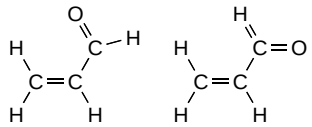
Part G. Flexible Molecules

1. Conformers for *n*-Butane. Obtain equilibrium geometries for both *anti* and *gauche* conformers of *n*-butane using the HF/6-31G* model. At what temperature does the minor conformer make up less than 1% of an equilibrium mixture? At what temperature does it make up more than 40%? Don't forget that 360° rotation about the central CC bond leads to two equivalent *gauche* conformers.

2. Dipole Moment of *n*-Butane. Using the results from the previous problem, calculate the value of the dipole moment for a sample of *n*-butane at room temperature. To what value does the dipole moment go as the temperature is raised? Elaborate.

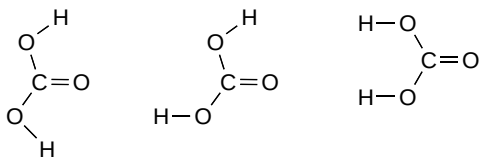
3. Infrared Spectra of Acrolein Conformers. Acrolein (propenal, $H_2C{=}CC(H){=}O$) exists as a mixture of *syn* and *anti* conformers.



Could these be distinguished using infrared spectroscopy, in particular, from the infrared frequency corresponding to the CO stretch? This requires both that the minor conformer contribute at least 5% to an equilibrium mixture and that the CO stretching frequencies of the conformers differ by at least 5 cm^{-1}. Use the B3LYP/6-31G* model to obtain geometries and infrared spectra for both conformers. Do not start with planar structures. Which conformer is lower in energy? What percentage of a room-temperature equilibrium mixture corresponds to the higher-energy conformer? If it less than 5%, what temperature would be needed to bring it to 5%? Compare the infrared spectra for the two conformers. Do the CO stretching frequencies differ by 5 cm^{-1} or more? Is there anything else that would help to distinguish the spectra? Elaborate.

4. Dipole Moment of Formic Acid. Formic acid (HCO_2H) incorporates one rotatable bond and may exist in either *cis* (HOC=O = 0°) or *trans* (HOC=O = 180°) conformers. Use the B3LYP/6-31G* model to obtain geometries for both conformers. Which is more stable and by how much? Rationalize the preference. What is the dipole moment of a sample at room temperature? Is it dominated by one conformer or do both conformers contribute significantly?

5. Carbonic Acid. Three "planar"conformers can be drawn for carbonic acid.



According to the HF/6-31G* model, which conformer is preferred? What is % abundance of the two higher-energy conformers room temperature? Does the ordering of dipole

moments for the three conformers parallel the ordering of energies? If it does, provide an explanation as to why.

6. Hydrazine and Tetrafluorohydrazine. Obtain an energy profile for rotation about the NN bond in hydrazine and obtain a Fourier fit. Use the HF/6-31G* model and step (:NN: dihedral angle) from 0 to 180^o in 20^o increments. (It is not necessary to step all the way to 360^o to identify the unique energy minima and to obtain the connecting barriers.) Which term(s) dominate the Fourier fit? Rationalize your result in terms of what you know about the relative "sizes" of bonds and lone pairs.

Repeat your calculations and analysis for tetrafluorohydrazine. Is this profile qualitatively similar to that for hydrazine insofar as the location of the energy minimum and the locations and heights of the rotational barriers? Which term(s) dominate the Fourier fit? Point out any significant differences between the two and provide a rationale.

7. Dinitrogen Tetraoxide. What is the preferred conformation of dinitrogen tetraoxide (O_2NNO_2) which results from oxidation of hydrazine? Are the nitro groups coplanar or perpendicular (or somewhere in between)? Use the B3LYP/6-31G* model to obtain the equilibrium geometry starting with a twisted geometry. Rationalize your result.

