Molecular Modeling Problems

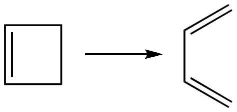
Part B. Molecular Stabilities and Reaction Energies

1. Pressure Affects Reaction Enthalpy. The heat (enthalpy) and energy of a chemical reaction are not the same, but are related through a pressure-volume term.

$\Delta H = \Delta E + P\Delta V$ at constant pressure

However, except for very high pressures, this term is very small and the energy and enthalpy are nearly identical.

Use the B3LYP/6-31G* model to obtain equilibrium geometries for 1,3-butadiene and cyclobutene. Calculate the energy of the ring opening reaction.



Based on space-filling models as a measure, which molecule takes up less volume? Increasing in pressure will drive the reaction toward reactants or toward products? What pressure would be required to make the energy and enthalpy differ by 1 kJ/mol? (Need to supply information on units.)

2. Zero-Point Energies Affect Reaction Energy. The energy resulting from a quantum chemical calculation refers to a molecule resting at the bottom of a potential energy well. On the other hand, a measured enthalpy refers to a molecule in its lowest ("zeroeth") vibrational state. The difference, known as the zero-point energy, is directly proportional to the sum of all vibrational frequencies, and it is straightforward to correct calculated reaction energies (or experimental reaction enthalpies). Is the correction significant?

Use the B3LYP/6-31G* model to calculate equilibrium geometries and vibrational frequencies for acetonitrile, CH_3CN, and its isomer, methyl isocyanide, CH_3NC. Evaluate the zero-point energy for each. Does this change in the energy of isomerism by more than 10%?

Repeat your calculations and analysis for propene and its isomer cyclopropane.

3. Temperature Affects Reaction Energy. Experimental thermochemical measurements are made at finite temperature (typically 298 K), whereas calculated energies pertain to molecules at 0 K. The change in enthalpy from 0K to a finite temperature (T) is given by:

$$\Delta H(T) = \Delta H_{tr}(T) + \Delta H_{rot}(T) + \Delta H_{vib}(T) + RT$$

$$\Delta H_{tr}(T) = 3/2\ RT$$

$$\Delta H_{rot}(T) = 3/2\ RT \quad \text{(RT for a linear molecule)}$$

$$H_{vib}(T) = H_{vib}(T) - H_{vib}(0) = Nh \sum_{i}^{\text{normal modes}} \frac{v_i}{(e^{hv_i/kT} - 1)}$$

This requires the vibrational frequencies, ν_i. R is the gas constant, k is Boltzmann's constant, h is Planck's constant and N is Avogadro's number.

Using the results from the calculations you performed in the previous problem, evaluate the change in the energy of acetonitrile and methyl isocyanide with change in temperature from 0 K to 298 K. Combine this with the difference in zero-point energies for the two isomers (see previous problem). Does the full correction (zero-point energy + temperature) change in the energy of isomerism by more than 10%?

Repeat your calculations and analysis for propene and its isomer cyclopropane.

4. Mass Affects Reaction Energy. While the Born-Oppenheimer approximation removes nuclear mass from the Schrödinger equation, the energy of a chemical reaction actually depends on mass. This is referred to as an equilibrium isotope effect, and may be attributed to the difference in zero-point energies the between reactants and products (an oversimplification that is adequate for our purpose). The most commonly measured (and largest) isotope effect is that resulting from substitution of deuterium for hydrogen.

Use the B3LYP/6-31G* model to determine the difference in zero-point energy (and the difference in bond energies) between H_2 and D_2. Is the change in bond energy likely to be noticed? Assume that a change in bond energy of 5% is detectable.

Repeat the calculations and the analysis for the change from ^{14}N to ^{15}N in nitrogen molecule.

