

Name: \_\_\_\_\_

Key

**Chemistry 386J**  
**Anslyn**  
**October 1, 2011**  
**Exam 1**

1. \_\_\_\_\_ (11 points)
2. \_\_\_\_\_ (26 points)
3. \_\_\_\_\_ (8 points)
4. \_\_\_\_\_ (12 points)
5. \_\_\_\_\_ (10 points)
6. \_\_\_\_\_ (21 points)
7. \_\_\_\_\_ (8 points)
8. \_\_\_\_\_ (7 points)
9. \_\_\_\_\_ (24 points)

Total. \_\_\_\_\_ (127 points)

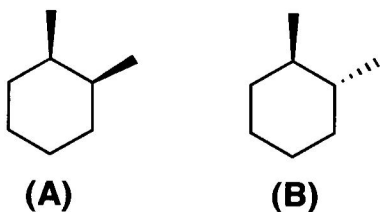
**Table 2.4**  
**Group Increments (in kcal/mol) for Fundamental Groupings\***

Group	$\Delta H_f^\circ$	Group	$\Delta H_f^\circ$	Group	$\Delta H_f^\circ$
C-(H) <sub>3</sub> (C)	-10.20	C-(O)(C <sub>d</sub> )(H) <sub>2</sub>	-6.5	C-(O) <sub>2</sub> (C) <sub>2</sub>	-18.6
C-(H) <sub>2</sub> (C) <sub>2</sub>	-4.93	C <sub>B</sub> -(O)	-0.9	C-(O) <sub>2</sub> (C)(H)	-16.3
C-(H)(C) <sub>3</sub>	-1.90	O-(C) <sub>2</sub>	-23.2	C-(O) <sub>2</sub> (H) <sub>2</sub>	-16.1
C-(C) <sub>4</sub>	0.50	O-(C)(H)	-37.9	C-(N)(H) <sub>3</sub>	-10.08
C <sub>d</sub> -(H) <sub>2</sub>	6.26	O-(C <sub>d</sub> ) <sub>2</sub>	-33.0	C-(N)(C)(H) <sub>2</sub>	-6.6
C <sub>d</sub> -(H)(C)	8.59	O-(C <sub>d</sub> )(C)	-30.5	C-(N)(C) <sub>2</sub> (H)	-5.2
C <sub>d</sub> -(C) <sub>2</sub>	10.34	O-(C <sub>B</sub> ) <sub>2</sub>	-21.1	C-(N)(C) <sub>3</sub>	-3.2
C <sub>d</sub> -(C <sub>d</sub> )(H)	6.78	O-(C <sub>B</sub> )(C)	-23.0	C <sub>B</sub> -(N)	-0.5
C <sub>d</sub> -(C <sub>d</sub> )(C)	8.88	O-(C <sub>B</sub> )(H)	-37.9	N-(C)(H) <sub>2</sub>	4.8
C <sub>d</sub> -(C <sub>B</sub> )(H)	6.78	C-(CO)(C) <sub>3</sub>	1.58	N-(C) <sub>2</sub> (H)	15.4
C <sub>d</sub> -(C <sub>B</sub> )(C)	8.64	C-(CO)(C) <sub>2</sub> (H)	-1.83	N-(C) <sub>3</sub>	24.4
C <sub>d</sub> -(C <sub>d</sub> ) <sub>2</sub>	4.6	C-(CO)(C)(H) <sub>2</sub>	-5.0	N-(C <sub>B</sub> )(H) <sub>2</sub>	4.8
C <sub>B</sub> -(H)	3.30	C-(CO)(H) <sub>3</sub>	-10.08	N-(C <sub>B</sub> )(C)(H)	14.9
C <sub>B</sub> -(C)	5.51	C <sub>B</sub> -(CO)	9.7	N-(C <sub>B</sub> )(C) <sub>2</sub>	26.2
C <sub>B</sub> -(C <sub>d</sub> )	5.68	CO-(C) <sub>2</sub>	-31.4	N-(C <sub>B</sub> ) <sub>2</sub> (H)	16.3
C <sub>B</sub> -(C <sub>B</sub> )	4.96	CO-(C)(H)	-29.1	N <sub>I</sub> -(H)	16.3
C-(C <sub>d</sub> )(C)(H) <sub>2</sub>	-4.76	CO-(H) <sub>2</sub>	-26.0	N <sub>I</sub> -(C)	21.3
C-(C <sub>d</sub> ) <sub>2</sub> (H) <sub>2</sub>	-4.29	CO-(C <sub>B</sub> ) <sub>2</sub>	-25.8	N <sub>I</sub> -(C <sub>B</sub> )	16.7
C-(C <sub>d</sub> )(C <sub>B</sub> )(H) <sub>2</sub>	-4.29	CO-(C <sub>B</sub> )(C)	-30.9	CO-(N)(H)	-29.6
C-(C <sub>B</sub> )(C)(H) <sub>2</sub>	-4.86	CO-(C <sub>B</sub> )(H)	-29.1	CO-(N)(C)	-32.8
C-(C <sub>d</sub> )(C) <sub>2</sub> (H)	-1.48	CO-(O)(C)	-35.1	N-(CO)(H) <sub>2</sub>	-14.9
C-(C <sub>B</sub> )(C) <sub>2</sub> (H)	-0.98	CO-(O)(H)	-32.1	N-(CO)(C)(H)	-4.4
C-(C <sub>d</sub> )(C) <sub>3</sub>	1.68	CO-(O)(C <sub>d</sub> )	-32.0	N-(CO)(C) <sub>2</sub>	—
C-(C <sub>B</sub> )(C) <sub>3</sub>	2.81	CO-(O)(C <sub>B</sub> )	-36.6	N-(CO)(C <sub>B</sub> )(H)	0.4
C-(O)(C) <sub>3</sub>	-6.6	CO-(C <sub>d</sub> )(H)	-29.1	N-(CO) <sub>2</sub> (H)	-18.5
C-(O)(C) <sub>2</sub> (H)	-7.2	O-(CO)(C)	-43.1	N-(CO) <sub>2</sub> (C)	-5.9
C-(O)(C)(H) <sub>2</sub>	-8.1	O-(CO)(H)	-58.1	N-(CO) <sub>2</sub> (C <sub>B</sub> )	-0.5
C-(O)(H) <sub>3</sub>	-10.08	C <sub>d</sub> (CO)(C)	7.5		
C-(O)(C <sub>B</sub> )(H) <sub>2</sub>	-8.1	C <sub>d</sub> -(CO)(H)	5.0		

C<sub>d</sub> = double bond; C<sub>B</sub> = benzene carbon; N<sub>I</sub> = imine nitrogen.

