Problem Set 1: This problem set is now available at (www.blackboard.utdl.edu). It will be due in class 21 days (02/13/18) from today (01/23/18). Grades will be administered as follows: 10 (exceptional effort), 8 (complete), 5 (incomplete or inadequate effort), 2 (poor effort), 0 (nonexistent). ***No late problem sets will be accepted.***

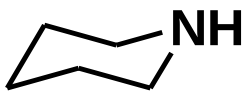
1. **Problem:** Consider the conformations about the O-C(=C) bond that are possible for methyl vinyl ether. (Draw the two lone pairs on oxygen as substituents in appropriate Newman projections.)

    a) What conformation would be preferred according to the σ, π description of bonding?
    b) What conformation would be preferred according to the bent bond description?
    c) After answering parts a) and b), use the literature to find a paper on methyl vinyl ether conformations. What do the experimental data tell you?

2. **Problem:** Construct a qualitative MO diagram showing how the π-molecular orbitals in the following molecules are modified by the addition of the substituent:

    a) Vinyl fluoride, compared to ethylene
    b) Acrolein, compared to ethylene
    c) Acrylonitrile, compared to ethylene
    d) Benzyl cation, compared to benzene
    e) Propene, compared to ethylene
    f) Fluorobenzene, compared to benzene

3. **Problem:** Cyclic amines such as piperidine and its derivatives show substantial differences in the properties of the axial C-2 and C-6 versus the equatorial C-2 and C-6 C-H bonds.



The axial C-H bonds are *weaker* than the equatorial C-H bonds as can be demonstrated by a strongly shifted C-H stretching frequency in the IR spectrum. Axial C-2 and C-6 methyl groups *lower* the ionization potential of the lone-pair electrons on nitrogen substantially more than do equatorial C-2 or C-6 methyl groups. Discuss the relationship between these observations and provide a rationalization in terms of qualitative MO theory.