NAME _____

Scoring: 1. _____ / 6 5. _____ / 14

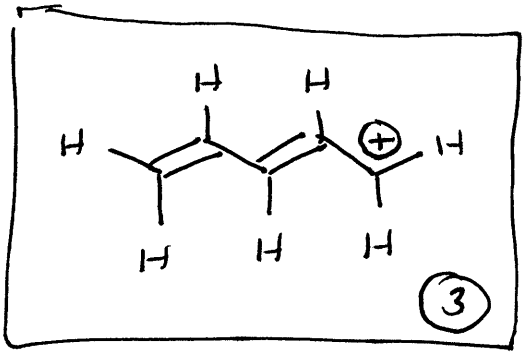
2. _____ / 15 6. _____ / 26

3. _____ / 17 7. _____ / 4

4. _____ / 18

Total Score: _____ / 100

1. (6 pts) **Draw Lewis dash-bond structures** for the two most stable constitutional isomers with molecular formula $C_5H_7^+$. Draw all atoms, bonds, and lone pairs of electrons. In each box, draw just one explicit structure; do not draw multiple resonance structures, and do not draw a resonance hybrid that is an average of multiple structures.

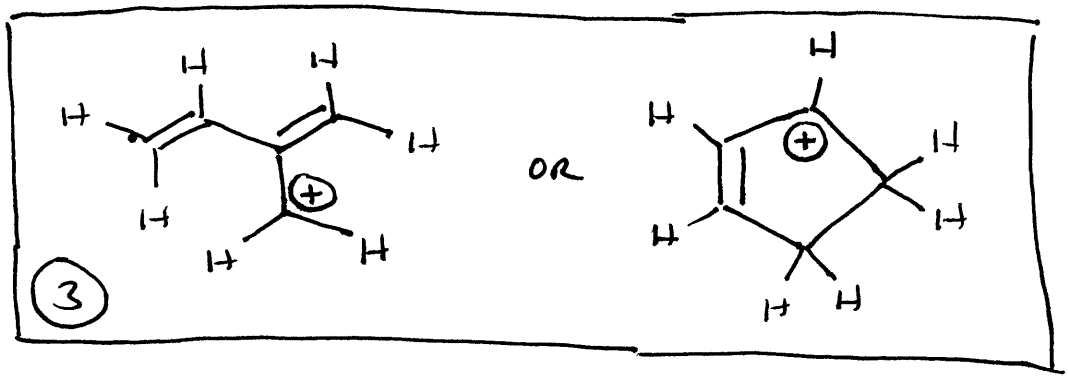


(OR ANY OTHER RESONANCE STRUCTURE OR SINGLE-BOND ROTAMER OF THIS STRUCTURE)

~~NOT THESE STRUCTURES~~

3

AND

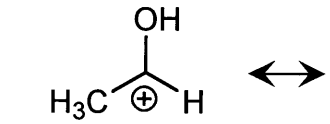


3

(2) POINTS PARTIAL FOR ANY OTHER $C_5H_7^+$ ISOMER.

(5) POINTS TOTAL FOR DRAWING BOTTOM TWO ANSWERS (AND NOT THE TOP ONE).

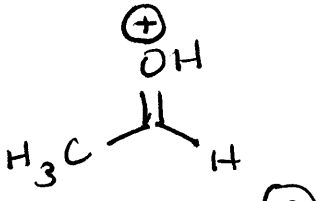
2. (15 pts) For each of the molecules on the left, draw as many of the best Lewis dash-bond resonance structures as there are boxes to put them in. (Feel free to omit lone pairs and C-H's, or draw them—your choice.) Then, below each resonance structure, describe whether each would be a major or minor contributor. Finally, draw a consensus structure that illustrates partial charges and multiple bonds.



contribution: minor (1)

(major/minor?)

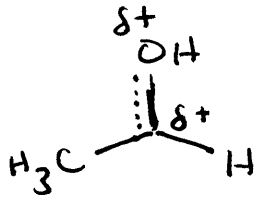
resonance structure



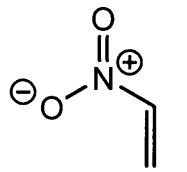
(3)

contribution: major (1)

consensus structure



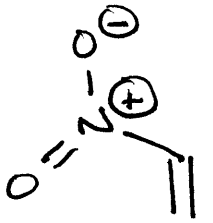
(3)



contribution: major (1)

(major/minor?)

