

Chem 220 - Organic Chemistry

Problem Set 2 - Solution Set

Chapter 3, Alkanes

Due: Monday, September 21, 2009



The Baeyer Laboratory, Munich, 1893

(This photograph is in the hallway across from 110 SCL)

- [Adolf von Baeyer](#) (1835-1917); Nobel Prize 1905. (center, seated with derby), who was a student of Kekulé, succeeded Liebig at Munich. In the photograph (second row; third from right) is [Henry Lord Wheeler](#) (1867-1914); Yale Faculty 1896-1911. As was the custom in the 19th century, many Americans, such as Wheeler, did advanced study in chemistry in Europe. Karl is the laboratory assistant. (The only person wearing an apron and no tie; upper left.)

In 1885, as an addendum to a paper on acetylenic compounds, Baeyer proposed that cyclopentane was the [least strained of the cycloalkanes](#). While he accepted the idea that the carbon atoms in cycloalkanes were tetrahedral, he treated the cycloalkanes as though they were flat. He argued that there is only one cyclohexane carboxylic acid, not two (axial and equatorial) as was predicted by a chair cyclohexane.

- [Equatorial](#) is frequently misspelled.
- A Projection of [Melvin Newman](#) (Son of Yale: 1929, BS; 1932, PhD)

Reading and Enrichment Assignments:

- Work through [How to Draw Cyclohexanes \(PowerPoint\)](#)
- The [Conformation Module](#) in the Study Aids will give you a good overview of the subject of conformation.
- View [The Evolution of Formulas and Structure in Organic Chemistry During the 19th Century \(PowerPoint\)](#).

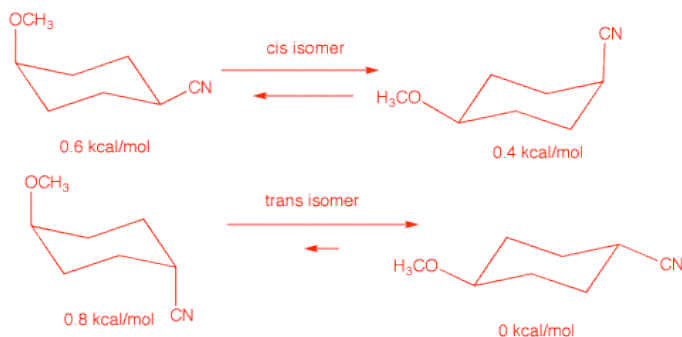
1. Redraw (line angle formula) and name (IUPAC) the hydrocarbon in this problem. For a dynamic view click [here](#). For a static view click [here](#). [How to manipulate Jmol structures](#). [What if there are two different longest chains? [Check here](#).] *IUPAC Rule 2.6 for hydrocarbons states that if there is more than one longest chain, the one with the greater number of substituents prevails. The hydrocarbon is clearly a nonane (longest chain). Is it 3,6-diethyl-2,5,5-trimethyl nonane or is it 6-ethyl-3-isopropyl-5,5-dimethyl nonane? Clearly the first nonane has five substituents while the second one has only four. The first one prevails.*

2. Compound A (MW=139.19), a 1,4-disubstituted cyclohexane, has the following composition: C, 69.03%; H, 9.41%; N, 10.07%. The difference in conformational energy for the two chair conformations of A is 0.4 kcal/mol. Using the [A-value](#) data (Energy Differences Between Cyclohexanes), determine the structure of A. Illustrate and explain. What is the conformational energy difference for the stereoisomer of A, ---namely A'. Explain and illustrate. Show the chair conformations of A and A' with the appropriate equilibrium arrows to illustrate the major and minor

conformations. Label each conformation with its energy. *The first order of business is to determine the molecular formula of the compound. Does compound A contain only C, H and N? No! The sum of the percentages adds up to 88.51%. Since oxygen is determined by difference it must constitute 11.49% of the remaining matter. For the calculation:*

Atom	At. Wt.	%/At. Wt.	%/At. Wt./0.72	Rounding
C	12.01	5.74	7.97	8
H	1.008	9.34	12.97	13
N	14.01	0.72	1	1
O	16	0.72	1	1