5. Carbon Isotope Effect on CH Bond Dissociation Energy in Methane. How much does the CH bond dissociation energy in methane change as a result of changing the mass of carbon (from ^{12}C to ^{13}C)? Use the B3LYP/6-31G* model to calculate equilibrium geometries and vibrational frequencies for methane and methyl radical and evaluate the change in zero-point energy for bond dissociation. Change the mass of carbon to (^{13}C) for both molecules, rerun the calculation and recalculate the change in zero-point energy for bond dissociation. Assuming an experimental precision of 1%, it this energy change like to be observable?

6. Hydrogen Isocyanide. Under "normal" (laboratory) conditions, hydrogen isocyanide (HNC) is in equilibrium with its more stable isomer, hydrogen cyanide (HCN). According to the B3LYP/6-31G* model, what is the room-temperature Boltzmann distribution of isomers? Assuming that 5% as the lower bound for detection, what is the lowest temperature that would be needed to see the minor isomer?

Radioastronomy confirms that both hydrogen cyanide and hydrogen isocyanide are present in interstellar clouds. The interesting observation is that they occur in similar amounts. Speculate why.

7. Ion-Molecule Equilibria. Ions resulting from protonation of neutral molecules in an ion cyclotron resonance spectrometer can be trapped for sufficiently long times to allow ion-molecule equilibria to be established. Measurement of the equilibrium abundance of the ions, together with knowledge of the relative amounts of the neutral molecules, allows determination of the equilibrium constant for the proton transfer reaction and, therefore, the relative proton affinities of the neutral molecules. For example, measurement of the equilibrium abundance of protonated dimethylamine and aziridine provides the relative proton affinities of the precursors.

dimethylamine-H^+ + aziridine $\rightarrow$ dimethylamine + aziridine-H^+

Use the B3LYP/6-31G* model to calculate equilibrium geometries and energies for the four molecules involved in this equilibrium. Which amine has the higher proton affinity and by how much? Assuming a 1:1 mixture of the two amines, and that the limit of detection of the "minor" ion is 5%, is it possible to directly establish the relative proton affinities of dimethylamine and aziridine? If it is not possible, in what ratio would the two amines need to be introduced in order for both ions to be seen?

8. CH Bond Dissociation in Propyne. A bond may dissociate either homolytically, leading to a pair of neutral radicals, or heterolytically, leading to a cation and an anion. Use the B3LYP/6-311+G** to obtain geometries for the two possible radicals resulting from homolytic CH bond dissociation in propyne. Are both radicals stable species? Elaborate. If they are, which is more stable? Rationalize your result. Is the less stable radical likely to be detectable in an equilibrium mixture at room temperature? (Assume that the minor radical needs to be at least 5% of the mixture in order to be seen.)

Heterolytic CH bond dissociation of propyne may either involve loss of a proton, leading to a hydrocarbon anion, or loss of hydride, leading to a hydrocarbon cation. Which is the less unfavorable (less *endothermic*) process? To decide, obtain geometries for the two hydrocarbon anions and two hydrocarbon cations, as well as for hydride anion. (The energy of proton is 0.) Are both hydrocarbon anions stable species? If they are, which is more stable? Attempt to rationalize your result. Is the less stable anion likely to be detectable in an equilibrium mixture at room temperature? Are both hydrocarbon cations stable species? If they are, which is more stable? Attempt to rationalize your result. Is the less stable cation likely to be detectable in an equilibrium mixture at room temperature?

Is homolytic or heterolytic CH bond dissociation of propyne less unfavorable?

9. Chlorine Nitrate: Chlorine nitrate, $ClONO_2$, possibly plays a role in the balance of ozone in the upper atmosphere, specifically as a "thermodynamic sink" for NO_2 and ClO radicals that are known to react with ozone and destroy ozone.

$$ClO^{\cdot} + NO_2^{\cdot} \rightarrow ClONO_2$$

However, were its isomer chlorine peroxynitrite (ClOONO) in equilibrium with chlorine nitrite, it might undergo cleavage of the OO bond. This would lead back to the NO_2 and ClO radicals, negating at least in part the scavenging ability of chlorine nitrate.