\*Data are from Benson, S. W. (1976) *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd ed., John Wiley & Sons, New York.

1. This question refers to the two alkanes, labeled (A) and (B), shown below.



- a) Please provide the IUPAC name for each of these alkanes. Do not be concerned about R or S descriptors. +2

(A): cis-1,2-dimethylcyclohexane

(B): trans-1,2-dimethylcyclohexane

- b) Using Benson group increments provided on the previous page, calculate the  $\Delta H_f^\circ$  values for these alkanes. +3

$$2 \times C(H)_3C = -20.40$$

$$4 \times C(H)_2(C)_2 = -19.72$$

$$2 \times C(H)(C)_3 = -3.80$$

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$$\Delta H_f^\circ = -43.92 \text{ kcal/mol}$$

- c) The A-value for the methyl group is 1.74, and the value for a gauche interaction is 0.9 kcal/mol. Given these values, please correct the  $\Delta H_f^\circ$  values that you calculated for the alkanes in part b) of this question. Make sure it is clear which new value of  $\Delta H_f^\circ$  belongs to structure (A) and which belongs to structure (B). +4

$$A: 1 \text{ A-value} + 1 \text{ gauche} = 1.74 + .9 = 2.64$$

$$-43.92 + 2.64 = -41.28 \text{ kcal/mol}$$

$$B: 1 \text{ gauche} = .9$$

$$-43.92 + .9 = -43.02$$

- d) Now predict whether (A) or (B) will burn the hottest, giving the most exothermic  $\Delta H_{\text{comb}}$  value. How much of a difference in the heats of combustion will there be?

A will burn the hottest by 1.74 kcal/mol

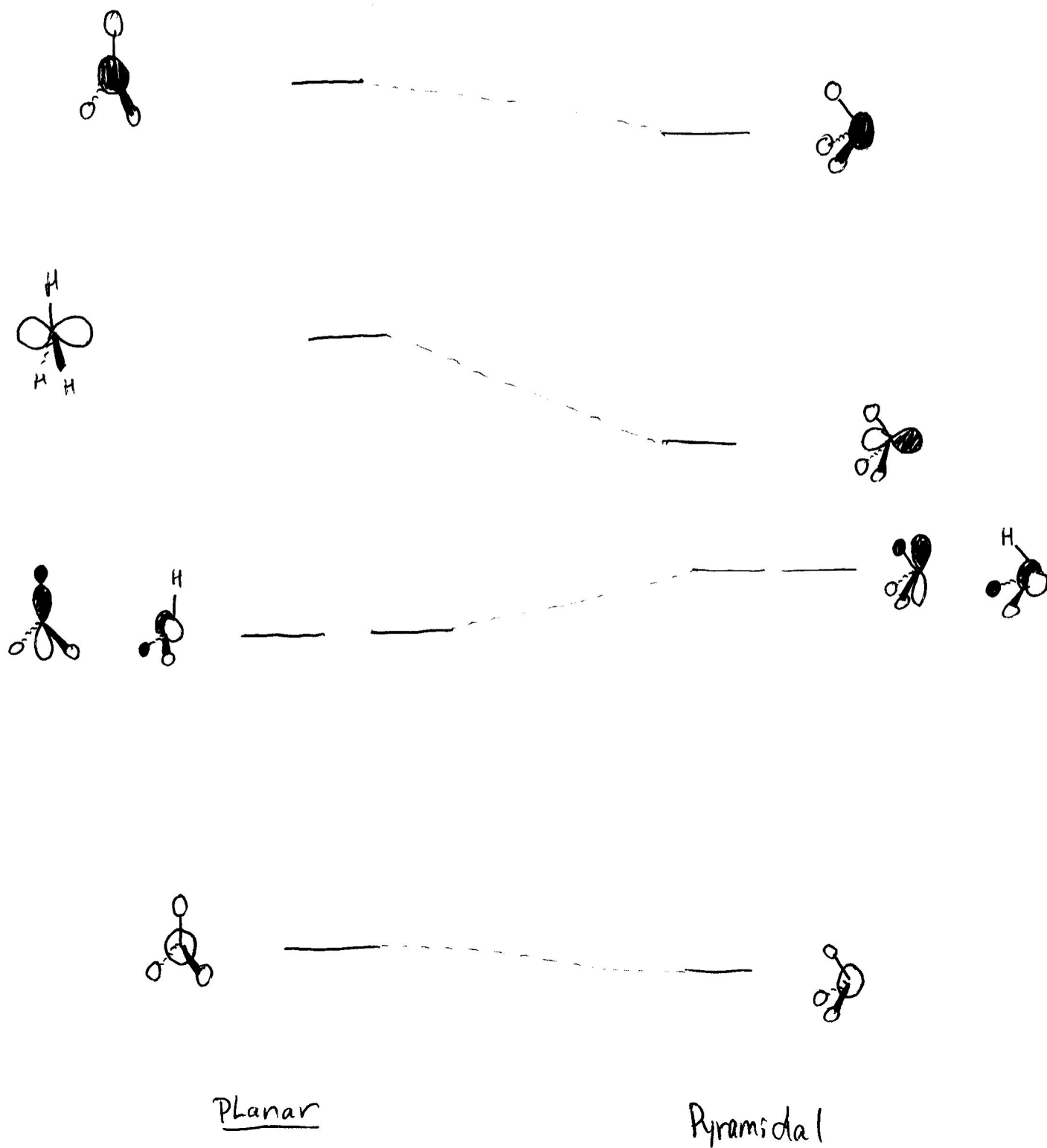
+2

↓  
-1 if wrong,  
value but correct  
by values in c)

2. One of the main topics of chapter 1 was qualitative molecular orbital theory (QMOT). The following question pertains to this theory.

a) Construct the Walsh diagram for a methyl group showing orbital energies for both planar and pyramidal forms (indicating which is which), as well as orbital phasing.

