

# Structure and Bonding

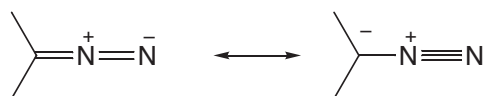
**1** While the Hartree-Fock model is remarkably successful in accounting for the structures of main-group compounds, Hartree-Fock geometries exhibit a number of systematic errors. The most conspicuous is that bond lengths are almost always shorter than experimental values. The magnitude of the error generally increases as the elements involved in the bond move from left to right in the *Periodic Table*.

- a. Optimize the geometries of ethane, methyl fluoride and fluorine molecule using the HF/6-311+G\*\* model. While your results will not fully represent the so-called Hartree-Fock limit, the 6-311+G\*\* basis set is flexible enough to approach this limit. Compare calculated CC, CF and FF bond distances with experimental values (1.531Å, 1.383Å and 1.412Å, respectively). Which if any of the calculated bond lengths fall within 0.02Å of the experimental distance (a typical error for a bond distance obtained by X-ray crystallography)?
- b. Repeat your calculations using the HF/6-31G\* model. This model is simple enough to allow its widespread application to sizeable molecules. Are the differences in bond lengths (from HF/6-311+G\*\* results) relatively constant, or do they change from one molecule to another? Are HF/6-31G\* bond lengths inside the 0.02Å error limits?

**2** Errors in (limiting) Hartree-Fock bond distances increase from single to double and triple bonds. For example, while Hartree-Fock carbon-carbon single bond lengths are quite close to experimental distances, the corresponding double and triple bond lengths are typically too short. This can be rationalized by recognizing that approaches beyond the Hartree-Fock model, in one way or another, “mix” ground and excited-state descriptions. Bond distances in excited states will tend to be longer than those in the ground state, meaning that any “mixing” of ground and excited states will lead to bond lengthening. Furthermore, as excited states will generally be more accessible (lower in energy) for unsaturated systems compared to saturated systems, it is reasonable to expect that changes from Hartree-Fock results will be greater.

- Optimize the geometries of ethane, ethylene and acetylene using the HF/6-311+G\*\* model. Compare calculated C–C, C=C and C≡C bond distances with experimental values (1.531Å, 1.339Å and 1.203Å, respectively). Is the error in the single bond distance smaller than the errors in the double and triple bond lengths?
- Display the HOMO and LUMO for ethylene. The first excited-state of ethylene might be viewed as resulting from excitation of an electron from the HOMO to the LUMO. Is the HOMO carbon-carbon bonding, non-bonding or antibonding? (See the essay “*Atomic and Molecular Orbitals*” for a description of terminology.) Is the LUMO carbon-carbon bonding, non-bonding or antibonding? Would you expect the carbon-carbon bond in the first excited state of ethylene to be longer, shorter or unchanged from that in the ground state? Elaborate. What effect, if any, on the carbon-carbon bond length in ethylene would be expected from mixing of excited states?

**3** Diazomethane is usually described as a composite of two Lewis structures, both of which involve separated charges.



Optimize the geometry of diazomethane using the HF/6-31G\* model. Also optimize the geometries of methylamine, CH<sub>3</sub>NH<sub>2</sub>, and methyleneimine, H<sub>2</sub>C=NH, as examples of molecules incorporating “normal” CN single and double bonds, respectively, and of *trans* diimide, HN=NH, and nitrogen, N≡N, as examples of molecules incorporating “normal” NN double and triple bonds, respectively. Which Lewis structure provides the better description for diazomethane or are both required for adequate representation?

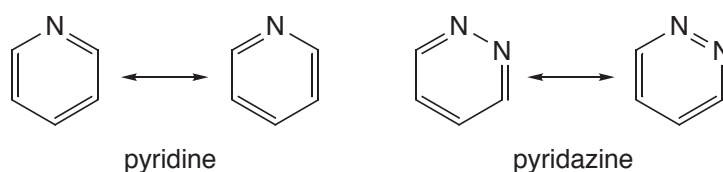
**4** Draw a Lewis structure for cyanide anion, CN<sup>−</sup>, and assign formal charges. (See page 133 for the “recipe”.) Does it incorporate a double bond like in methyleneimine, H<sub>2</sub>C=NH, or a triple bond like in hydrogen cyanide, HC≡N? On which atom does the negative charge reside?

To see if your Lewis structure presents a “realistic” picture, obtain equilibrium geometries for cyanide anion, methyleneimine and

hydrogen cyanide using the HF/6-31G\* model. According to your calculations, is the CN bond in cyanide anion closer to double or triple (compare it to bond lengths in methyleneimine and hydrogen cyanide)? Which atom bears the negative charge, or is it distributed over both carbon and nitrogen?

**5** Draw two different “reasonable” geometries for ozone, O<sub>3</sub>. For each, provide Lewis structures and assign formal charges to the oxygen atoms. Obtain the equilibrium geometries for both using the HF/6-31G\* model. Which structure is lower in energy? Is it in accord with the experimentally known equilibrium geometry? Is the higher-energy structure actually an energy minimum? Elaborate. If the preferred structure has more than one distinct oxygen atom, which is most positively charged? Most negatively charged? Is your result consistent with formal charges?