Use the B3LYP/6-311+G** model to obtain equilibrium geometries and energies for chlorine nitrate and chlorine peroxynitrite and calculate the room-temperature Boltzmann distribution between the two isomers. Is chlorine peroxynitrite likely to be a significant factor? Elaborate

10. Singlet and Triplet Carbenes. Molecules incorporating divalent carbon are referred to as carbenes or methylenes. The parent compound, CH_2 (methylene), is known to possess a triplet ground state, with one unpaired electron residing in an in-plane σ orbital and the other in an out-of-plane π orbital. The lowest-energy singlet state (with both electrons in the σ orbital) has been established experimentally to be approximately 42 kJ/mol higher in energy.

Use the B3LYP/6-31G* model to obtain equilibrium geometries of both singlet and triplet states of methylene, difluoromethylene (CF_2), dichloromethylene (CCl_2) and dibromomethylene (CBr_2). Adjust the calculated singlet-triplet energy differences for CF_2, CCl_2 and CBr_2 to account for the error in the singlet-triplet difference for CH_2. Use the corrected energies to assign the ground state for CF_2, CCl_2 and CBr_2. Rationalize any change in preferred ground state (relative to the parent compound) that you uncover.

11. Singlet and Triplet Cyclobutadiene. The singlet state of cyclobutadiene (C_4H_4) has four π electrons, formally making it an antiaromatic molecule. Does its exhibit a "rectangular" structure with localized single and double bonds or a "square" structure in which the four carbon-carbon bond lengths are all the same? Use the B3LYP/6-31G* model to decide. (Be sure to start with a rectangular structure.) Rationalize your result.

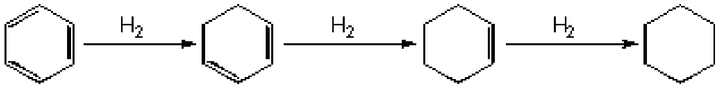
Obtain the geometry of the triplet state of cyclobutadiene. Does this exhibit the same structure (square or rectangular) as singlet cyclobutadiene? Rationalize your result. Calculate the singlet-triplet energy difference in cyclobutadiene, and correct it to account for the error in the corresponding difference in methylene (experimentally the triplet is favored by 42 kJ/mol). Is the ground state of cyclobutadiene a singlet or a triplet? Rationalize your result.

12. Singlet and Triplet Cyclopropylidene. Use the B3LYP/6-31G* model to obtain the equilibrium geometry of the singlet state of cyclopropylidene (C_3H_2).

Is the molecule properly represented by the Lewis structure shown above, that is, does it incorporate "normal" carbon-carbon single and double bonds? If it does not, provide an explanation as well as an alternative structure drawing. It might help you to examine the occupied molecular orbitals, in particular, the π orbitals.

Obtain the geometry of the corresponding triplet state of cyclopropylidene and calculate the singlet-triplet energy difference. Correct your value to account for the error in the corresponding difference in methylene (experimentally the triplet is favored by 42 kJ/mol). Is the ground state different from that for methylene? If it is different, suggest why.

13. Aromaticity of Benzene. The 4n+2 rule suggests that benzene with six π electrons in a ring should be unusually stable ("aromatic"). One way to "measure" the aromatic stabilization of benzene is to compare the energy of adding H_2 (leading to 1,3-cyclohexadiene) with the energy of adding H_2 to 1,3-cyclohexadiene (leading to cyclohexene), or alternatively the energy of adding H_2 to cyclohexene (leading to cyclohexane).



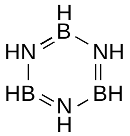
Each of these reactions trades a CC π bond and an HH bond for two CH bonds. All three reactions would normally be expected to be *exothermic* (σ bonds are stronger than π bonds). However, the first reaction also results in loss of aromaticity, which suggests that any difference in energy between the first and second (or third) reactions should reflect the aromatic stabilization of benzene.