The formula is C₈H₁₃NO. M.W. calculated: 139.19, which agrees with the given value. [Note: A compound composed of these four elements must, if it has an odd number of hydrogens, have an odd number of nitrogens. [Check here.](#)] Compound A is a 1,4-disubstituted cyclohexane. Cyclohexane is C₆H₁₂. Subtracting two hydrogens for the positions of the two substituents leaves a cyclohexane nucleus of C₆H₁₀. Subtracting: C₈H₁₃NO - C₆H₁₀ = C₂H₃NO for the sum of the composition of the two substituents. Linking to the A-values tables shows only one functional group containing a single nitrogen, namely, cyano (-CN): 0.2 kcal/mol. We are left with CH₃O- for the composition of the remaining substituent, which is the group methoxy (CH₃O-): 0.6 kcal/mol. The energy difference agrees with the given value. Compound A is the cis-isomer because the trans isomer A' would have an energy difference between its two chair conformations of 0.6 kcal/mol + 0.2 kcal/mol - 0 kcal/mol = 0.8 kcal/mol. See below:



3. Predict the heat of formation of n-nonane using the data presented [here](#). Explain. *The heats of formation of the n-alkanes differ by approximately -5 kcal/mol per -CH₂- group increase. Since n-octane has $\Delta H_f^\circ = -49.8$ kcal/mol, n-nonane would be expected to have a value of $\Delta H_f^\circ = \sim -55$ kcal/mol.*

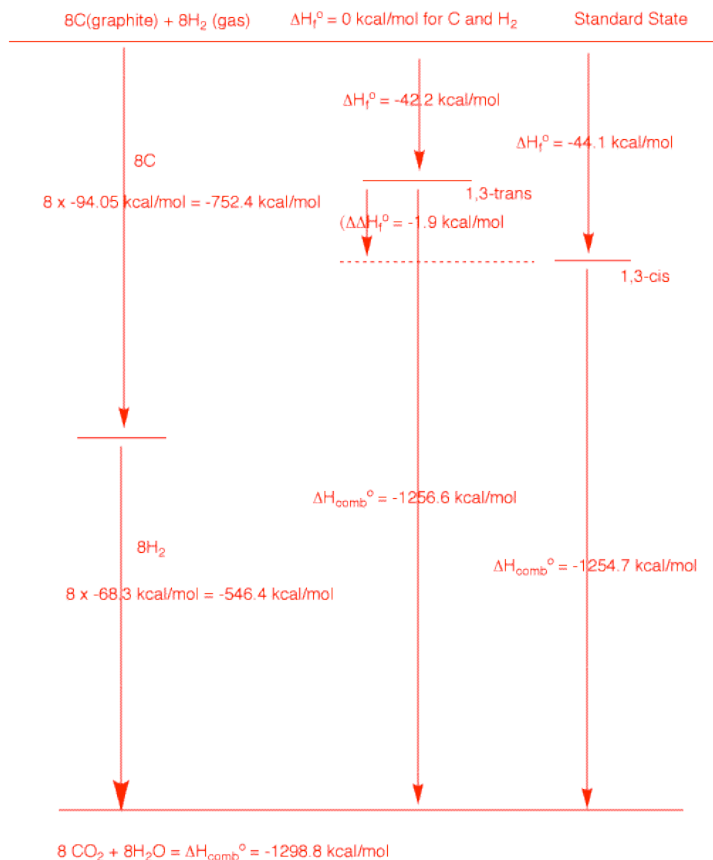
4. Using the [heats of formation tables](#), explain the difference in the heats of formation of cis- and trans-1,3-dimethylcyclohexane. The difference in the heat of formation of these stereoisomers is the same as the difference in their heats of combustion. Justify and illustrate with a diagram.

Not surprisingly, the cis-1,3-isomer is more stable ($\Delta H_f^\circ = -44.1$ kcal/mol) than the 1,3-trans-isomer ($\Delta H_f^\circ = -42.2$ kcal/mol).

($\Delta H_f^\circ = -72.2 \text{ kcal/mol}$).

The trans isomer has one axial methyl group while the 1,3-cis-isomer has none. Their difference in ΔH_f° is 1.9 kcal/mol, close to the value of 1.8 kcal/mol used for equatorial and axial methyl cyclohexane ([Look here](#)).