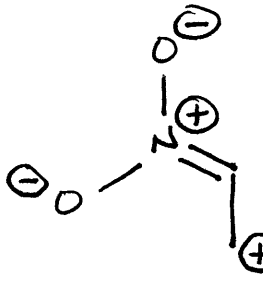
resonance structure



(3)

contribution: major (1)

resonance structure



(3)

contribution: minor (1)

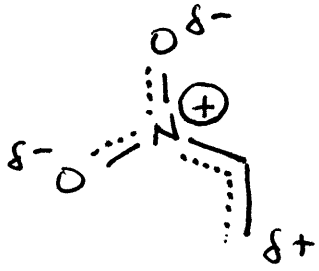
RUBRIC:

(3) POINTS FOR EACH STRUCTURE.

2 POINTS FOR ALL CHARGES CORRECT AND INTERNALLY CONSISTENT.

1. POINT FOR CORRECT BOND ORDERS.

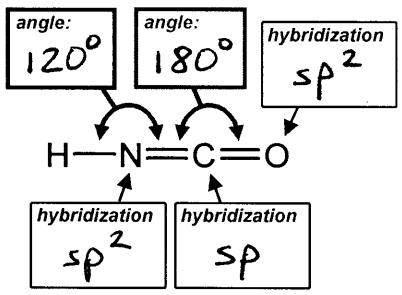
consensus structure



(1) POINT FOR CONTRIBUTIONS. NO PARTIAL CREDIT. MUST HAVE CORRECT STRUCTURE TO GET POINT.

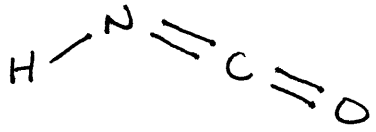
4. (17 pts) For each of the Lewis structures drawn below, in the boxes provided:
   - Draw Lewis wedge/dashed-bond structures that illustrate the most stable three-dimensional structure of the molecule. Draw all atoms, but feel free to omit lone pairs.
   - In the boxes provided, write the hybridization state for any atom heavier than hydrogen.
   - In the boxes provided, give any bond angle indicated by curved arrows in the original Lewis structure.

(1) each.

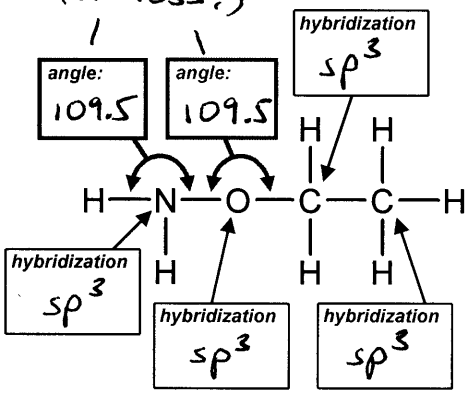


wedge/dashed-bond (3D) structure

(3)

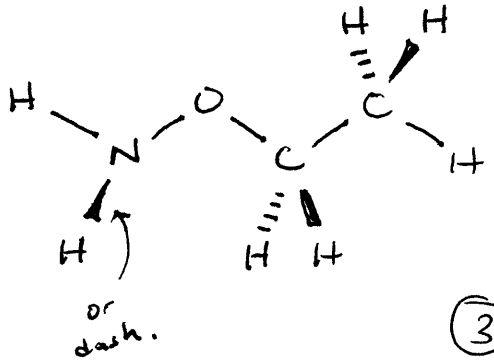


(or less.)