Use the B3LYP/6-31G* model to obtain energies for the three reactions. Are the second and third reactions *exothermic* as expected? Is the first reaction *exothermic* or *endothermic*? What is the difference between the energy of the first and the average of second and third reactions? What is your estimate of the aromatic stabilization of benzene?

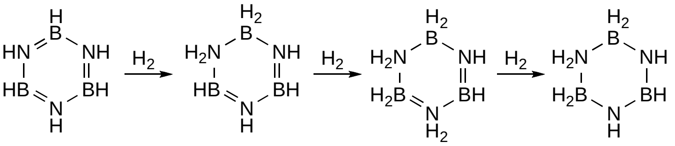
14. Antiaromaticity of Cyclobutadiene. Use the same reasoning applied in the previous problem to assess loss of stability ("antiaromaticity") of cyclobutadiene, a molecule with 4n π electrons. Specifically, compare the energy of adding H_2 to cyclobutadiene (leading to cyclobutene) with the energy of adding H_2 to cyclobutene (leading to cyclobutane). While each reaction trades an HH bond and a CC π bond for two CH bonds, only the first reaction removes interaction of the coplanar double bonds. Use the B3LYP/6-31G* model. You can assume that cyclobutadiene is planar, but do not assume that all four carbon-carbon bonds are the same length. What is the difference in the energies of the two reactions? Is there evidence for significant destabilization of cyclobutadiene? If there is, is the magnitude comparable to the stabilization of benzene (see previous problem)?

15. Aromaticity of 1,3,5-Cyclohexatriene. It is well known that the six carbon-carbon bonds in benzene are identical, midway in length between "normal" single and double bonds. Is this a necessary condition for benzene to be aromatic? To decide, compare energies of benzene and 1,3,5-cyclohexatriene, a hypothetical molecule with alternating single and double bonds. Use the B3LYP/6-31G* model. While you can obtain the equilibrium geometry for benzene, you cannot do this for 1,3,5-cyclohexatriene. This molecule ***is not an energy minimum*** and, given the chance, will collapse to benzene. Assume a fixed geometry with alternating single and double bonds set to 1.54Å and 1.32Å. Is the energy difference roughly the same as the aromatic stabilization of benzene (see previous problem), or is it significantly smaller? Do all carbon-carbon bonds in benzene need to be the same in order for the molecule to be aromatic?

16. Aromaticiy of Borazine. Borazine ($B_3N_3H_6$) is isoelectronic with benzene. Both are planar and both have six π electrons. Is borazine an aromatic molecule?



To help you decide, calculate energies for successive addition of one, two and three equivalents of hydrogen. This is analogous to analysis previously carried out for benzene. Use the B3LYP/6-31G* model

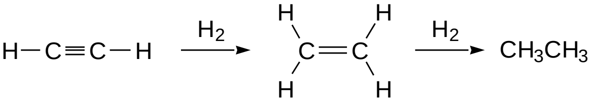


Is the first hydrogenation step significantly more difficult (more *endothermic*) than the second and third steps? If it is, estimate the “aromaticity” of borazine and compare this to the value for benzene obtained previously.

17. Krypton Difluoride. While numerous compounds of xenon are known, the only ***neutral*** krypton compound to have been reported to date is krypton difluoride (KrF_2). Is its dissociation into krypton atom and fluorine molecule *endothermic* or *exothermic*? Obtain equilibrium structures of KrF_2, F_2 and (the energy of) Kr with the B3LYP/6-31G* model. Also obtain data for XeF_2 and atomic xenon. How does the calculated reaction energy compare with that for the corresponding xenon compound? Does thermodynamic stability (with regard to dissociation) a cause for the fact that XeF_2 is known whereas KrF_2 is not? Elaborate.