+6

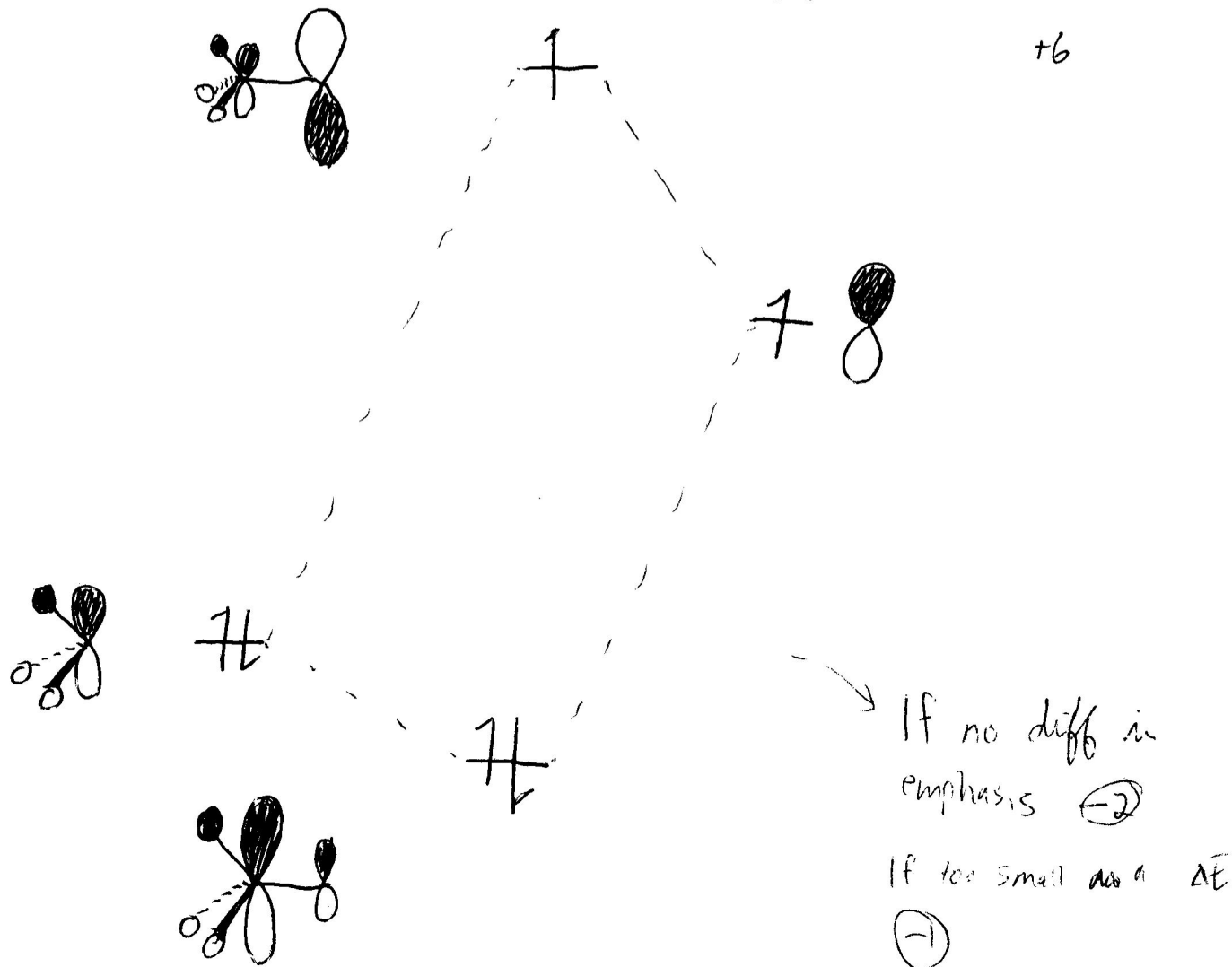


- b) Recall that the methyl group can have either a planar or pyramidal geometry depending on the number of electrons in the molecule. Referring to the Walsh diagram that you just drew, what would you expect the geometry of  $\text{BH}_3$  to be? Briefly explain your answer.

+2

Planar - higher energy of the degenerate  $\pi(\text{CH}_3)$  orbitals destabilizes the pyramidal version.