(1) each.

wedge/dashed-bond (3D) structure

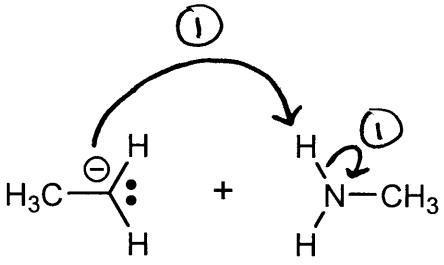


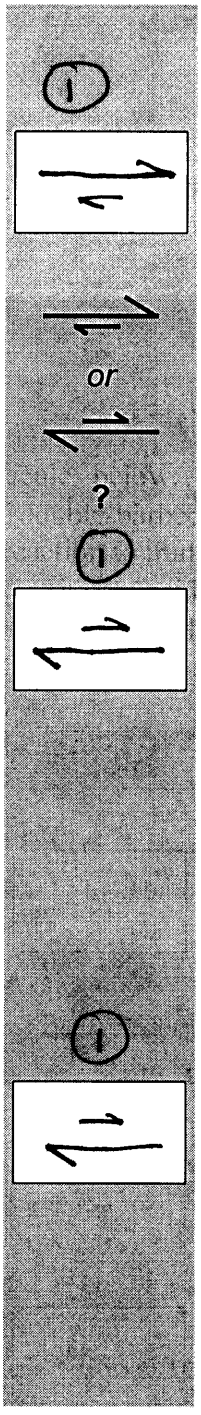
(3)

OKAY TO DRAW LONE PAIRS, BUT THEY MUST BE CORRECT.

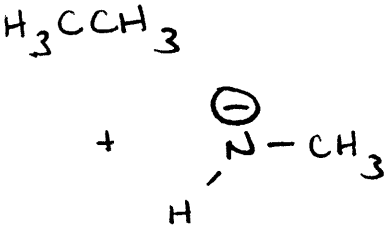
Rubric:
1 point for each bond angle and hybridization (12 total).
3 points for each 3-D structure (6 total).
-1 for each incorrect center or bond rotation (up to 3).

4. (18 pts) For each of the sets of molecules below:
   - Using "electron pushing" (with double-barbed arrows), show how the molecules on the left would react in an acid-base reaction to transfer a proton from one to the other.
   - In the box on the right, draw the conjugate acid and base products of each reaction.
   - In the middle, draw an equilibrium arrow that shows whether you feel the acid-base equilibrium would lie on the left or the right.

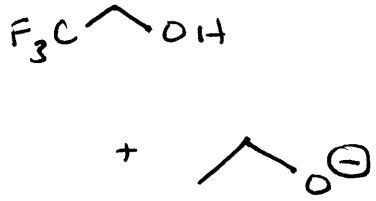




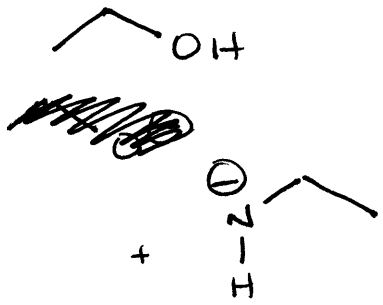
products (3)



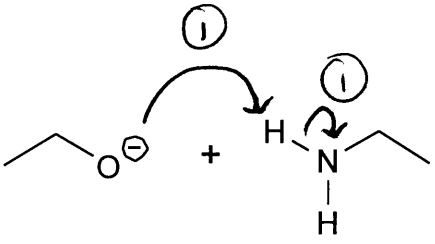
products (3)



products (3)

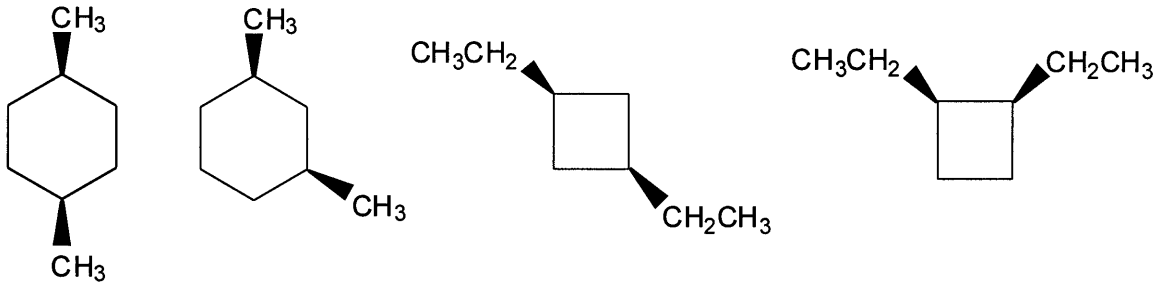


(2) FOR ONE, (1) FOR THE OTHER



5.