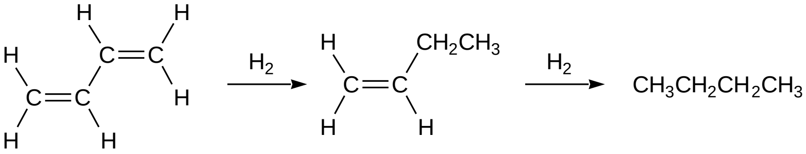
18. Energy Content of Hydrazine Fuels. Combustion of which fuel, hydrazine or tetramethylhydrazine, delivers the greater amount of energy on a per gram basis? Use the B3LYP/6-31G* model to obtain energies for the two oxidation reactions. (The products are N_2 and water for hydrazine and N_2, water and CO_2 for tetramethylhydrazine). Make certain to include the mass of the oxidizer (O_2) in your calculations. How does the better of the two fuels compare with molecular hydrogen on a per gram basis?

19. Hydrogenation of Acetylene. Both steps in the hydrogenation of acetylene to ethane are *exothermic*, each trading an HH bond and a π bond for two CH bonds.



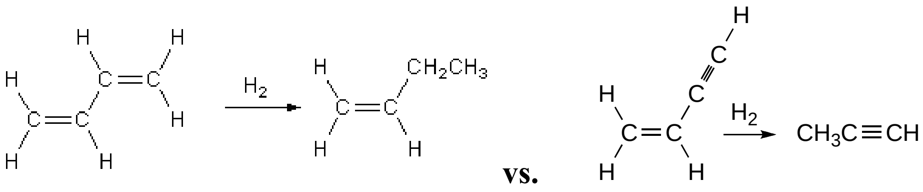
Which step is the more *exothermic*? To decide, use the B3LYP/6-31G* model to obtain equilibrium geometries and energies for all reactants and products. What (if anything) does your result say about the relative strengths of the first and second π bonds in acetylene? What have you assumed to reach your conclusion?

20. Hydrogenation of 1,3-Butadiene. Both steps in the hydrogenation of *trans*-1,3-butadiene to *n*-butane involve formation of two new CH bonds at the expense of an HH bond and a π bond.



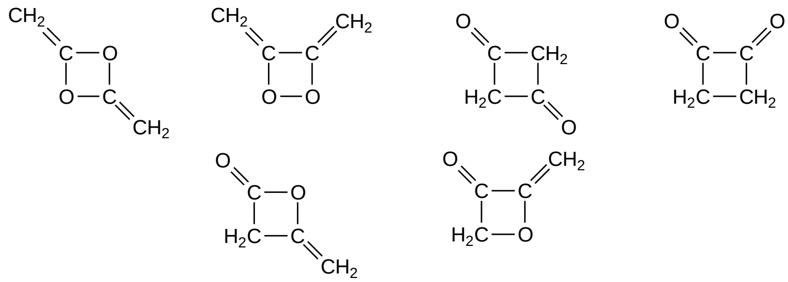
Which step is the more *exothermic*? To decide, use the B3LYP/6-31G* model to obtain equilibrium geometries and energies for *trans*-1,3-butadiene, 1-butene and *n*-butane as well as molecular hydrogen. Does your result support the idea that adjacent (conjugated) double bonds are stronger than isolated double bonds? Elaborate.

21. Hydrogenation of 1,3-Butadiene vs. But-1-yne-3-ene. Compare the energy of the first step in the hydrogenation of 1,3-butadiene (see previous problem) with that of hydrogenation of the ***double bond*** in but-1-yne-3-ene. Use the B3LYP/6-31G* model to obtain equilibrium geometries for all molecules in the two reactions.



Which reaction is more *exothermic*? What, if anything, does your result say about the interaction (conjugation) energy of adjacent double bonds vs. that of a double bond adjacent to a triple bond?

22. Ketene Dimer. There are six “cyclic” structures for the dimer of ketene, $H_2C=C=O$.



Before you do any calculations, guess which structure is likely to be the most stable based on what you know about the relative stabilities of CC and CO π bonds (lost in the dimerization) and CC and CC σ bonds (gained in the dimerization). According to the B3LYP/6-31G* model, which structure is actually preferred? Are two or more structures likely to be seen in an equilibrium mixture at room temperature? Assume 5% as the limit of detection of any structure. Is the dimerization *exothermic* or *endothermic*? Is this consistent with changes in bond strengths and the strain of the resulting four-membered ring? Elaborate.