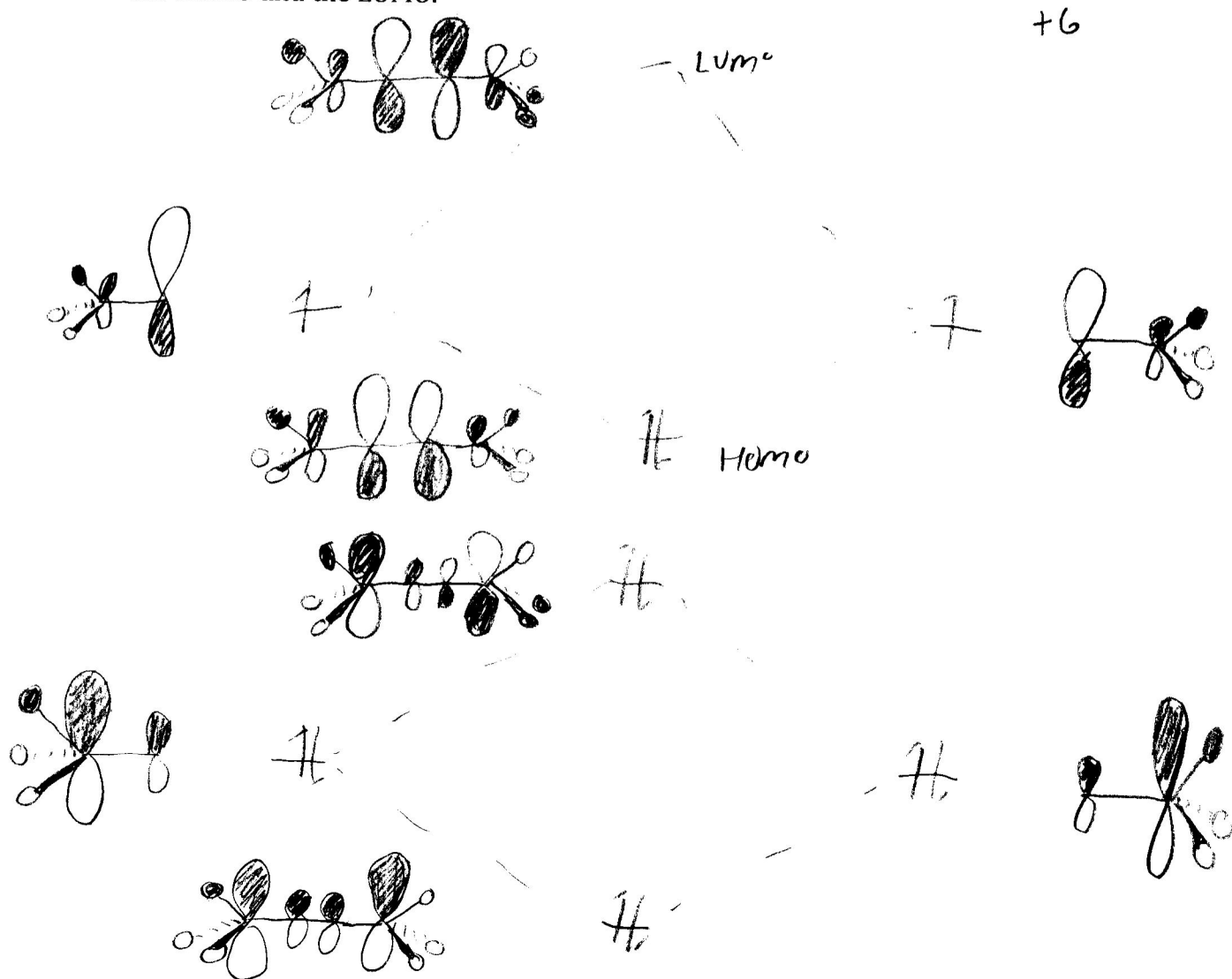
- c) Using an orbital mixing diagram, mix one of the  $\pi(\text{CH}_3)$  group orbitals with a p-orbital in order to create a delocalized  $\pi$ -system of ethyl radical. Be sure to place the starting orbitals at the proper relative energy levels. Then make cartoon representations of what these new orbitals look like, and populate with electrons.



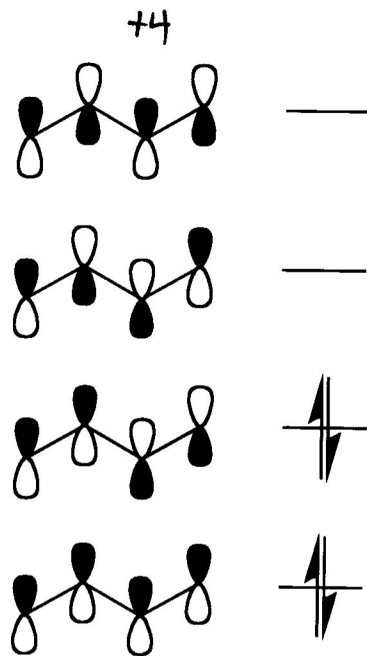
d) Use the diagram that you just created to explain hyperconjugation.

Some electron density is delocalized from the  $\pi(Cu_3)$  orbital of the radical, stabilizing this radical to a small extent. +2

e) Using the two orbitals you created in the mixing diagram from part c), make the extended  $\pi$ -system of 2-butene consisting of four molecular orbitals. Then make cartoon representations of what these new orbitals look like. Fill in the molecular orbitals with the number of electrons you would expect for 2-butene. Finally, label the HOMO and the LUMO.



f) We give below the  $\pi$ -molecular orbitals of 1,3-butadiene. Make a comparison between your answer to part e) and these orbitals. Explain how they are most similar, and how they are most different.