8. Hydrogen Peroxide and Hydrogen Disulfide. Obtain an energy profile for rotation about the OO bond in hydrogen peroxide and obtain a Fourier fit. Use the HF/6-31G* model and step the HOOH dihedral angle from 0 to 180^o in 20^o increments. (It is not necessary to step all the way to 360^o to identify the unique energy minima and to obtain the connecting barriers.) Which term(s) dominate the Fourier fit? Rationalize your result in terms of what you know about the relative "sizes" of bonds and lone pairs.

Repeat your calculations and analysis for rotation about the SS bond in hydrogen disulfide. Is the profile qualitatively similar to that for hydrogen peroxide insofar as the location of the energy minimum and the locations and heights of the rotational barriers? Which term(s) dominate the Fourier fit? Point out any significant differences between the two and provide a rationale.

9. 1-Butene. Use the HF/6-31G* model to obtain an energy profile for rotation about the central CC single bond in 1-butene (CH_3CH_2─CH=CH_2). Step from 0 to 180^o in 20^o increments. (It is not necessary to step all the way to 360^o to identify the unique energy minima and to obtain the connecting barriers.) How many distinct energy minima are there? If more than one, which is favored? Which term(s) dominate the Fourier fit?

10. 1,3-butadiene. Use the HF/6-31G* model to obtain an energy profile for rotation about the central CC single bond in 1,3-butadiene. Step from 0 to 180^o in 20^o increments. (It is not necessary to step all the way to 360^o to identify the unique energy minima and to obtain the connecting barriers.) Is this profile qualitatively similar to that for 1,3-butadiene insofar as the location of the energy minima? Specifically, is there a *trans* coplanar minimum? Is there a *cis* minimum that is actually slightly distorted from planarity? Is the *trans* minimum lower in energy than the *cis* minimum? Which term(s) dominate the Fourier fit?

11. Acrolein and Glyoxal. Use the HF/6-31G* model to obtain an energy profile for rotation about the central CC single bond in acrolein (H_2C=C(H)-C(H)=O). Step from 0 to 180^o in 20^o increments. (It is not necessary to step all the way to 360^o to identify the unique energy minima and to obtain the connecting barriers.) Is this profile qualitatively similar to that for 1,3-butadiene insofar as the location of the energy minima (see previous problem)? Specifically, are the CC and CO double bond in the "*cis*" structure of acrolein coplanar or (as in the case of 1,3-butadiene) and the locations and heights of the rotational barriers? Which term(s) dominate the Fourier fit? Point out any significant differences between the two and provide a rationale.

Repeat your calculations and analysis for glyoxal (O=(H)C-C(H)=O) and answer the analogous questions.

12. λ_{max} vs. Diene Conformation. A very simple way to model the energy of an electronic transition from ground to excited state (λ_{max} in the UV/vis spectrum) is to assume that it parallels the difference in energy between the highest-occupied and lowest-unoccupied molecular orbitals (the HOMO-LUMO gap). To what extent does this gap (and λ_{max}) for a diene depend conformation? To what extent does the change in the gap parallel the change in energy of the ground-state molecule with change in conformation?

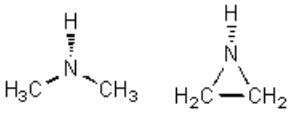
Use the energy profile for 1,3-butadiene obtained in a previous problem (varying the CCCC dihedral angle in each from 0° to 180° in 20° steps) to plot both the energy and the HOMO/LUMO gap as a function of dihedral angle. At what dihedral angle is the HOMO/LUMO gap the largest? At what dihedral angle is it the smallest? Is there much difference in the HOMO/LUMO gap between *cis* and *trans*-planar diene conformers? Does the variation in total energy closely follow the HOMO-LUMO gap or are the two uncorrelated?

13. Twist-Boat Cyclohexane. In addition to the familiar chair structure, there is a second stable form of cyclohexane. This structure is usually described as "twist boat", insofar as the CH_2 groups on the opposite side of the six-member ring point in the same direction. Obtain equilibrium geometries for both chair and twist boat conformers of cyclohexane using the HF/6-31G* model, and calculate the room-temperature equilibrium distribution of the two. Is the higher-energy conformer sufficiently abundant (>5% of the total) such that it is likely to be seen? Elaborate.