23. Molecular Phosphorous. The most stable arrangement of molecular phosphorus is tetrahedral P_4 (***white phosphorus***). Dissociation into two molecules of P_2 is estimated to be endothermic by >200 kJ/mol, and can only be detected upon heating to 1000 K. To the contrary, the stable form of molecular nitrogen is N_2. N_4 has never been detected.

Use the B3LYP/6-31G* model to obtain equilibrium geometries and energies for tetrahedral P_4 and N_4 (as well as P_2 and N_2) and calculate energies for the two dissociation reactions. Are your results consistent with what is known (or unknown) about the two systems? Is tetrahedral N_4 actually a stable molecule? Explain your reasoning.

24. Dimerization of Alkylboranes. Borane (BH_3) exists in equilibrium with its dimer, diborane (B_2H_6), an equilibrium that strongly favors the dimer.

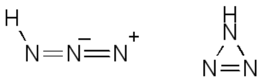
$$BH_3 + BH_3 \rightleftharpoons B_2H_6$$

Trimethylborane also coexists with its dimer, although here equilibrium stongly favors the monomer.

$$BMe_3 + BMe_3 \rightleftharpoons B_2Me_6$$

What is the reason for the change? Is it that a hydrogen bridge is strongly favored over a methyl bridge? To help you decide obtain geometries and energies for methylborane and the four possible dimers of methylborane: *cis* and *trans* isomers with both methyl groups terminal, with both methyl groups bridged and with one methyl group terminal and the other bridged. Use the B3LYP/6-31G* model. Which dimer is favored? Is dimerization to one or both of the isomers with the two methyl groups in terminal positions *exothermic* (as with dimerization of borane)? Is dimerization to the isomer with both methyl groups in bridged positions *endothermic* (as with dimerzation of hexamethyldiborane)? Summarize your results to come up with an explanation for the difference in the two equilibria.

25. Hydrogen Azide. It is not unreasonable to expect that hydrogen azide might have a high-energy cyclic isomer, cyclotriazine. While such a structure is likely to be highly strained, its Lewis structure does not involve separated positive and negative charges.



Attempt to obtain equilibrium geometries for both hydrogen azide and cyclotriazene using the B3LYP/6-311+G** model. (Start from a non-planar geometry for the cyclic isomer.) Are both acyclic and cyclic structures energy minima? Justify you answer. If both structures are energy minima, which is more stable? What temperature would be required in order for both to be observed in an equilibrium mixture? (Assume that the minor isomer must be at least 5% of the mixture in order to be detected.)

26. Relative Acidities of Propene and Propyne. Is propene or propyne the stronger acid in the gas phase? Use the B3LYP/6-311+G** model to calculate the geometries for the reactants and product of the reaction. Be certain to consider all possible anions resulting from deprotonation of propene and propyne.

$$\text{propene} + \text{propyne-H}^+ \rightarrow \text{propene-H}^+ + \text{propyne}$$

Rationalize your result. Is it anticipated by comparison of electrostatic potential maps for propene and propyne? Elaborate.

27. Why is Cyclopentadiene a Strong Acid? In the gas phase, cyclopentadiene is a much stronger acid than 1,3-pentadiene, that is, proton-transfer between cyclopentadiene and 1,3-pentadiene is *exothermic*.

$$\text{cyclopentadiene} + \text{1,3-pentadiene} - H^+ \rightarrow \text{cyclopentadiene-}H^+ + \text{1,3-pentadiene}$$

Use the B3LYP/6-31G* model to obtain equilibrium geometries for cyclopentadiene and cyclopentadienyl anion (the deprotonated form of cyclopentadiene). Are there any conspicuous structural changes between the two molecules that might help to rationalize the high acidity? Elaborate.

