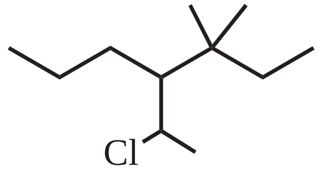
Chemistry 125   Third Examination Answers

Novemer 13, 2002

1. (2 minutes) Give systematic (IUPAC) names for the following molecule.

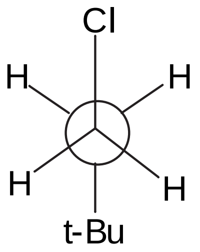


4-(1-chloroethyl)-3,3-dimethylheptane

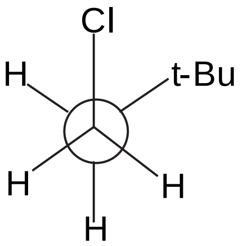
2. (5 minutes) Consider **1-chloro-3,3-dimethylbutane**.

A) Use **Newman projections** to show two conformational isomers generated by rotation about the C(1)-C(2) bond of this molecule. Use an appropriate abbreviation for the alkyl radical substituent on C(2).

B) Name these two conformational isomers.



anti



gauche

C) The energy difference between these isomers is 1.67 kcal/mole (according to Chem3D). What is their equilibrium ratio at room temperature?

anti should be favored by a factor of $10^{(3/4 * 5/3)} = 10^{1.25} \cong 17$

[Note that 101.25 is $10 * 10^{1/4}$ = 10 * sqrt(sqrt (10)) ≅ 10 * sqrt(~3) ≅ 10 * 1.7. It's very handy to be able to approximate a value without using a calculator, especially when you're just using an approximate formula anyway.]

[Note also that "eclipsed" is not properly a conformational **isomer**, but rather the high point in energy separating two isomeric "valleys" in the plot of energy vs. rotation angle. Isomers are (at least meta)stable compounds, denoted by such valleys. You'll soon learn the abbreviations of the common alkyl groups, such at t-Bu.]

3 . (5 min) **Name** three plausible choices for the "zero" reference point of a scale of energy for organic compounds. For each choice give a reason that would make it plausible.

1. The products of combustion (CO_2, H_2O, etc.). This scale is convenient because it is directly based on an experiment that is straightforward (burning in a calorimeter).

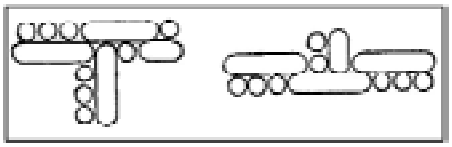
2. The elements in their standard states (graphite, 1 atm of H_2, O_2, etc.). This scale is convenient because it generates relatively small numbers, even though the values are not directly accessible to experiment.

3. The isolated atoms (ground state C, H, O, etc.). This scale is convenient for simple theory, because one can hope (rather naively, but remarkably successfully) to calculate the energy by adding contributions from the individual bonds formed among the atoms.

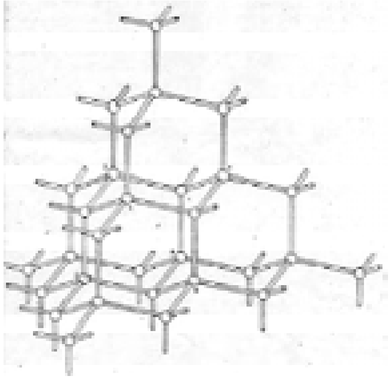
Note: 10 points were assigned to this questions. Credit was apportioned as 3 points for each part with the final 1 point given for clarity of presentation. Note that it was important to give the reason for choosing each of the zero points.

4. (17.5 min) Tell what experimental fact(s) each of the following chemical formulae/models was meant to rationalize. Be as specific as possible.

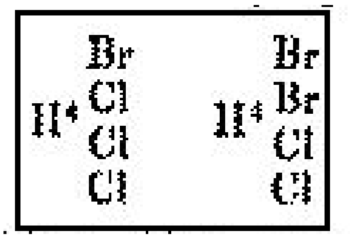
Answers were good, but a common problem was not citing specific experimental facts related to the models.