These two isomers have the molecular formula C_8H_{16} . The maximum amount of heat (ΔH°) that can be generated from combusting 8 moles of graphite and 8 moles of hydrogen is -1298.8 kcal/mole (see the left side of the diagram). The trans and cis isomers liberate -1256.6 and 1254.7 kcal/mol of heat, respectively, upon combustion. Their respective heats of formation are simply the difference of each of these numbers from the maximum value. Clearly from the diagram the difference in the heats of formation of each isomer is equal to the difference of their heats of combustion.



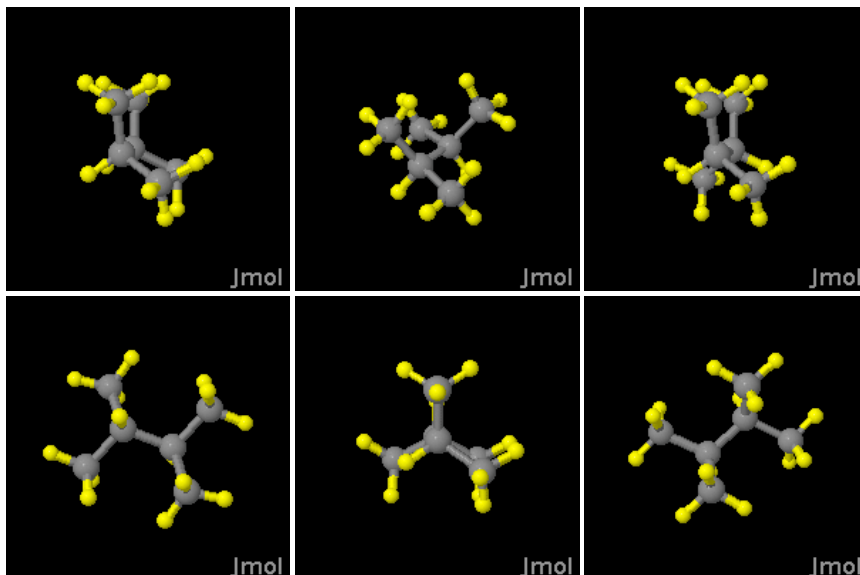
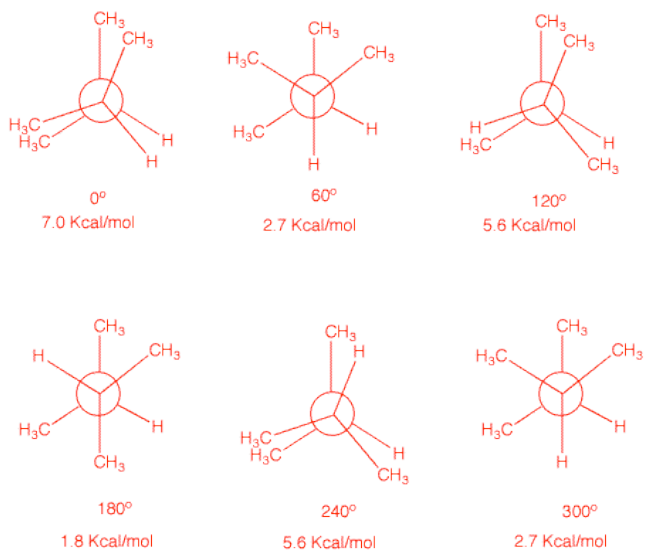
5. Calculate the heat of combustion of cyclopentane using the data (ΔH_f° of cyclopentane, CO₂ and H₂O) in the [heats of formation tables](#). Compare your value with the value in Table 3-5. From the Tables: ΔH_f° (cyclopentane) = -18.3 kcal/mol; ΔH_f° (CO₂) = -94.05 kcal/mol; ΔH_f° (H₂O) = -68.3 kcal/mol. Cyclopentane = C₅H₁₀. ΔH_f° (max) = 5 x [(-94.0) + (-68.3)] = -811.75 kcal/mol.

$$\Delta H_{\text{comb}}^\circ (\text{cyclopentane}) = \Delta H_{\text{max}}^\circ (\text{cyclopentane}) - \Delta H_f^\circ (\text{cyclopentane})$$

$$\Delta H_{\text{comb}}^\circ (\text{cyclopentane}) = -811.8 - (-18.3) = -793.4 \text{ kcal/mol}$$

You can use a diagram as in #4. Your text lists a value of 3320 kJ/mol. $3320 \text{ kJ/mol} \times 4.18 \text{ kJ/Kcal} = -794.3 \text{ Kcal/mol}$. Close enough!