**6** Pyridine and pyridazine are each represented by two Lewis structures.



While the two structures are the same for pyridine, they are different for pyridazine. Compare carbon-nitrogen bond distances in pyridazine (using those in pyridine as a “reference”) obtained from optimized structures using the HF/6-31G\* model. Should its two Lewis structures be given equal weight? If not, which structure is the more important? Elaborate.

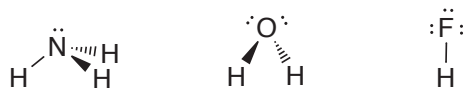
**7** Acyl cation, CH<sub>3</sub>CO<sup>+</sup>, adds to benzene and other aromatics. According to B3LYP/6-31G\* calculations, which atom in acyl cation is the most positively-charged? Draw the Lewis structure for acyl cation that is most consistent with its charge distribution. Is the calculated geometry of acyl cation consistent with its Lewis structure? Which atom (carbon or oxygen) would you expect to add to benzene? Draw a Lewis structure of the acyl cation - benzene adduct.

8 Nitronium cation,  $\text{NO}_2^+$ , is the active reagent in the nitration of benzene and other aromatics. According to B3LYP/6-31G\* calculations, is it linear or bent? What common neutral molecule has the same number of electrons as  $\text{NO}_2^+$ ? Is this molecule linear or bent? Examine the charges on the nitrogen and oxygen atoms in  $\text{NO}_2^+$ . Is nitrogen or oxygen more positive? Draw a Lewis structure for nitronium cation that is most consistent with the calculated geometry and charges. Display an electrostatic potential map for  $\text{NO}_2^+$ . What atom (nitrogen or oxygen) would you expect to add to benzene? Draw a Lewis structure of the nitronium cation - benzene adduct.

9 Molecular geometry depends not only on the constituent atoms, but also on the total number of electrons. Molecules with the same stoichiometry but with varying numbers of electrons may prefer different geometries. Optimize geometries of 2-methyl-2-propyl cation, radical and anion using the HF/6-31G\* model. What changes, if any, to the local geometry of the central carbon do you observe with increasing number of valence electrons? What is the origin of these changes?

10 What happens to electron pairs that are “left over” after all bonds have been formed? Is each electron pair primarily associated with a single atom or is it “spread out”?

- a. Optimize the geometries of ammonia, water and hydrogen fluoride using the HF/6-31G\* model and examine electrostatic potential surfaces. (A value of -80 kJ/mol for electrostatic potential isosurfaces will demark highly electron-rich regions.) Describe the three surfaces and relate them to the Lewis structures.

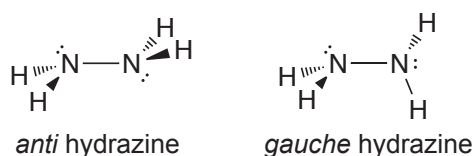


Rationalize the unusual shape of the potential for water, and clarify the difference in the shapes of the ammonia and hydrogen fluoride potentials (that might first appear to you to be nearly identical).

- b. Optimize the geometries of methyl anion, ammonia and hydronium cation using the HF/6-31G\* model and examine electrostatic potential surfaces. For which does the potential extend furthest away from the nuclei? For which is the extension the least? What

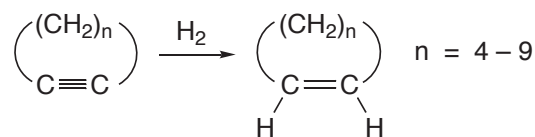
do the relative sizes (extensions) of the potential tell you about the relative abilities of these three molecules to act as electron sources (“nucleophiles”)?

- c. Optimize the geometries of *anti* and *gauche* conformers of hydrazine using the HF/6-31G\* model. Note the energies of the two highest-energy occupied molecular orbitals (the HOMO and the orbital immediately below the HOMO) and examine electrostatic potential surfaces.



Is there a noticeable difference in the extent to which the two electron pairs interact (“delocalize”) between the two conformers? Interaction should result in the “spreading out” of the potential over both nitrogens and in the “splitting” of the energies of the two highest-energy occupied orbitals. If there is a difference, is the “more delocalized” conformer lower or higher in energy than the “less delocalized” conformer?

**11** Examine structures obtained from HF/3-21G calculations for cycloalkynes from cyclohexyne,  $\text{C}_6\text{H}_8$ , to cycloundecyne,  $\text{C}_{11}\text{H}_{18}$ . What is the minimum ring size needed to allow a nearly linear geometry (within  $10^\circ$ ) of the incorporated  $\text{C}-\text{C}\equiv\text{C}-\text{C}$  structural unit? Optimize geometries for the corresponding *cis*-cycloalkenes and calculate energies for addition of hydrogen to the cycloalkynes.



$\equiv\text{C}$  bond

angle?

**12** The HNH bond angle in ammonia is  $106.7^\circ$ , somewhat less than the tetrahedral value ( $109.5^\circ$ ). So too is the HOH bond angle in water ( $104.5^\circ$ ). The usual rationale is that the lone pair on nitrogen and the two lone pairs on oxygen “take up more space” than NH and OH bonds, respectively. As seen from the experimental data below, HXH bond angles in second-row and heavier main-group analogues of ammonia and water deviate even more from tetrahedral.

