5.53 (Molecular Structure and Reactivity I) Problem Sets

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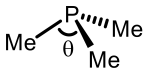
October 12, 2024

Contents

1 Applications of Molecular Orbitals

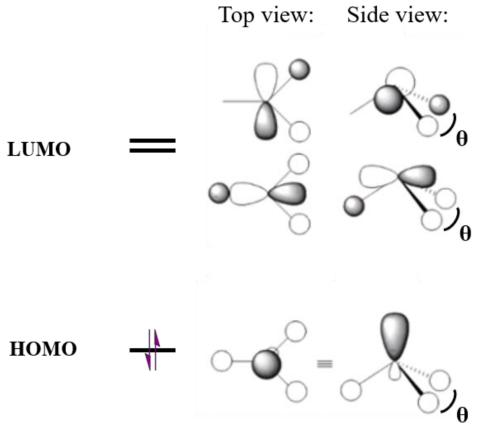
9/25: The questions pertain to the material we have covered from Introduction (Sep 5) to Pericyclic Reactions (Sep 19). For the molecular orbital (MO) diagrams, please draw the MOs with appropriate energy levels, fill in the electrons, and draw cartoons that illustrate the orbital interactions.

1. The geometry of PMe_3 (**1**) is known to be pyramidal.



1

A qualitative MO diagram for the frontier orbitals of PMe_3 can be drawn as follows.



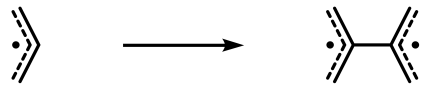
a) How will the energies of the frontier orbitals change if we decrease one C−P−C angle, denoted as θ, by symmetrically moving the two methyl groups closer to each other? Draw a Walsh diagram for the frontier orbitals to explain. Assume that the bond lengths are unchanged.

b) How will the energies of the frontier orbitals change if we instead increase θ while maintaining the bond lengths? Draw a Walsh diagram for the frontier orbitals to explain.

c) Rank the relative nucleophilicity and electrophilicity of the following molecules, and rationalize your hypotheses.

2 **3** **4**

2. Consider the combination of two allyl fragments (**1**) joined at the center carbons, leading to diradical (**2**).

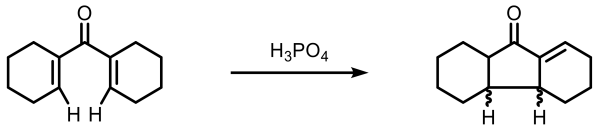


1 **2**

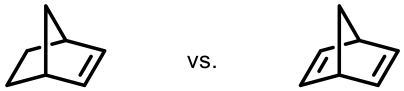
a) Construct a π MO interaction diagram for **2** that predicts the symmetries of the combined MOs and their energies relative to carbon p-orbitals. Please assume that only interactions between AOs on adjacent atoms are significant.

b) Can the two radical centers delocalize via resonance? Explain using the MO diagram from part (a).

3. Predict the stereochemistry of the product and rationalize your answer based upon MO theory.

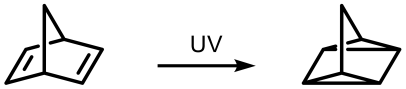


4. Norbornadiene is known to be more reactive towards electrophiles than norbornene.



norbornene norbornadiene

   a) Rationalize this difference using an MO diagram.
   b) Norbornadiene derivatives can be converted to quadricyclane derivatives under UV irradiation. Quadricyclanes are highly strained molecules, yet they are thermally stable.



norbornadiene quadricyclane

   Provide a frontier MO analysis to explain why quadricyclane is thermally stable.

5. Please use computational tools to complete this question. We will be using a browser-based quantum chemistry platform (Rowan) for this course.

   a) Create an account on Rowan (https://rowansci.com/) using your MIT email.
      - To learn how to submit a job on Rowan, please watch this video tutorial: https://docs.rowansci.com/web-interface/run-a-simple-job and/or read this overview: https://docs.rowansci.com/web-interface/submit/geometry-optimization.
      - More information on how to use Rowan (as well as additional tools) can be found here: https://docs.rowansci.com/web-interface.
   b) Ethane (H_3CCH_3).
      i. Using any means, build a molecular model for ethane in Rowan. Then, perform a geometry optimization using the PBE0 functional and the def2-SVP basis set. Take a screenshot of the webpage before submitting the job and paste it here.
         - Note: this job should not take more than 1 minute to run (not including queue time). If it takes significantly longer, consider adjusting your initial bond lengths/angles.
      ii. Convert the optimized structure into Cartesian (XYZ) coordinates and paste them here.
      iii. What is the calculated optimized C–C bond distance? What is the H–C–H bond angle(s)?
   c) Ethyl cation ($H_3CCH_2^+$).
      i. Using any means, build a molecular model for the ethyl cation in Rowan. Then, perform a geometry optimization using the PBE0 functional and the def2-SVP basis set. Take a screenshot of the webpage before submitting the job and paste it here.
         - Note: this job should not take more than 1 minute to run (not including queue time). If it takes significantly longer, consider adjusting your initial bond lengths/angles.
      ii. Convert the optimized structure into Cartesian (XYZ) coordinates and paste them here.
      iii. What is the calculated optimized C–C bond distance? What is the H–C–H bond angle(s)?
   d) Now, using qualitative MO arguments based on your calculations, discuss at least two factors contributing to the differing C–C bond lengths in ethane vs ethyl cation.