1,3-butadiene

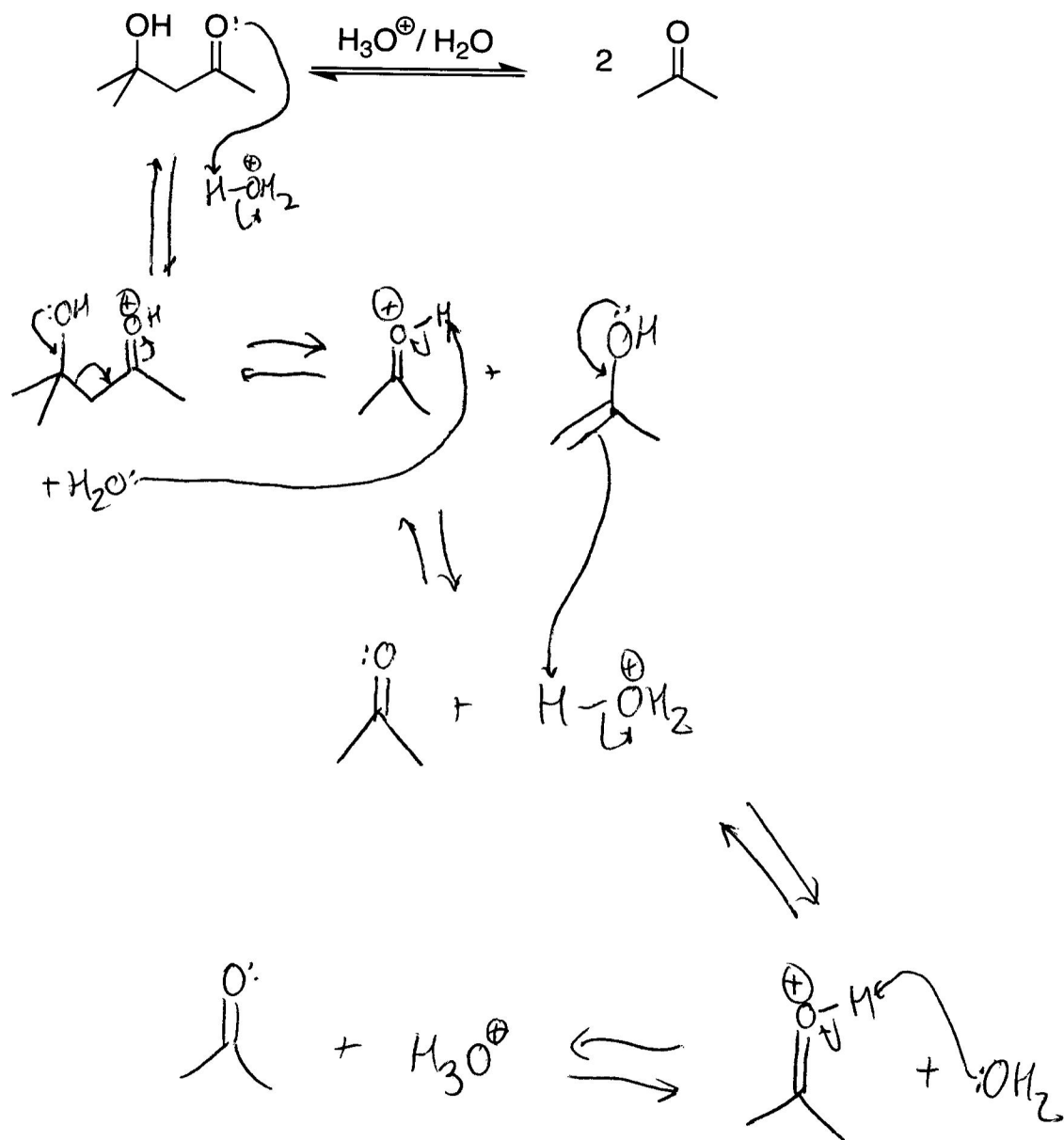
Similar: phasing of the p-orbitals are the same. Same amount of nodes between orbitals.

Different: The phasing between the (size) p-orbitals is the the same in butadiene, but unequal in the case of 2-butene. The HOMO has the most character between the central carbons, consistent with a  $\pi$  bond



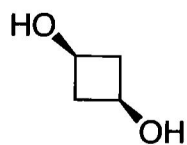
3. Draw the mechanism for the following reaction, making sure to show all participating lone pairs, applicable formal charges, and required arrow pushing to indicate the flow of electrons.

+8

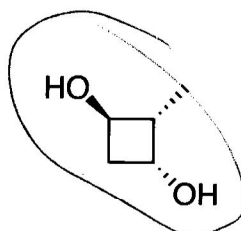


4. The next question refers to the set of diols that are drawn below. Circle the diols that are chiral. Next, put a (\*) near any structure that is meso. Then, state the relationship of the alcohol groups (homotopic, enantiotopic, diastereotopic) on the line below each diol.

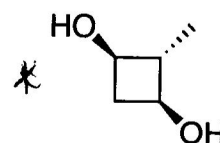
+12



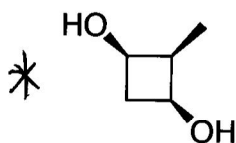
Homotopic



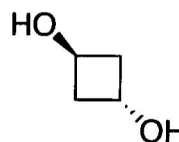
Diastereotopic



Enantiotopic



Enantiotopic



Homotopic

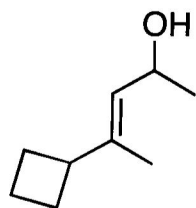
8 total

17

$\frac{1}{2}$  for each one wrong

5. Each of the molecules pictured is destabilized by at least one of the different types of strain discussed in class. In each molecule, indicate each type of strain that is present. Indicate where on the molecule that this strain occurs. +10

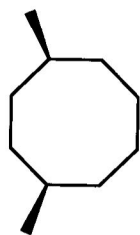
a)



(1,3)A strain

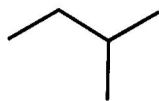
Small Ring strain

b)



Transannular strain

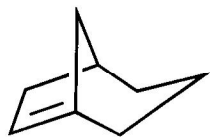
c)



Gauche

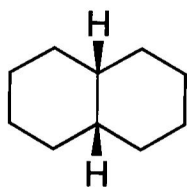
(gem dimethyl)

d)



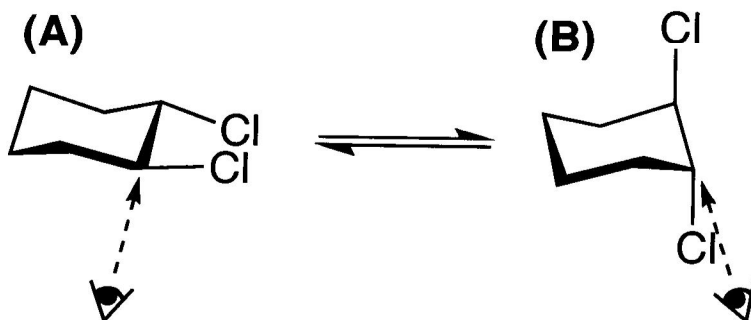
Anti-Bredt strain

e)



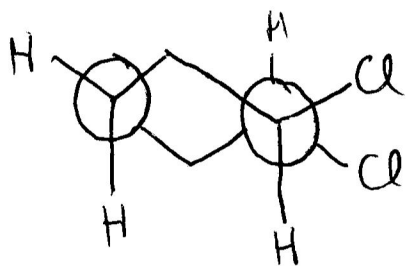
Gauche (1,3-diaxial strain)