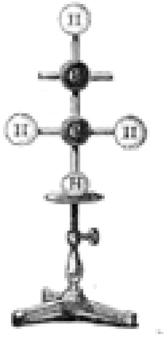
Kekulé's sausage formulae were designed to display constitution, the "nature and sequence of bonds". That the system could give two different formulae for "methylethylic alcohol" and "acetonic alcohol" seemed an advantage when it was thought that there were two such isomers, but in fact only demonstrated a shortcoming of the scheme, since there is in fact only one isomer of isopropyl alcohol.



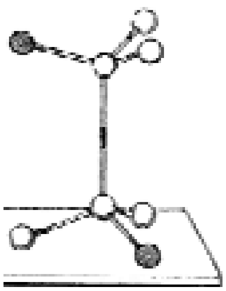
Mohr's clear "ball and stick" representation of the arrangement of carbons atoms in diamond, as determined by an early x-ray diffraction experiment, showed that six-membered rings of singly bonded carbon atoms do indeed have the "chair" conformation predicted for cyclohexane by Sachse almost 30 years earlier.



Couper used the "type-like" formulae to argue that marsh gas (methane, CH_4, or C_2H_4 as he wrote initially) must have a central carbon nucleus attached to the four substituent H atoms that could be replaced by halogens. If the H_4 grouping were central, as suggested by these formulae, one would expect the "molecules" shown to have independent existence, whereas experimentally one finds only mixtures of HBr and HCl, not these larger aggregares.



Hofmann used this model of "the olefiant gas" to explain its reactivity with Br_2 to generate "the oil of the Dutch chemists". The idea was that unsatisfied valences should make a molecule especially reactive toward other atoms. [Of course Hofmann made an unlucky choice by assigning both dangling bonds from the same carbon atom. Otherwise this would have been a prescient model of the bromination of ethylene to give 1,2-dibromoethane.]



Paternó's model of 1,2-dibromoethane was designed to explain the possibility of three isomers of dibromoethane "supposing that they really exist". He also showed 1,1-dibromoethane, and a second "isomer" of 1,2-dibromoethane in which there had been 120° rotation about the central C–C bond.

5 . (5 minutes) List the types of contribution to strain energy that are consideredby a molecular mechanics program like Chem3D. If the furthest right model in Question 4 had precisely the conformation suggested by the formula, which two contributions should dominate its strain energy,

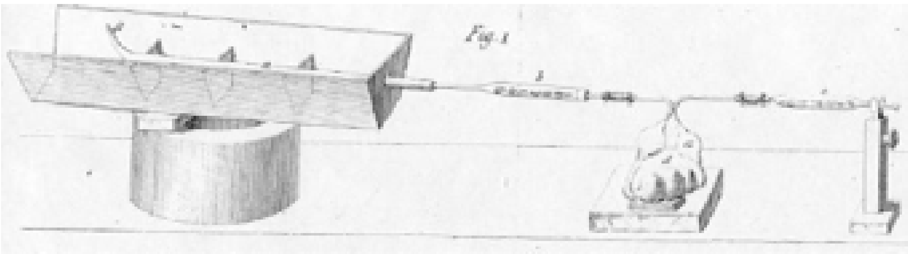
Contributions: bond stretch, bond angle bend, stretch-bend interaction, torsion,
van der Waals (1,4 and non-1,4)

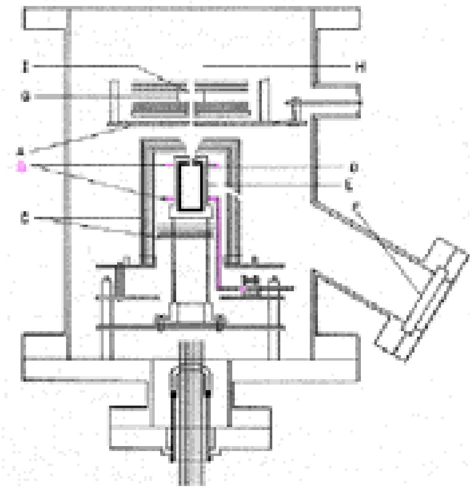
As you can confirm for yourself with Chem3D, the dominant sources are torsion (3.5 kcal/mole) and 1,4-van der Waals (1.76 kcal/mole), both due to the eclipsed conformation chosen by Paternó.

[These strains could be relieved by stretching and bending the bonds, but the cost would be too high, because these are “stiffer springs” than the torsion and van der Waals potentials, so stretching and bending strain account for only 0.1 and 0.7 kcal/mole.]