5. (14 pts) This problem deals with the following four isomers of C_8H_{16}:



A **B** **C** **D**

(2)

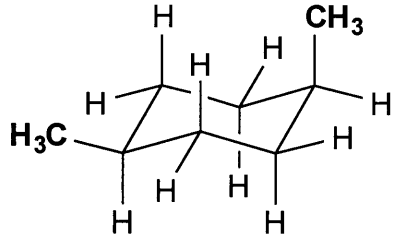
(a) Are these cycloalkanes (**cis-**) or ***trans-*** substituted? (Circle one.)

"*cis*" means "same side" or "same face". All of these are functionalized on the same (top) face, so they are *cis*-substituted.

(b) For each of the molecules **A** and **B**, draw the most stable chair conformation. Include all hydrogens on the cyclohexane ring, but you can abbreviate the methyl groups as "-CH_3".

most stable chair conformation for **A**

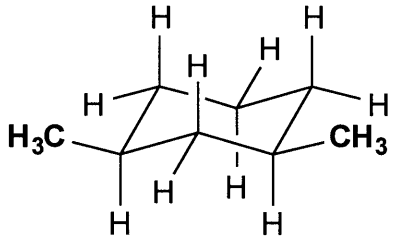
(3)



You can put the methyl groups on any carbons, as long as they are across from each other (1,4), and on either face (top or bottom), as long as they are on the same face.

most stable chair conformation for **B**

(3)



Similar comments to left: Substituents can be on any two carbons, as long as they are 2 away from each other (1,3), and on either face (top or bottom), as long as they are on the same face.

(2)

(c) Which of these two molecules is more stable, **A** or (**B**) ? (Circle one.)

In molecule **B**, both groups are equatorial in the most stable chair conformer. In molecule **A**, there is always one group axial.

most exothermic (most negative ΔH_c^0)

D	C	A	B

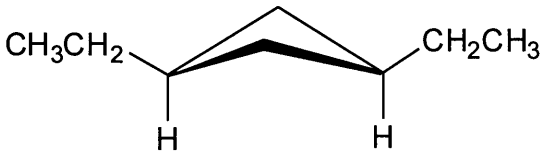
least exothermic (least negative ΔH_c^0)

(least stable) **(most stable)**

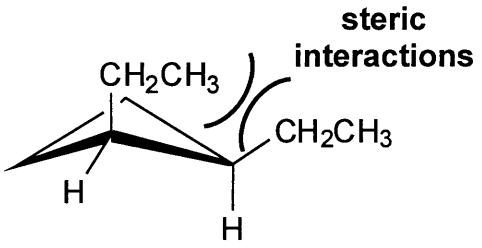
4

The heat of combustion is a measure of molecule stability; the more exothermic combustion is, the more energy the molecule gives off when it burns, the more energy the molecule had bottled up inside of it at the beginning—and the less stable the molecule is. So, the least stable molecule will have the most exothermic ΔH_c^0, and the most stable will have the least exothermic ΔH_c^0.

In this problem, the two cyclobutanes are going to be less stable than the two cyclohexanes, because of ring strain (25 kcal/mol or so). Out of cyclobutanes **C** and **D**, cyclobutane **D** is going to have additional steric interactions between the two adjacent ethyl groups, whereas the ethyl groups in **C** are across from each other:



molecule **C**



molecule **D**

This means **D** is least stable, followed by **C**, then **A** then **B**.

Rubric:

2 points for circling correct answers in parts (a) and (c). *No partial credit.*

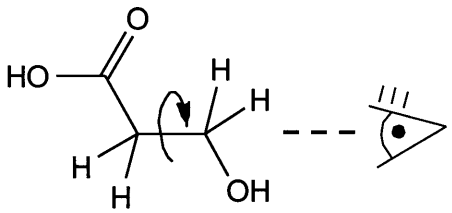
3 points for each chair in part (b).

