we discussed the cis-trans isomerism of the alkene retinal that allows our eyes to detect light. Suppose that a friend of yours decides to design an artificial eye. Instead of using an alkene, your friend decides to use the isomerization between anti and gauche butane structures to detect light.

i.)What problems do you foresee in this design?

There is rapid rotation around the single bond in butane. Therefore, the light cannot be used to trigger an isomerization that is already happening rapidly

ii) Under what conditions might this design be effective?

If the temp is lowered (a lot) then the rotation will be slowed & stopped. When rotation is stopped, then light can be used to trigger isomerization


ChemGlobe - Periodic table of elements
http://periodictable.tsx.org
Lanthanoids
Actinoids