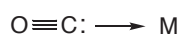
|                        |                       |                        |                        |
|------------------------|-----------------------|------------------------|------------------------|
| NH <sub>3</sub> 106.7  | PH <sub>3</sub> 93.3  | AsH <sub>3</sub> 92.1  | SbH <sub>3</sub> 91.6  |
| H <sub>2</sub> O 104.5 | H <sub>2</sub> S 92.1 | H <sub>2</sub> Se 90.6 | H <sub>2</sub> Te 90.3 |

Is this further reduction in bond angle due to increased size of lone pairs on the heavy elements or are other factors involved? Do electrostatics (Coulomb’s law) or changes in orbital hybridization play a role?

- Optimize the geometries of the eight hydrides shown above using the HF/3-21G model and also calculate electrostatic potential surfaces. (Set the isovalue for each to -10.) These surfaces demark the “most available” electrons that may loosely be interpreted as the lone pair electrons. What is the ordering of sizes of lone pairs (as indicated by the electrostatic potential surfaces) in the series NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub>? In the series H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se, H<sub>2</sub>Te? Is the size ordering consistent with the observed bond angles? Elaborate.
- Examine hydrogen charges in ammonia and its analogues. Do they increase (hydrogen becoming more positive), decrease or remain about the same in moving to heavier analogues? Rationalize your result in terms of the electronegativities of nitrogen and its heavier analogues (relative to the electronegativity of hydrogen). Use Coulomb’s law to predict the trend in HXH bond angle in the series NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub>. Repeat your analysis for water and its analogues.
- The bonds in ammonia, water and their heavier analogues may be described in terms of sp<sup>3</sup> hybrids. The “p contribution” to these bonds should increase as the energy of the (atomic) p orbitals move closer to the energy of the s orbital and should result in a decrease in bond angle. In order to get a measure of relative valence s and p orbitals (2s, 2p for first-row elements, 3s, 3p for second-row elements, etc.) perform HF/3-21G calculations on Ne, Ar, Kr and Xe. Do valence s

and p orbitals move closer together, move further apart or are their relative positions unchanged in going from Ne to Xe? If they do change their relative positions, how would you expect the HXH bond angles to change in moving from NH<sub>3</sub> to SbH<sub>3</sub> and from H<sub>2</sub>O to H<sub>2</sub>Te? Elaborate.

**13** Carbon monoxide is the most common molecule to appear in organometallic compounds. CO bonds “end on” from carbon, and contributes two electrons to the metal.



As the electrons from carbon monoxide are non-bonding, it might be expected that their loss will not have significant consequences. However, it is well known that the infrared stretching frequency of “complexed” CO is smaller than that in free carbon monoxide.

- a. Optimize the geometry of carbon monoxide using the B3LYP/6-31G\* model and examine both the HOMO and LUMO. Is the HOMO bonding, antibonding or essentially non-bonding between carbon and oxygen? What, if anything, would you expect to happen to the CO bond strength as electrons are donated from the HOMO to the metal? Elaborate. Is this consistent with the changes seen in the infrared stretching frequency of carbon monoxide?

The LUMO is where the next (pair of) electrons will go. Is it bonding, antibonding or essentially non-bonding between carbon and oxygen? What if anything would you expect to happen to the CO bond strength were electrons to be donated (from the metal) into this orbital? Elaborate. Is this consistent with the changes seen in the infrared stretching frequency of carbon monoxide?

To see if the metal center incorporates a high-energy filled molecular orbital properly disposed to donate electrons into the LUMO of CO, you need to perform calculations on a molecule from which carbon monoxide has been removed. Iron tetracarbonyl, resulting from loss of CO from iron pentacarbonyl is one such molecule.

- b. Optimize the geometry of iron pentacarbonyl (a trigonal bipyramid) using the B3LYP/6-31G\* model.\* Then, delete one of the *equatorial* CO ligands to make iron tetracarbonyl and perform a single-point energy calculation using the B3LYP/6-31G\* model.

Is the HOMO of the iron tetracarbonyl fragment properly disposed to interact with the LUMO in CO? Elaborate. Would you expect electron donation to occur?

14 Two “limiting” structures can be drawn to represent ethylene “bonded” to a transition metal. The first may be thought of as a “weak complex” in that it maintains the carbon-carbon double bond, while the second destroys the double bond in order to form two new metal-carbon  $\sigma$  bonds, leading to a three-membered ring (a so-called “metallacycle”).



The difference between the two representations is only one of degree, and “real” metal-alkene complexes might be expected to span the full range of possible structures.

- a. Optimize the geometry of ethylene using the B3LYP/6-31G\* model and examine both the HOMO and LUMO. Is the HOMO bonding, antibonding or non-bonding between the two carbons? What if anything should happen to the carbon-carbon bond as electrons are donated from the HOMO to the metal? Do you expect the carbon-carbon bond length to decrease, increase or remain about the same? Elaborate.