6. The following problem refers to the compound *trans*-1,2-dichlorocyclohexane.



a) Make Newman projections for both of these conformations, looking down the bond that is indicated in the equilibrium. +4

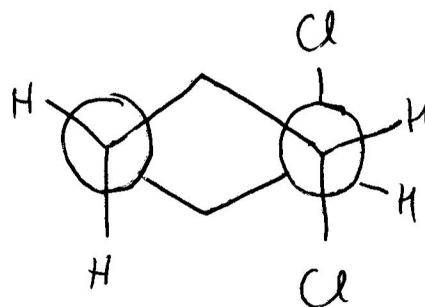
(A)



Gauche strain

Syn Clinal

(B)



1,3-diaxial strain

Anti periplanar

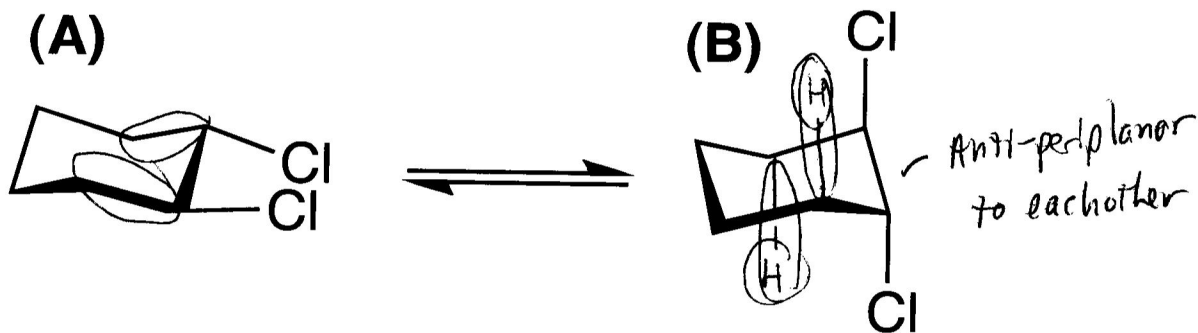
b) Identify strains that are associated with these conformations. List them with your drawing in part a). +2

c) Using the Klyne-Prelog system, list under the heading in part a) the relationship between the chlorine atoms for each conformation. Do not be concerned with the + or - designation. +2

- d) Recall that a weaker bond has electrons in higher energy orbitals. Given that the BDE of a C-Cl bond is around 84 kcal/mol, and that a C-C bond is around 90 kcal/mol, which bond has electrons in the higher energy orbital? +2

C-Cl bonds are in higher orbitals because they are weaker bonds.

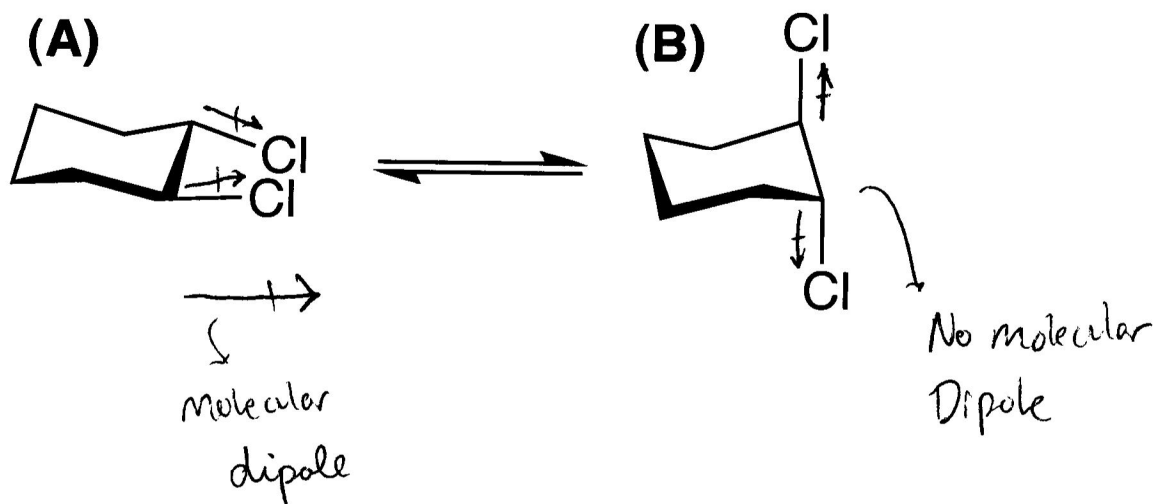
- e) Structures (A) and (B) are redrawn below. In each drawing please point out the bonds that are anti-periplanar to the C-Cl bonds. If the C-Cl bonds are anti-periplanar to each other point that out also. +4



- f) In the gas phase, there is a slight preference for the diaxial compound (60:40). Given the knowledge you developed from parts d) and e), how can you rationalize this preference for the diaxial species? +2

Donation to the  $\sigma^*$  orbital from either the C-Cl bond next door or the C-H bond. This is a manifestation of the anomeric effect.

- g) We again redraw structures (A) and (B) below. Please draw the bond dipoles and the resulting molecular dipoles for each conformation. If there is no molecular dipole, please state this. +3

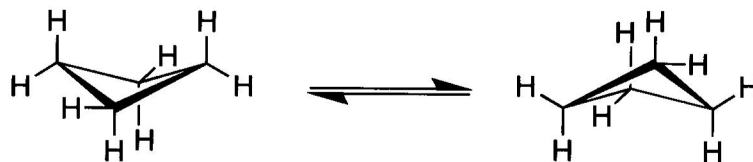


- h) As mentioned in part f), the preference for (B) is noted in the gas phase. This is also true in non-polar solvents, but goes away as the polarity of the solvent is increased and (A) begins to dominate. Given that the higher polarity solvents will better solvate polar molecules, how can you account for the reverse in conformational preference?

