Chem 220 - Organic Chemistry

Problem Set 2

Chapter 3, Alkanes

Due: Monday, September 20, 2010

The Baeyer Laboratory, Munich, 1893

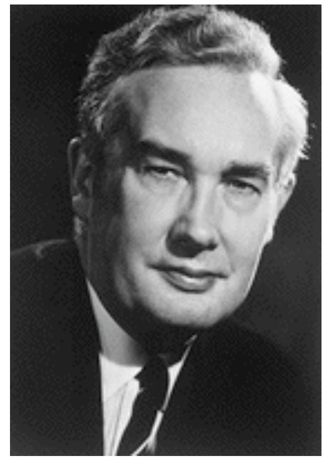
(This photograph is in the hallway across from 110 SCL)

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.

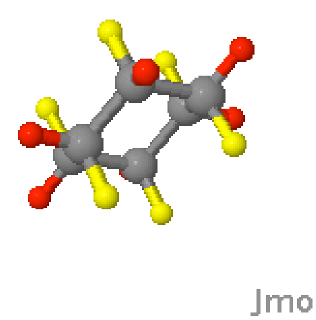
- A Projection of Melvin Newman (Son of Yale: 1929, BS; 1932, PhD)



Sir Derek H. R. Barton (1918-1998)

1969 Nobel Prize with Odd Hassel for their work on conformational analysis

For a video of Barton talking about conformational analysis, click here.



Cyclohexane in the chair conformation

(How to manipulate Jmol structures)

Reading and Enrichment Assignments:

a. Work through How to Draw Cyclohexanes (PowerPoint)

b. The Conformation Module in the Study Aids will give you a good overview of the subject of conformation.

c. View The Evolution of Formulas and Structure in Organic Chemistry During the 19th Century (PowerPoint).

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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.]

2. Compound **A** (MW=162.61), a 1,4-disubstituted cyclohexane, has the following composition: C, 51.70%; H, 6.82%; Cl, 21.80%. The difference in conformational energy for the two chair conformations of **A** is 1.9 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 comformations of **A** and **A'** with the appropriate equilibrium arrows to illustrate the major and minor conformations. Label each conformation with its energy.

3. Predict the heat of formation of 2-methyloctane using the data presented here. Explain.

4. Examine the heats of formation of the four octanes listed in the heats of formation tables.

a)What trend do you notice?

b) Draw a diagram that shows the heat of formation and heat of combustion of the two extreme cases: n-octane and 2,2,3,3-tetramethylbutane. Show calculations.

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5. a) Calculate the heat of combustion of cyclobutane using the data (ΔH_f^o of cyclobutane, CO_2 and H_2O) in the heats of formation tables. Compare your value with the value in Table 3-5 in your text.

b) Calculate the strain energy in cyclobutane given the heat of combustion of cyclohexane (Table 3-5 in your text) and the knowledge that cyclohexane is strain-free.

6. Draw Newman projections for the eclipsed and staggered conformations of 2-methylbutane viewed along the C_2-C_3 axis. Calculate the energy of each conformation, both staggered and eclipsed.