28. Gas and Aqueous-Phase Basicities of Amines. The relative proton affinities of free amines differ significantly from those in water. For example, in the gas-phase the proton affinity of trimethylamine is 84 kJ/mol greater than that of ammonia, whereas in water the two are nearly the same.

$$Me_3N + NH_4^+ \rightarrow Me_3NH^+ + NH_3 \qquad \Delta E_{gas} = -84 \text{ kJ/mol}; \Delta E_{aq} = xx \text{ kJ/mol}$$

Use the B3LYP/6-31G* model to obtain equilibrium geometries for ammonia, trimethylamine, ammonium ion and trimethylammonium ion, and calculate the energy of proton transfer between the two amines. Is your result in reasonable accord with the experimental value?

You can't actually perform the calculations in water. However, you can model the energy of the reaction in water by explicitly including water molecules in the calculation. At the minimum it is necessary to attach enough water molecules to account for all possible amine-water hydrogen bonds. This number is four for ammonia and ammonium ion, but only one for trimethylamine and trimethylammonium ions. Obtain equilibrium geometries for the four amine/ammonium ion complexes involved in the reaction below and calculate the relative "aqueous-phase" proton affinities of trimethylamine and ammonia.

$$Me_3N \ldots H_2O + NH_4^+ \ldots (H_2O)_4 \rightarrow Me_3NH^+ \ldots H_2O + NH_3 \ldots (H_2O)_4$$

Do the results show the observed trend in proton affinities in moving from the gas phase into water? Elaborate. Is there a serious flaw in the model? Elaborate.

29. Boiling Points of Ethanol and Ethylamine. While ethanol and ethylamine have similar molecular weights and molecular structures and while both can participate in up to three hydrogen bonds, the two molecules have very different boiling points. Ethanol is a liquid at STP whereas ethylamine is a gas. Is this because ethanol forms stronger intermolecular hydrogen bonds than ethylamine? To tell, obtain equilibrium geometries for ethanol and ethylamine and their respective hydrogen-bonded dimers, and compare hydrogen-bond energies. Use the B3LYP/6-31G* model.

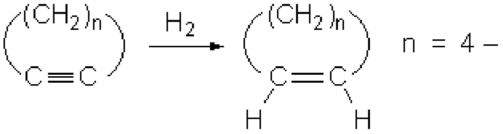
ethanol + ethanol → ethanol … ethanol

ethylamine + ethylamine → ethylamine … ethylamine

Which dimer is more tightly bound? Is your result consistent with the ordering of boiling points? Elaborate.

30. Cycloalkynes. The fact that the C-C≡C bond angles in acyclic alkynes want to be linear makes it unlikely that triple bonds will easily incorporate into small rings. Identify the smallest cycloalkyne with both C-C≡C bond angles 170° or larger? Start with cyclohexyne and use the B3LYP/6-31G* model to obtain equilibrium geometries.

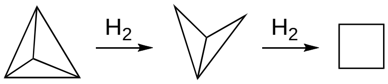
Obtain geometries of the corresponding cycloalkenes as well as for hydrogen molecule, calculate energies of hydrogenation reactions.



Is there a relationship between C-C≡C bond angle and hydrogenation energy?

31. Tetrahedrane. Tetrahedrane, $(CH)_4$ in the form of a tetrahedron, has yet to be experimentally characterized, although X-ray crystal structures exist for derivatives, for example, tetra-*tert*-butyltetrahedrane. Somewhat surprising is the observation that the carbon-carbon bond length short for a linkage between sp^3 carbons, and nearly identical to that found in cylopropane (1.49Å vs. 1.50Å).

Use the B3LYP/6-31G* model to obtain the geometry of tetrahedrane itself. Does it also incorporate a short carbon-carbon bond? Next, obtain geometries for all remaining molecules involved in hydrogenation of tetrahedrane, first to bicyclo[1.1.0]butane and then to cyclobutane.



Are both steps *exothermic*? Is the first step more or less favorable (*exothermic*) than the second step? Rationalize your result.