14. Inversion in Phosphine and Trifluorophosphine. Phosphine (PH_3) is pyramidal and inverts via a planar transition state. Use the HF/6-31G* model to obtain geometries for both pyramidal and planar forms. Also perform analogous calculations on the two structures of ammonia (NH_3). Is this barrier in phosphine smaller, larger or about the same as that for ammonia? Provide a rationale if it is markedly different.

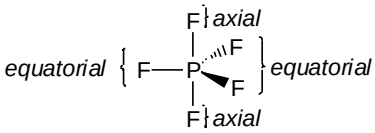
Repeat your calculations for trifluorophosphine (PF_3). Is there a significant increase or decrease in inversion barrier relative to that for phosphine. Obtain planar and pyramidal structures for trifluoroamine (NF_3). Is any change in inversion barrier from ammonia similar to the change found in the phorphorus compounds?

15. Inversion in Aziridine. Is pyramidal inversion of a nitrogen that is part of a three-member ring expected to be more or less difficult that inversion of an acyclic amine. To decide, use the HF/6-31G* model to obtain geometries for dimethylamine (to act as a reference), aziridine and their respective inversion transition states.

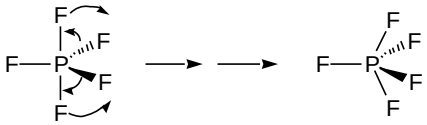


Calculate inversion barriers (difference between pyramidal and planar forms) for both molecules. Is the barrier in aziridine significantly larger than that in dimethylamine? Provide a rational for your results.

16. Pseudorotation in Phosphorus Pentafluoride. Pseudorotation exchanges *equatorial* and *axial* positions of a five-coordinate, trigonal-bipyramidal center, for example, the phosphorus in phosphorus pentafluoride (PF_5).



The process, known as pseudorotation, simultaneously decreases the FPF angle involving two *axial* fluorines and increases the FPF angle involving two of the *equatorial* fluorines. The transition state is a structure in which (what were) the two *axial* fluorines and two of the *equatorial* fluorines form the base of a square-based pyramid. Continuing the motion returns to the stable trigonal-bipyramidal geometry but with *axial* and *equatorial* fluorines exchanged. Repeated pseudorotation moves fully scramble the fluorines.



Use the HF/6-31G* model to obtain geometries for both trigonal bipyramidal (D_{3h} symmetry) and square-based pyramidal (C_{4v} symmetry) forms of PF_5 and calculate the barrier to pseudorotation. Even though the latter is presumed to be a transition state, you can obtain its geometry by starting from a structure with C_{4v} symmetry. Is your result consistent with failure of ^{19}F NMR spectroscopy to distinguish between *equatorial* and *axial* sites even at temperatures as low as -100^o C? Elaborate/

17. Pseudorotation in Iron Pentacarbonyl. Iron pentacarbonyl, $Fe(CO)_5$, adopts a trigonal bipyramidal (D_{3h} symmetry) geometry with distinct *equatorial* and *axial* positions. However, *equatorial* and *axial* positions these are assumed to rapidly exchange by way of a square-based pyramid (C_{4v} symmetry) structure, in process known as pseudorotation. Use the B3LYP/6-31G* density functional model to obtain geometries for both forms. (Even though the square-based pyramid is presumed to be a transition

state, if you start with a C_{4v} symmetry structure, this will be maintained in the geometry optimization.) Calculate the activation energy for pseudorotation. Is it significantly higher than that for PF_5 (xx kJ/mol)? Is it likely that the ^{13}C NMR spectrum likely to exhibit one or two resonances? Elaborate.

18. Nitroamide. Is the amino group in nitroamide (O_2N-NH_2) planar or pyramidal? While the inherent preference is for a pyramidal geometry, delocalization of the lone pair on the amino group into the nitro group is best accommodated by a planar structure. Use the B3LYP/6-31G* model to determine the equilibrium geometry of nitroamide, starting from a non-planar structure. If you find that the molecule is non-planar, calculate the barrier to inversion.