The LUMO is where the next (pair of) electrons will go. Is this orbital bonding, antibonding or non-bonding between the two carbons? What, if anything, should happen to the carbon-carbon bond as electrons are donated (from the metal) into the LUMO? Is the expected change in the carbon-carbon bond due to this interaction

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\* To save computer time, you could use the PM3 model to optimize the geometry of iron pentacarbonyl.



in the same direction or in the opposite direction as any change due to interaction of the HOMO with the metal? Elaborate.

To see if the metal center incorporates appropriate unfilled and filled molecular orbitals to interact with the HOMO and LUMO of ethylene, respectively, perform B3LYP/6-31G\* calculations on iron tetracarbonyl, arising from loss of ethylene from ethylene iron tetracarbonyl.

- b. Optimize the geometry of ethylene iron tetracarbonyl (a trigonal bipyramid with ethylene occupying an *equatorial* position with the CC bond in the *equatorial* plane) using the B3LYP/6-31G\* model.\* Then, delete the ethylene ligand and perform a single-point B3LYP/6-31G\* calculation on the resulting (iron tetracarbonyl) fragment. Examine both the HOMO and LUMO of this fragment.

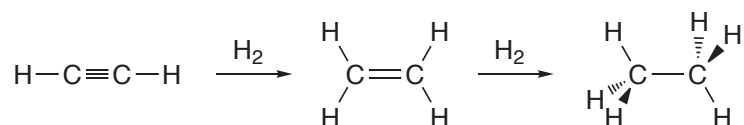
Is the LUMO of the iron tetracarbonyl fragment properly disposed to interact with the HOMO of ethylene? Elaborate. Would you expect electron donation from ethylene to the metal to occur? Is the HOMO of the fragment properly disposed to interact with the LUMO of ethylene? Elaborate. Would you expect electron donation from the metal to ethylene to occur?

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\* To save computer time, you could use the PM3 model to optimize the geometry of ethylene iron tetracarbonyl.

# Thermochemistry

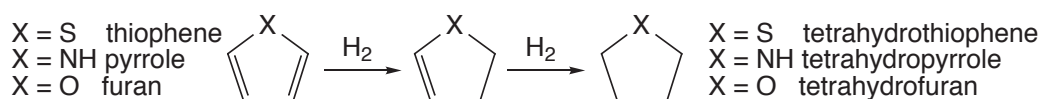
15 Which step in the hydrogenation of acetylene to ethane is the more *exothermic*?



Is a triple bond as strong as two double bonds? Use energies based on optimized geometries from B3LYP/6-31G\* calculations.

16 Compare the B3LYP/6-31G\* energy of the hypothetical molecule, 1,3,5-cyclohexatriene, with alternating single and double bonds, with that of benzene. 1,3,5-cyclohexatriene is not an energy minimum (it collapses to benzene). To calculate its energy, you need to set the carbon-carbon bonds to alternating single (1.54Å) and double (1.32Å) lengths. (**Do not optimize.**) Is the difference in energy roughly the same as the aromatic stabilization afforded benzene (~ 160 kJ/mol), or significantly smaller? Does your result suggest that aromatic stabilization occurs at least in part without structural change? Elaborate.

17 Addition of one equivalent of hydrogen to thiophene (X=S) not only breaks one of the double bonds but also destroys any aromaticity. On the other hand, addition of a second equivalent only breaks the remaining double bond. Therefore, the difference in energy between the first and second hydrogenation steps provides a measure of the aromatic stabilization afforded thiophene.

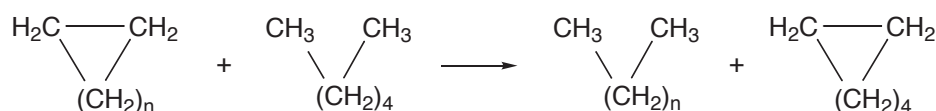


- a. Optimize geometries for hydrogen, for thiophene and for its first and second hydrogenation products using the B3LYP/6-31G\* model, and calculate the difference in hydrogenation energies between thiophene (leading to dihydrothiophene) and dihydrothiophene (leading to tetrahydrothiophene). Is this difference comparable to that between the first and second hydrogenation energies of benzene

(~160 kJ/mol from calculations using the B3LYP/6-31G\* model) or is it significantly smaller or greater?

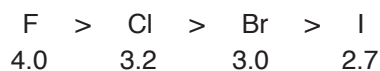
- b. Repeat for pyrrole (X=NH) and furan (X=O). Order the aromatic stabilities of the three molecules.

**18** Small-ring cycloalkanes are less stable than the corresponding  $n$ -alkanes. This is usually attributed to CCC bond angles that deviate from tetrahedral and eclipsing interactions between CH bonds. The destabilization or “ring strain” of cycloalkanes, relative to  $n$ -alkanes, is provided by the energy of a hypothetical reaction in which one equivalent of hydrogen is added leading to the analogous  $n$ -alkane, relative to the corresponding hydrogenation of cyclohexane (assumed to be an unstrained molecule).



- a. Use this reaction to obtain strain energies for cyclopropane, cyclobutane and cyclopentane from geometries optimized using the HF/6-31G\* model. Which is the most strained cycloalkane? Is any cycloalkane less strained than cyclohexane? If so, why?
- b. Obtain the strain energy for cycloheptane. Is it significantly less or greater than the strain energy of cyclohexane? If so, suggest why.

