CHEM 433

Turn your work in on a separate set of paper. Your sheets must be stapled, and if torn from a spiral-bound notebook, must be free of the little paper frills that are present if you just rip it out of the book without using the perforations.

1. Label the hybridization of the non-hydrogen atoms in the following structures.



2. Draw the σ and σ\* molecular orbitals diagrams for the discrete and localized σ bond formed between the carbon and chlorine in chloroethane. Indicate any polarization this bond may have in your diagram by drawing the shapes of the discrete bonding and antibonding orbitals.

3. Draw the π and π\* molecular orbitals for the discrete and localized π bond in acetone (propan-2-one). Indicate any polarization this bond may have in your diagram by drawing the shapes of the discrete bonding and antibonding orbitals.

4. Formaldehyde has a very large dipole moment (2.33 Debye) whereas carbon monoxide has a very small dipole moment (0.11 Debye). Use resonance and electronegativity arguments to explain these results.

5. Consider bond dipoles to predict which conformer of formic acid should have the higher dipole moment: A or B?



6. It is known that bulky substituents prefer the equatorial to the axial position in cyclohexane. Nevertheless, the equilibrium shown lies to the right. Provide an explanation for this:



7. Explain why the cyclohexane derivative shown prefers the conformation with the methyl group axial (B) rather than equatorial (A).



8. Sketch a Newman projection of what you think would be the preferred conformation of hydrazine (H2NNH2), and briefly explain your choice.

9. Bicyclopentyl shows a strong preference for the conformation with the highlighted hydrogens anti. Using any relevant chemical arguments, rationalize this result.



This next one might be a bit tough:

10. Usually cyclohexane *A* values are reported at ΔGo values, but for some substituents, ΔHo and ΔSo values are also available. Such values are shown below for methyl and isopropyl (equatorial to axial interconversion). Consider the two chair conformers of *cis*-1-methyl-4-isopropylcyclohexane. Calculate the percentage of each form present at (A) 300K, (B) 100K, and (C) 75K.

|  |  |  |
| --- | --- | --- |
| Subsitituent | ΔHo (kcal/mol) | ΔSo (cal/mol·K) |
| methyl | 1.75 | 0 |
| isopropyl | 1.52 | -2.31 |

11. Predict the preferred conformation of fluoromethanol, FCH2OH, around the carbon/oxygen bond and briefly rationalize your choice.

12. Provide an explanation as to why cyclopentene is ***less*** strained than cyclopentane.

13. Rationalize the trends in the table using the following equilibrium reaction:

|  |  |  |
| --- | --- | --- |
| R-group | s-trans | s-cis |
| Methyl | 0.7 | 0.3 |
| Ethyl | 0.55 | 0.45 |
| Isopropyl | 0.3 | 0.7 |
| Tert-butyl | ~0 | ~1 |



14. I know we didn’t do anything like this in lecture but give it a try. Predict the most stable conformation of the following molecule (Hint: think intramolecular interactions).



This next one will be tough, too.

15. Given that the A value for a methyl group on cyclohexane is 1.8 kcal/mol, draw the energy diagram for the ring interconversion that takes the methyl group from an equatorial to an axial position. What is your prediction as the relative energies for the different twist-boat conformations, and how does this affect your prediction to the lowest energy pathway for the ring interconversion (use a model kit if you need to).

16. Do a full stereochemical analysis of the following molecule. Label all stereoisomeric relationships (enantiomers, diastereomers and/or meso/identical).



Bonus: what is the name of this molecule (trade name, not IUPAC)