- *1 point partial for drawing a chair. Any chair.*
- *1 point partial for drawing every hydrogen correctly. Every hydrogen must be identifiable as axial/equatorial.*
- *1 point partial for drawing both methyls correctly.*

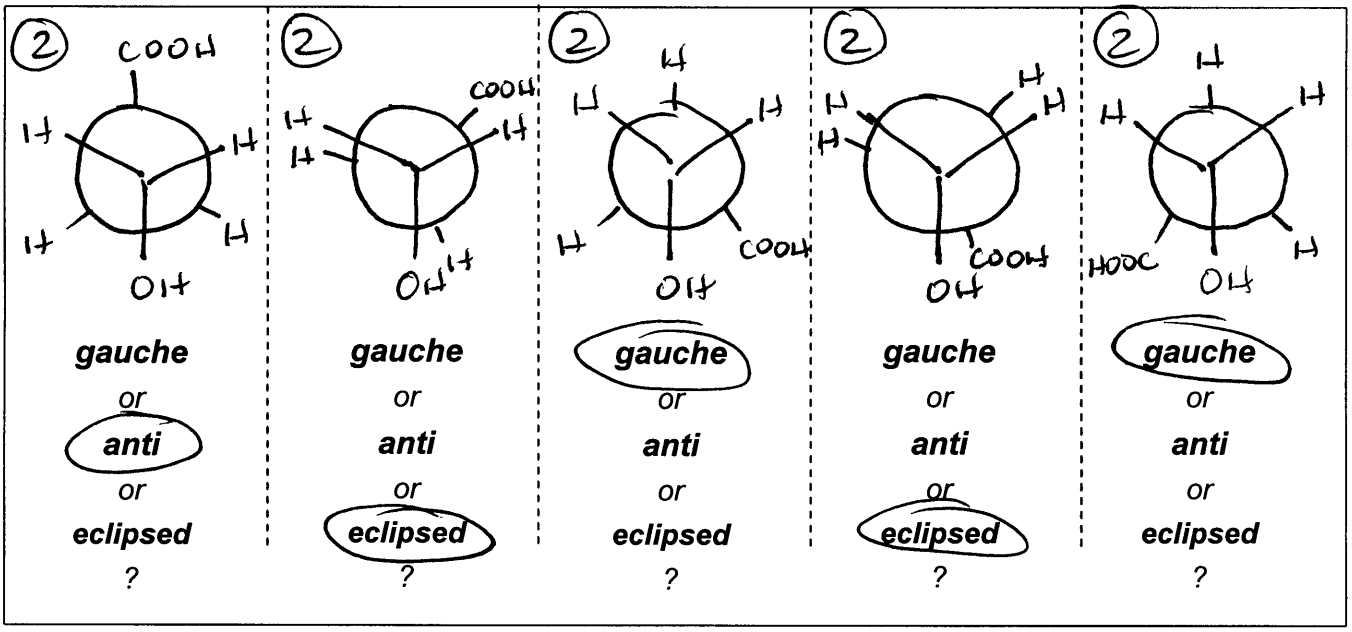
4 points for boxes in (d).

- *2 points partial for (C and D) before (A and B).*
- *1 point partial for D before C.*
- *1 point partial for A before B.*
- *2 points partial for **perfectly** reverse order (B-A-C-D). No other partial credit in this case.*

6. (26 pts) For the molecule 3-hydroxypropionic acid (drawn on the right):



(a) Draw Newman projections for <u>three</u> staggered and <u>two</u> eclipsed conformers accessed by rotation of the central C-C bond. Use the perspective I've indicated. Then, indicate whether each of your structures represents a ***gauche***, an ***anti*** ,or an ***eclipsed*** conformer by circling one answer.