6. Draw Newman projections for the eclipsed and staggered conformations of 2,3-dimethylbutane viewed along the C₂-C₃ axis. Calculate the energy of each conformation, both staggered and eclipsed. The Newman projections on the left below have C₂ in the front and C₃ in the rear. The degrees refer to clockwise rotation of C₃ about the C₂ axis. The energies are based upon the following data: H/H, gauche, 0 kcal/mol; CH₃/H, gauche, 0 kcal/mol; CH₃/CH₃, gauche, 0 kcal/mol; H/H, eclipsed, 1 kcal/mol; CH₃/H, eclipsed, 1.3 kcal/mol; CH₃/CH₃, eclipsed, 3.0 kcal/mol. The Jmol structures on the right match the Newman projections. [Move the Jmol structures](#) to see the Newman projections. If you are having trouble with these energy issues, [go here](#) and do methane through butane in the Conformation Module.



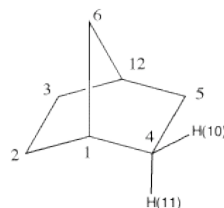
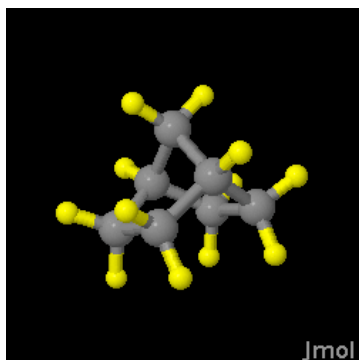
7. The structures on the right represent norborane.

a) Provide its IUPAC name.

b) Identify the bridgehead carbons by number. (The numbers on the far right are unrelated to the IUPAC numbering system.)

c) Click on the Jmol logo, select "style", "labels" and then "with atom numbers". Only the numbered hydrogens appear.

d) Measure the C(1)-C(6)-C(12) and the C(1)-C(2)-C(3) bond angles. (Click on "How to manipulate Jmol structures" for instructions on measuring.)



[How to manipulate Jmol structures.](#)

[Larger Version](#)

e) Measure the corresponding H-C(2)-H and H-C(6)-H bond angles in d). What has happened to these bond angles as a consequence of the C-C-C bond angles?

f) Measure the same angles for C(2) of the unstrained hydrocarbon, [propane](#).

g) Make a chart of the six measurements. Explain the trend.

7a. *Bicyclo[2.2.1]heptane. Its in your text. pg.*

118, 6th ed.

7b. Bridgehead carbons are 1 and 12.

7d. Measurements give 93.5° and 103° , respectively.

7f. Measurements give 108.2° and 109.7° , respectively.

7g. Chart: Propane is unstrained compared to norbornane. The C-C-C bond angle is slightly larger than the H-C-H bond angle in propane. Compare these two values with the bond angle of 109.5° in methane. The C(1)-C(2)-C(3) bond angle (103°) in norbornane is contained in both a 6- and 5-membered ring. It is more strained than the same bond angle in propane. At the same time, its corresponding H-C(2)-H bond angle increases (108.2°). The C(1)-C(6)-C(12) is contained in two 5-membered rings. Its bond angle has been reduced to 93.5° while its H-C-H bond angle has increased to 109.7° , greater than the bond angle in methane. In the chart the C-C-C bond angles are in blue; the H-C-H bond angles in green. As you move down the Compound column, the C-C-C bond angles contract while the corresponding H-C-H bond angles increase.

Compound	Bond Angle (degrees)
Propane C(1)-C(2)-C(3)	111.5
Propane H-C(2)-H	107.3
Norbornane C(1)-C(2)-C(3)	103.0
Norbornane H-C(2)-H	108.2
Norbornane C(1)-C(6)-C(12)	93.5
Norbornane H-C(6)-H	109.7