**19** HF is a much stronger acid than H<sub>2</sub>O, that in turn is a stronger acid than NH<sub>3</sub>. This parallels a decrease in the electronegativity of the atom bonded to hydrogen (F > O > N) and presumably a decrease in bond polarity. Hydrogen in HF is more positive than the hydrogens in H<sub>2</sub>O, that are in turn more positive than the hydrogens in NH<sub>3</sub>. Therefore, acid strength would be expected to decrease from HF to HI, paralleling the decrease in electronegativity of the halogen.



The opposite is true, HI is the strongest acid and HF is the weakest.

Acid strength relates to the energy of heterolytic bond dissociation into separated positive and negative ions.



Gas-phase heterolytic bond dissociation energies are much larger than the corresponding energies in a solvent such as water. This is because the solvent acts to stabilize the charged dissociation products much more than it does the uncharged reactants.

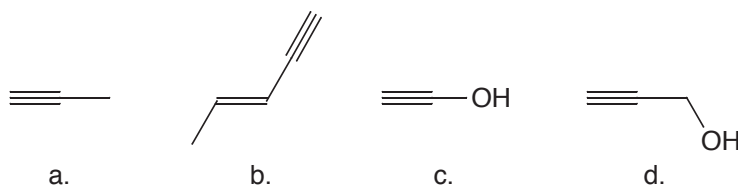
- a. Optimize geometries for HF, HCl, HBr and HI using the HF/3-21G model. Also, perform single-point energy calculations on  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ . Compute heterolytic bond dissociation energies for the four molecules. (The energy of the proton is 0.) Is the ordering of calculated bond dissociation energies the same as the ordering of acidities observed for these compounds?

Heterolytic bond dissociation in these compounds leads to separated ions, one of which,  $\text{H}^+$ , is common to all. Is it reasonable that bond energy will follow the ability of the anion to stabilize the negative charge. One measure is provided by an electrostatic potential map.

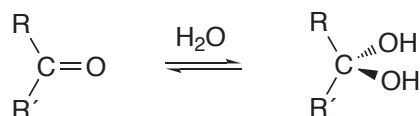
- b. Calculate electrostatic potential maps for  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ . Which ion, best accommodates the negative charge? Which most poorly accommodates the charge? Is there a correlation between the “size” of the ion and its ability to accommodate charge? Is the ability to accommodate charge in the anion reflected in the heterolytic bond dissociation energy of the corresponding hydride?

**20** Is the energy required to deprotonate acetylene less or greater than the energy required to deprotonate ethylene? Which molecule is the stronger acid? Use optimized geometries from B3LYP/6-31G\* calculations to decide.

**21** What anion results from deprotonation of the following alkynes? Optimize geometries using the B3LYP/6-31G\* model.

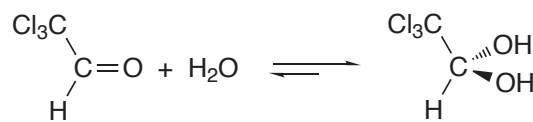


## 22 Aldehydes and ketones add water to form hydrates.

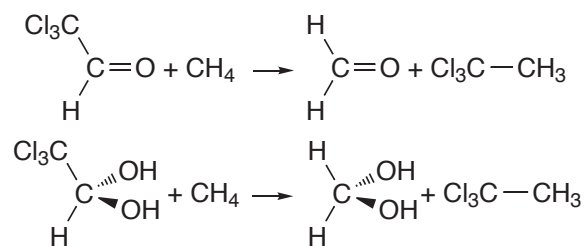


Equilibrium constants vary over an enormous range. Some compounds exist solely as the carbonyl, while others exist entirely as the hydrate.

- Use the HF/6-31G\* model to calculate reaction energies for addition of water to acetaldehyde, acetone and hexafluoroacetone. Which is the least likely to exist as a hydrate? Which is the most likely? Explain your results in terms of your knowledge of electron donating/accepting effects of methyl and trifluoromethyl substituents.
- For trichloroacetaldehyde (chloral) the equilibrium lies almost entirely in favor of the hydrate, chloral hydrate. Does the trichloromethyl group destabilize the carbonyl, stabilize the hydrate or both?

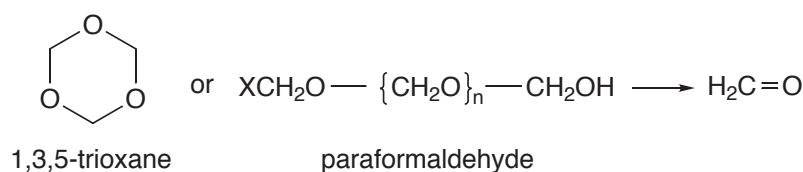


To tell, use the HF/6-31G\* model to calculate the energies of the reactions:



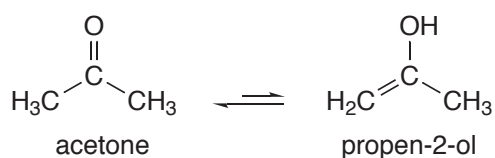
These compare the effect of a trichloromethyl group relative to that of hydrogen on both chloral and its hydrate. What do you conclude is the reason for the preference for hydrate formation?