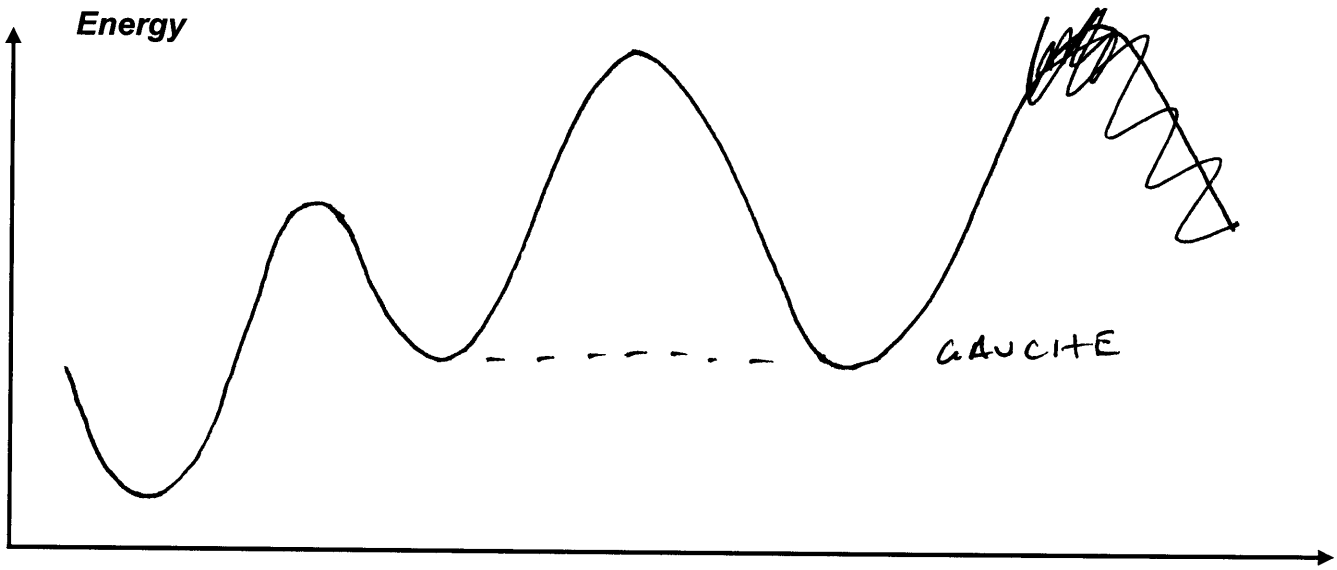


(2) POINTS FOR EACH COMBINATION OF NEWMAN PROJECTION AND CIRCLE.

CAN BE IN ANY ORDER.

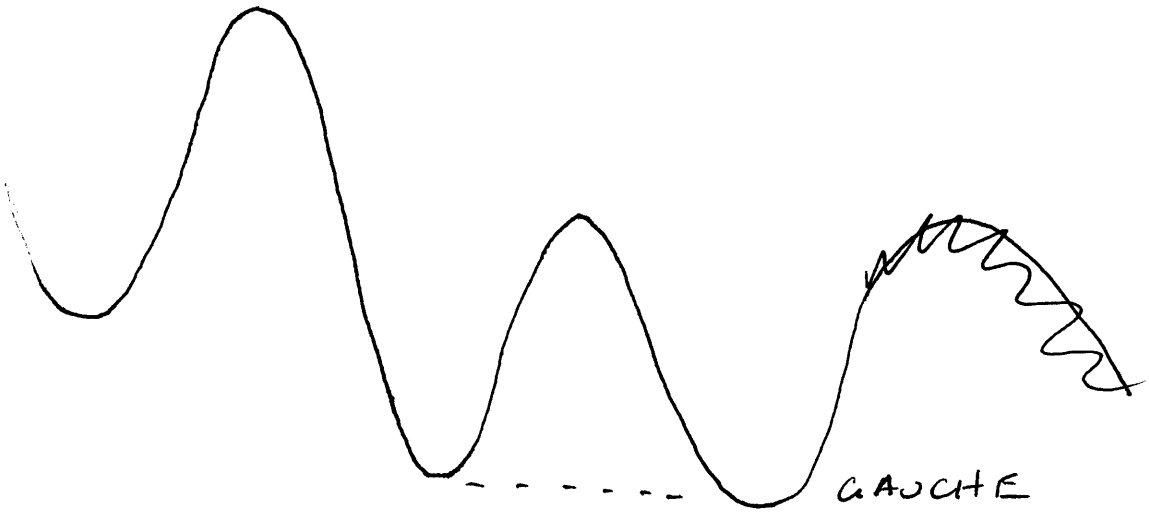
(10 POINTS TOTAL)

(b) In the space below, draw a potential energy diagram that illustrates the different relative energies of your five conformers.