+2

Like dissolves like.

7. Cyclobutane cannot exist as a planar ring, since that would produce C-H and C-C bonds that were fully eclipsed. Thus, this molecule puckers to relieve some of this strain. A picture of puckered cyclobutane is shown below for your reference. Both possible conformations interconvert rapidly, with a barrier to rotation of 1.45 kcal/mol.



- a) Draw the possible conformations of puckered trans-1,3-dimethylcyclobutane (pictured to the right).

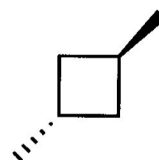
f2



A



B

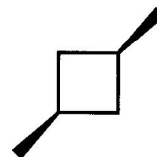
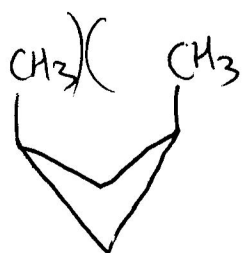


- b) Label the conformations you drew above, and denote which one (if any) would be the most stable. Briefly explain your designation.

Same types of strain present, so they are degenerate.



c) Draw the possible conformations of puckered *cis*-1,3-dimethylcyclobutane (pictured to the right).

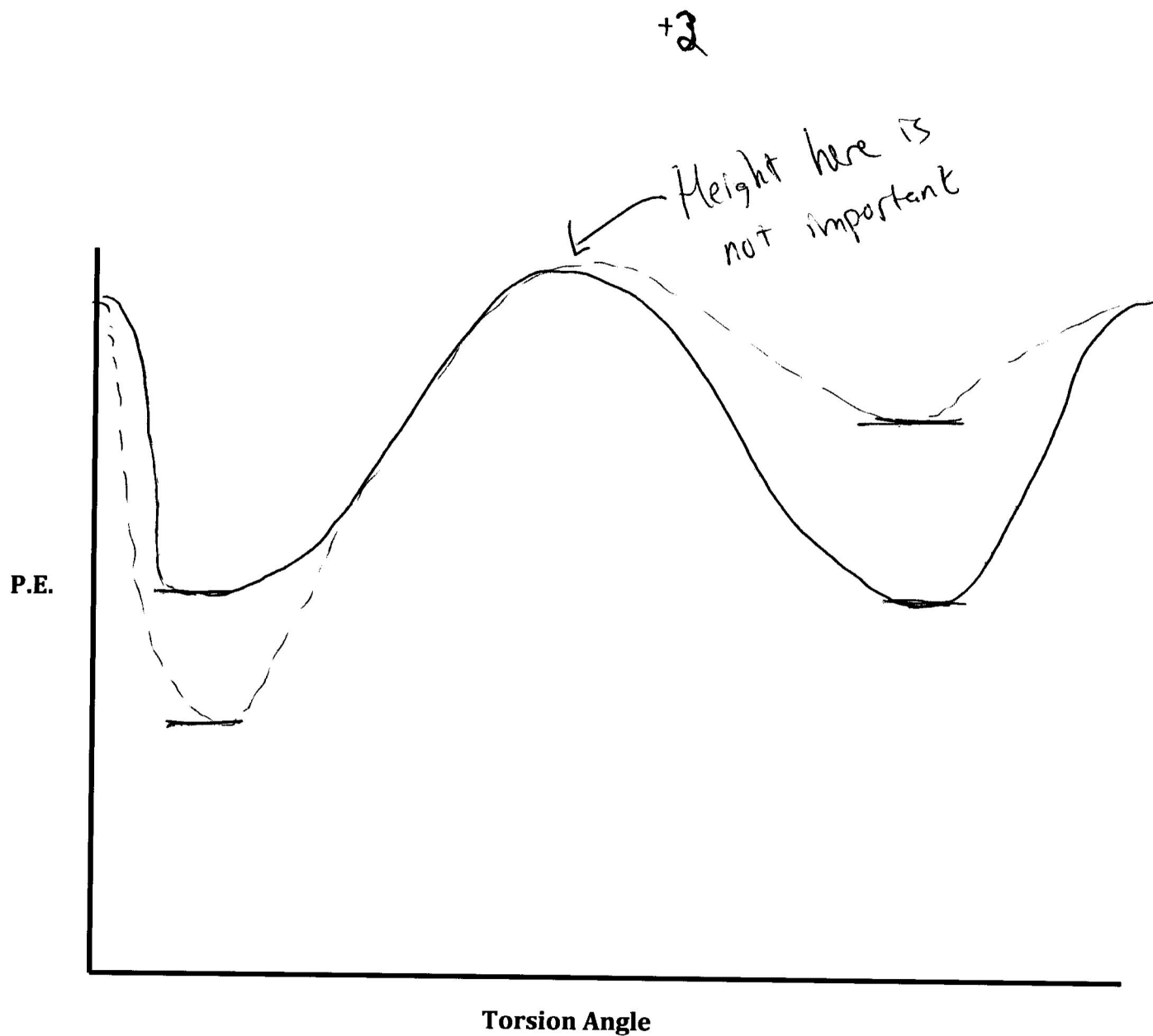


d) Label the conformations you drew above, and denote which one (if any) would be the most stable. Briefly explain your designation.

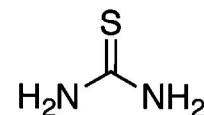
+1

B is more stable - groups not directed towards each other.

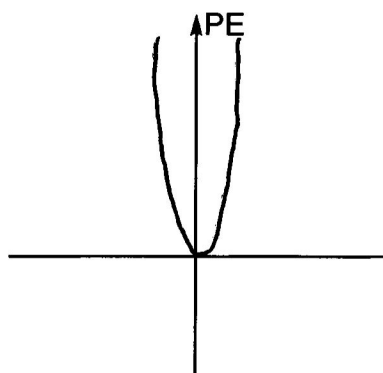
- e) Construct a potential energy diagram for the interconversion of the forms of the *trans*- isomer (represent this as a solid line), as well as the *cis*- isomer (represent this as a dashed line). Be sure to indicate the proper relative energies of the species.