## 23 Formaldehyde cannot be purchased as a pure substance. Instead it needs to be prepared *in situ* by “cracking” either 1,3,5-trioxane or paraformaldehyde.

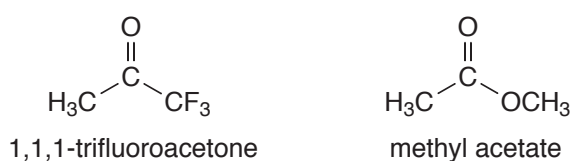


Is “cracking” 1,3,5-trioxane *endothermic* or *exothermic*? Use B3LYP/6-31G\* optimized geometries to tell. Is the entropy change for the cracking reaction likely to be positive or negative? Explain.

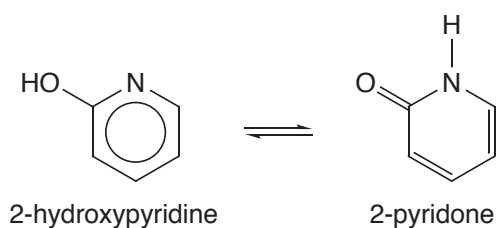
**24** The equilibrium between ketones and their corresponding alcohols (“enols”), for example, between acetone and propen-2-ol, almost always favors the ketone.



- Use the Boltzmann equation and energies from optimized B3LYP/6-31G\* structures to calculate the room temperature distribution of acetone and its enol.
- Repeat your calculations for 1,1,1-trifluoroacetone and methyl acetate and their respective enol forms. For which system is the equilibrium abundance of the enol form the highest? For which is it the lowest? Rationalize your result.

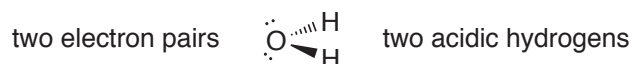


**25** Use B3LYP/6-31G\* optimized geometries to calculate the equilibrium abundance of 2-hydroxypyridine and its “keto form” (2-pyridone) at room temperature.



# Hydrogen Bonding and Intermolecular Interactions

**26** Water incorporates an equal number of electron pairs (electron-donors) and “acidic hydrogens” (electron-acceptors).



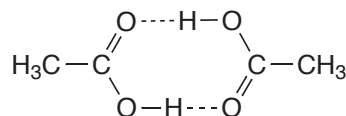
Water molecules use these two “complementary resources” fully to form a three-dimensional network of hydrogen bonds.

- a. What is the maximum number of hydrogen bonds that each water molecule can make to its neighbors in liquid water? Build a cluster of 30-50 water molecules\*, optimize using molecular mechanics and display hydrogen bonds. Are the molecules “in the middle” involved in the “maximum” number of hydrogen bonds? Do hydrogen bond lengths fall in a narrow range ( $\pm 0.05\text{\AA}$ )? Is this consistent with the fact that hydrogen bonds are much weaker than covalent bonds? Display the cluster as a space-filling model. How much “empty space” is there in liquid water?
- b. Add a molecule of ammonia into (the center of) your water cluster and reoptimize. How many hydrogen bonds are there to ammonia? On average, how many hydrogen bonds are there to the water molecules immediately surrounding ammonia? Does the situation appear to be similar or different from that for the “pure” water cluster? Has your cluster noticeably expanded or contracted in the vicinity of ammonia? (Examine it as a space-filling model.) Would you expect water to dissolve ammonia? Elaborate.
- b. Replace ammonia by methane and reoptimize. Has the cluster noticeably expanded or contracted in the vicinity of methane? Rationalize your result in terms of changes in hydrogen bonding (relative to the “pure” water cluster). Would you expect water to dissolve methane? Elaborate.

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\* With  $sp^3$  oxygen selected, hold down the **Insert** key (**option** key on Macintosh) and *click* at different locations on screen. Turn the cluster every few molecules to obtain a three-dimensional structure.

27 Acetic acids forms a symmetrical hydrogen-bonded dimer.



Compare its structure with that of “free” acetic acid. Use the HF/6-31G\* model. Point out any significant changes in bond lengths and angles. Have the hydrogens involved in the hydrogen bonds moved to positions halfway between the oxygens or have they remained with one oxygen (as in acetic acid)? Do the structural changes (or lack of structural changes) suggest that hydrogen bonds are comparable to normal (covalent) bonds or are they weaker? Elaborate.

28 Explain the difference in boiling points of ethylamine ( $17^\circ\text{C}$ ) and ethanol ( $79^\circ\text{C}$ ) in terms of hydrogen bonding. Examine the geometries of hydrogen-bonded dimers of both molecules and compare hydrogen-bond energies. Use the HF/6-31G\* model.

29 Examine the geometry, atomic charges and electrostatic potential map for lithium aluminum hydride,  $\text{LiAlH}_4$ . Use the B3LYP/6-31G\* model. Is it better described as an ion pair, that is, a “loose complex” between lithium cation and aluminum hydride anion or as a molecule where the two components are covalently bonded? Compare its structure and atomic charges with aluminum hydride anion,  $\text{AlH}_4^-$ .

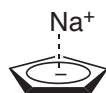
Repeat your analysis for sodium borohydride,  $\text{NaBH}_4$ .