8

OR



(8) POINTS TOTAL:

(2) POINTS FOR ANTI & GAUCHE BEING MINIMA;

(2) FOR ECLIPSED BEING MAXIMA

(2) POINTS FOR GAUCHE ENERGIES MATCHING

(2) POINTS FOR ECLIPSED ENERGIES MATCHING / NOT MATCHING

(c) 3-Hydroxypropionic acid experiences both hydrogen-bonding and torsional strain, and that makes it difficult to predict what conformer is most stable for this molecule. In your diagram, was the energetic effect of hydrogen bonding

GREATER *or* **LESSER**

than torsional strain? (Circle one.)

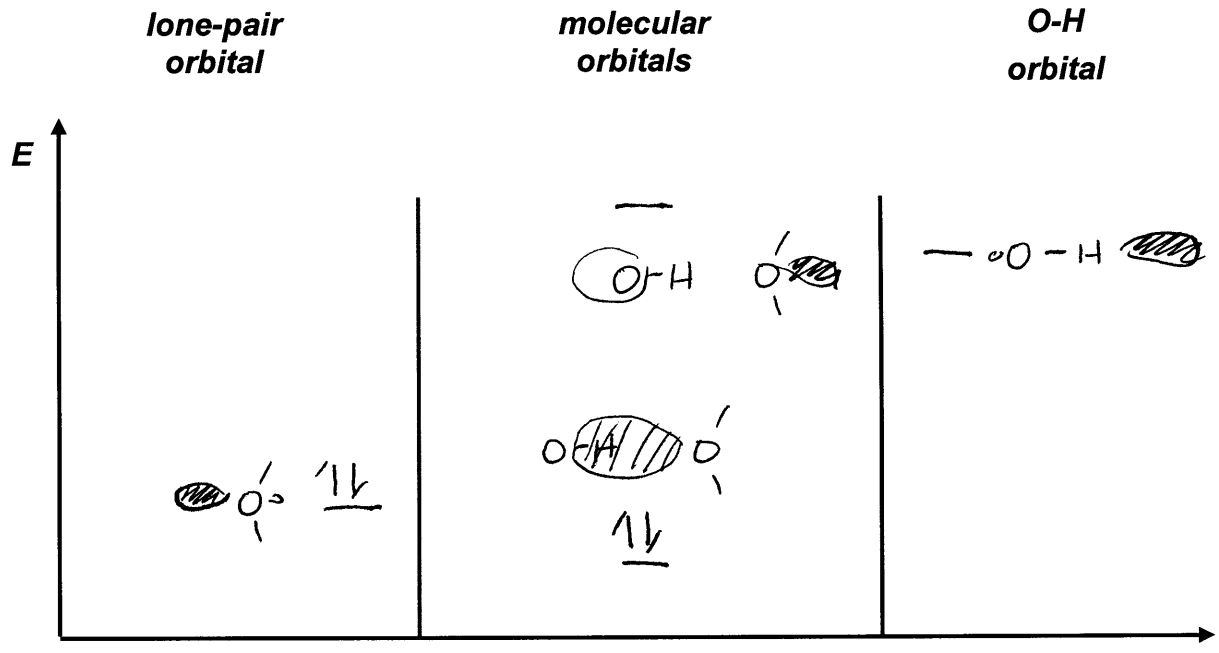
(2) POINTS, DEPENDING ON ANSWER TO POTENTIAL ENERGY DIAGRAM:

GREATER IF GAUCHE CONFORMERS ARE LOWER IN ENERGY;

LESSER IF ANTI IS LOWER.

(d) Hydrogen bonding has been described as a molecular orbital interaction between a lone-pair orbital on one atom and an antibonding X-H orbital on another. In the space below, draw a molecular orbital "mixing" diagram that depicts this interaction in 3-hydroxypropionic acid. In your diagram, show:

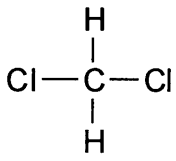
- the starting orbitals in the absence of H-bonding;
- new molecular orbitals that result from mixing; and
- energy levels and electron filling for all orbitals.



(4) POINTS FOR ~~EACH~~ EACH ORBITAL ENERGY LEVEL

(2) POINTS FOR ELECTRON FILLING

7. (4 pts) For each of the molecules below, circle whether the molecule is polar or non-polar.

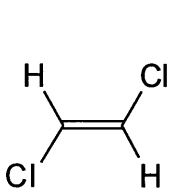


non-polar

or

polar *?*

2



non-polar

or

polar *?*

2