8. Thiourea, drawn below, has several different stretches in the IR spectrum. These absorption bands represent different degrees of freedom associated with this molecule. Three selected peaks can be found at 2955, 1620, and 1378  $\text{cm}^{-1}$ .

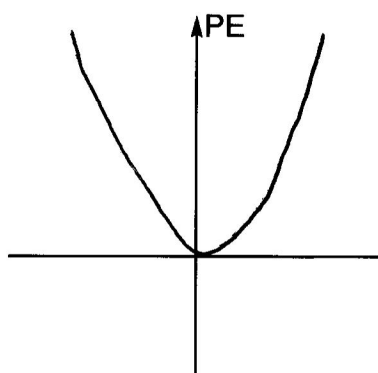


A. 2955  $\text{cm}^{-1}$



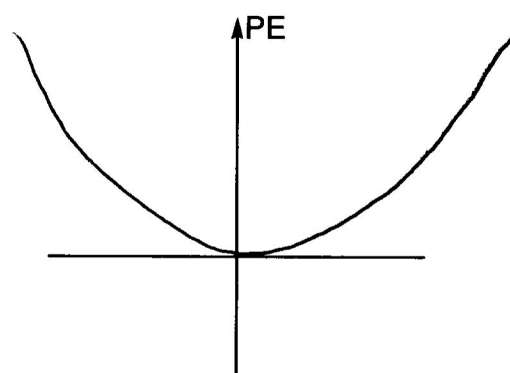
N-H Stretch

B. 1620  $\text{cm}^{-1}$



C=S Stretch

C. 1378  $\text{cm}^{-1}$



C-N Stretch

- a) On the potential energy surface, draw the surface that represents these degrees of freedom. The exact curves are not important, but the relative shapes of the curve should be correct.

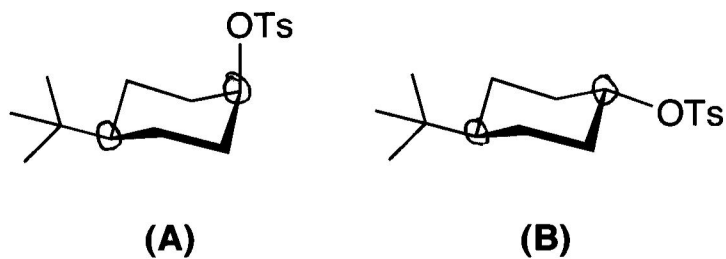
- b) Of your potential diagrams, which represents a motion with the most entropy?

C

- c) Of your potential diagrams, which motion has the largest force constant?

A

9. The following question refers to the two cyclohexane derivatives that are drawn below.



a) Are these molecules chiral? +2

No

b) Circle any stereocenters in both of these molecules.

+2

c) What stereochemical relationship does (A) have relative to (B)?

+2

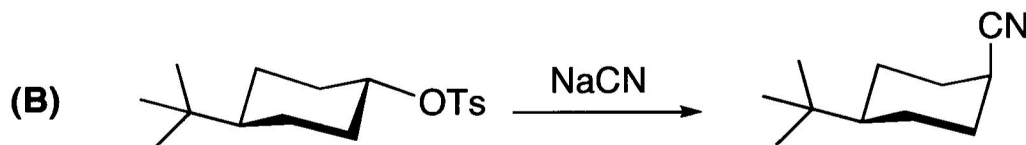
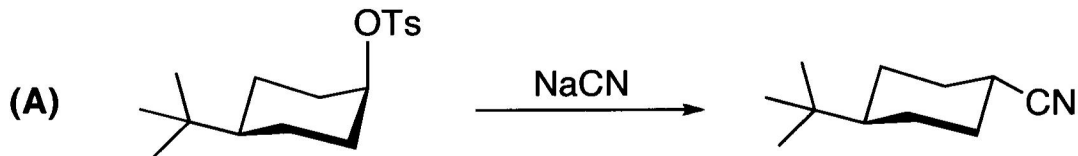
Diastereomers

d) If you were giving the IUPAC names, would you need to describe each stereocenter with an (*R*)- or an (*S*)- descriptor? Please briefly explain your answer.

+2

No - two groups have the same priority (not chiral)

Sodium cyanide reacts with (A) and (B) in an  $S_N2$  fashion to give the products that are shown.



e) Are these  $S_N2$  reactions stereoselective? Please explain your answer.

+2

Yes.

f) Are these reactions stereospecific? Please explain your answer.

+2

Yes.

Only 1 if they don't  
Say diff. prod ratio

j) Are these reactions stereoselective? Please explain your answer.

+2

No

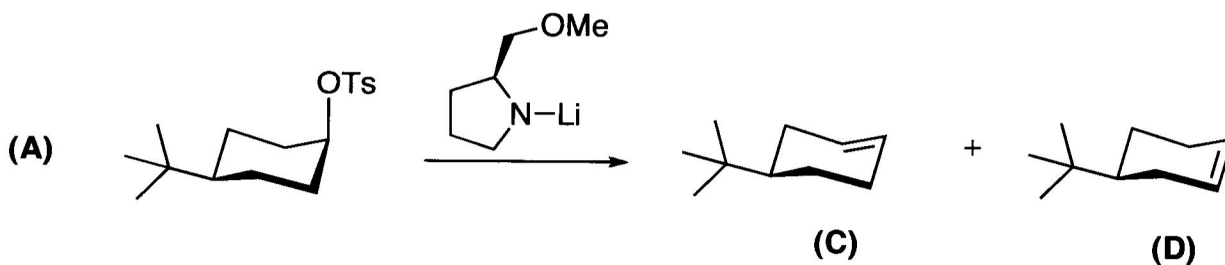
k) Are these reactions stereospecific? Please explain your answer.

+2

No

l) If the elimination reaction of (A) is carried out with a chiral base, as indicated below, do you expect the ratio of (C) to (D) to be 1:1 or something different? Explain your reasoning using your answer to part g).

+2



Something different.