30 The mixture of antimony pentafluoride,  $\text{SbF}_5$ , and hydrogen fluoride, HF, turns out to be a very strong acid (a so-called “superacid”). Optimize the geometry of the  $\text{SbF}_5/\text{HF}$  system using the HF/3-21G model, and calculate vibrational frequencies to insure that the structure you have found is an energy minimum. (See the essay “*Finding and Verifying Equilibrium and Transition State Geometries*” for a discussion.) Is the system better described as a complex between neutral antimony pentafluoride and neutral hydrogen fluoride or between  $\text{SbF}_6^-$  anion and a proton? (Compare with geometries of  $\text{SbF}_5$ ,  $\text{SbF}_6^-$  and HF.) Compare charges at hydrogen and electrostatic potential



maps for the  $\text{SbF}_5/\text{HF}$  system and for “free” HF. Is the hydrogen (in HF) “more positive” because of its association with  $\text{SbF}_5$ ?

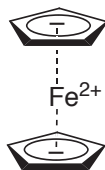
**31** Optimize the geometry of cyclopentadienyl sodium using the PM3 model. Is the charge on sodium consistent with representation of the system as a complex between sodium cation and cyclopentadienyl anion?



cyclopentadienyl sodium

Does the geometry of the incorporated cyclopentadienyl fragment also fit such a description? (Compare with cyclopentadienyl anion.)

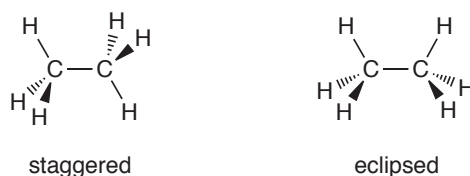
Repeat your calculation for ferrocene. (Again use the PM3 model.)



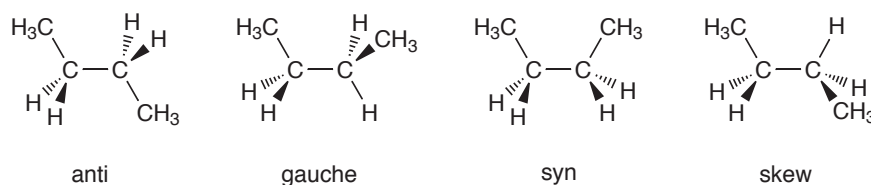
ferrocene

# Conformation

**32** Ethane adopts a geometry whereby CH bonds stagger each other. The structure in which CH bonds eclipse is an energy maximum.



Similarly, single (CH and CC) bonds in *n*-butane stagger each other leading to two distinct minimum energy forms (*anti* and *gauche* conformers), and two distinct maximum energy forms (*syn* and *skew*).

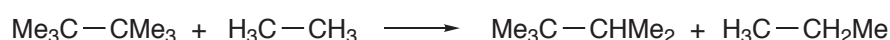


The observed conformations in these and in other molecules involving  $sp^3$  hybridized centers have been codified “single bonds stagger”. Does the “staggered rule” extend to bonds involving  $sp^2$  hybridized elements, most important,  $sp^2$  hybridized carbon?

- Use the HF/3-21G model to calculate the energy of 1-butene with change in the C=CCC dihedral angle from  $0^\circ$  to  $180^\circ$  in  $20^\circ$  steps. Plot the energy of 1-butene as a function of the C=CCC dihedral angle. How many energy minima are there? How many energy minima would there be if you had varied the dihedral angle from  $0^\circ$  to  $360^\circ$  instead of from  $0^\circ$  to  $180^\circ$ ? Elaborate. Characterize the structures of the energy minima as “staggered” or “eclipsed” relative to the CC double bond. Characterize the structures of the energy maxima. Formulate a “rule” covering what you observe.
- Build *cis*-2-butene. Lock both HCC=C dihedral angles to  $0^\circ$  (eclipsed). You will see that hydrogens on the two methyl groups are in close proximity. Next, define a range of values for **only one** of these dihedral angles from  $0^\circ$  to  $180^\circ$  in  $20^\circ$  steps. As with 1-butene,

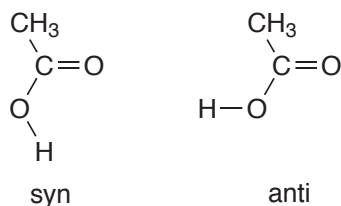
obtain the energy of *cis*-2-butene as a function of this dihedral angle using the HF/3-21G model, and construct a plot. Characterize the structure of the energy minima as “staggered” or “eclipsed” relative to the CC double bond. Have other structural parameters significantly altered in response to rotation?

**33** The central CC bond in 2,2,3,3-tetramethylbutane is  $\sim 75$  kJ/mol weaker than the CC bond in ethane. One explanation is that bond cleavage relieves the crowding of the methyl groups. A measure of this should be provided by the energy of the reaction:



- According to HF/6-31G\* calculations, is the reaction *exothermic* as written? If so, is the reaction energy large enough to account for the difference in bond strengths between the 2,2,3,3-tetramethylbutane and ethane? If not, or if the energy change is too small, suggest another reason for the difference in bond strengths.
- Compare the calculated geometries of ethane and 2,2,3,3-tetramethylbutane. Do both systems prefer geometries in which all single bonds are staggered? Be careful not to start your optimization of 2,2,3,3-tetramethylbutane with a staggered structure.

**34** Use optimized geometries from the B3LYP/6-31G\* model to assign the preferred conformation of acetic acid, with the OH bond *syn* or *anti* to the CO bond.



Rationalize your result. Hint: look at the dipole moments of both conformers. Is the difference small enough that the minor conformer might be observable at room temperature ( $> 1\%$ )?

**35** To what extent does  $\lambda_{\max}$  (the “color”) for a diene depend on its conformation? To what extent does  $\lambda_{\max}$  parallel the energy of the ground-state molecule with change in conformation?

Calculate the energy of 1,3-butadiene, 2-methyl-1,3-butadiene and 2-*tert*-butyl-1,3-butadiene with change in C=C–C=C dihedral angle starting from 0° going to 180° in 20° steps. Use the HF/3-21G model. For each diene, plot both the energy and the HOMO/LUMO gap as a function of dihedral angle. (To a reasonable approximation, changes in the HOMO/LUMO gap should mirror changes in  $\lambda_{\max}$ .)

For each diene: 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? Is there much difference among the three dienes? For each diene: Does the variation in total energy closely follow the HOMO/LUMO gap or are the two uncorrelated? What (if anything) does your result say about the importance of conjugation (double bonds coplanar) on diene conformation?

# Dipole Moments and Charges

**36** Atomic charges obtained from Hartree-Fock models are generally larger than those from MP2 models. While it is not possible to say which charges are more “realistic”, it is possible to say which model provides the better description of overall polarity as characterized by the dipole moment.

- Optimize the geometry of formaldehyde using the HF/6-311+G\*\* model. Is the calculated dipole moment smaller, larger or about the same as the experimental moment (2.34 debyes)?
- Repeat your calculations using the MP2/6-311+G\*\* model. Relative to the Hartree-Fock calculations, do you see a reduction, an increase, or no change in the calculated dipole moment? Is the dipole moment calculated from the MP2 model in better or poorer agreement with the experimental value? Compare Hartree-Fock and MP2 charges (on CH<sub>2</sub> as a unit vs. O). Is the change consistent with the change in dipole moment?
- Examine the HOMO and LUMO of formaldehyde (from the Hartree-Fock calculation). Where is the HOMO more concentrated, on the CH<sub>2</sub> group or on oxygen? Where is the LUMO more concentrated? Would electron promotion from HOMO to LUMO be expected to lead to an increase or a decrease in charge separation? An increase or decrease in dipole moment? Given that the MP2 model involves a “mixing” of ground and excited states, is your result consistent with the change in dipole moment in going from Hartree-Fock to MP2 models? Elaborate.

**37** The dipole moment provides a measure of the extent to which charge is distributed in a molecule. In a molecule like H<sub>2</sub>, with both “sides” the same, the charge on the two atoms is equal and the dipole moment is zero. Increasing the difference in charge increases the dipole moment. The magnitude of the dipole moment also depends on the extent to which charge is separated. The larger the separation of charge, the larger the dipole moment. For a diatomic molecule, the dipole moment is proportional to the product of the absolute difference in charge between the two atoms,  $|q_A - q_B|$ , and the bond length,  $r_{AB}$ .

$$\text{dipole moment} \propto |q_A - q_B| r_{AB}$$

- a. Obtain dipole moments for hydrogen fluoride, hydrogen chloride, hydrogen bromide and hydrogen iodide using geometries optimized with the HF/3-21G model. Use the electronegativities provided below to correlate calculated dipole moments with the product of bond length and electronegativity difference.

|    |     |    |     |
|----|-----|----|-----|
| H  | 2.2 | F  | 4.0 |
| Li | 1.0 | Cl | 3.2 |
| Na | 0.9 | Br | 3.0 |
|    |     | I  | 2.7 |

Does the correlation line reproduce the fact that the dipole moment of a homonuclear diatomic is zero?

- b. Repeat your analyses for the series: lithium hydride, lithium fluoride, lithium chloride, lithium bromide and lithium iodide and for the series: sodium hydride, sodium fluoride, sodium chloride, sodium bromide and sodium iodide.

**38** Optimize geometries for compounds X–CN, where X is halogen (F, Cl, Br, I) using the HF/3-21G model, and assign the direction of the dipole moment in each. Given that the more electronegative “group” (CN or X) will be at the negative end of the dipole, what can you say about the electronegativity of the cyano group?

Repeat for X–NO<sub>2</sub> compounds (X = F, Cl, Br, I). What can you say about the electronegativity of the nitro group?

**39** Optimize geometries for the six heteronuclear diatomics X–Y, where X, Y are halogens (F, Cl, Br, I) using the HF/3-21G model, and assign the direction of the dipole moment in each. Given that the more electronegative element will be at the negative end of the dipole, order the electronegativities of the halogens. Is the ordering you obtain the same as usually given, that is, F > Cl > Br > I?

Repeat for compounds X–C≡C–Y where X, Y are (different) halogens. Do you reach the same conclusions with regard to the ordering of electronegativities of the halogens?