[Incidentally, in discussing hydrocarbons we did not mention electrostatic dipole interactions, which are also considered when the bonds are polar, as in this dichloride, where the second largest contribution to strain energy is dipole-dipole interaction (2.2 kcal/mole).]

6. (7.5 min) Explain what **ONE** of these two pieces of apparatus is used to measure, and how it works. **Choose ONE only**.





Liebig's Combustion Analysis Set-Up Scoring Scheme:

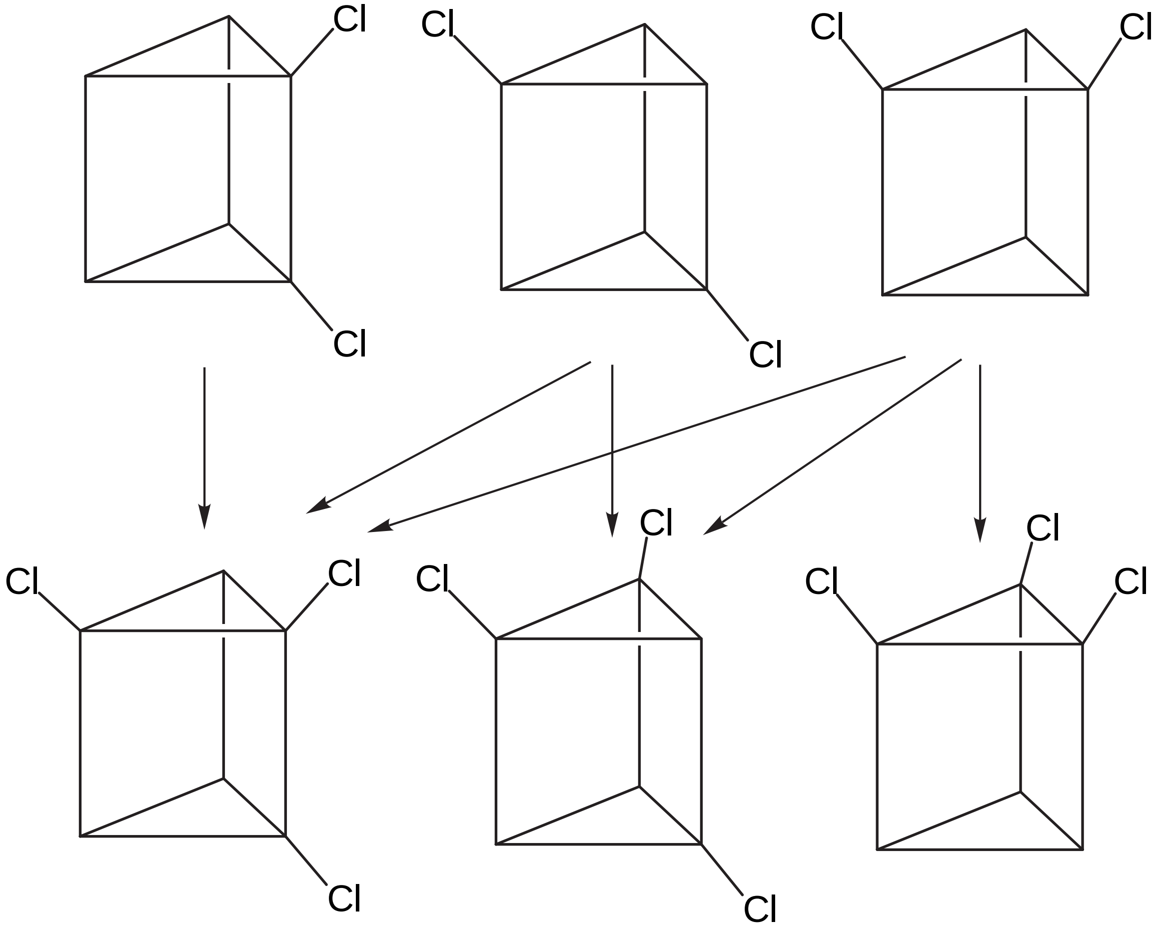
3 points each for:
- saying it's for elemental analysis by combustion,
- describing how C composition is determined by weight after absorbing CO_2 in kali-apparat and weighting water lost from kali-apparat
- describing how H composition is determined by weight after absorbing H_2O on $CaCl_2$.
- describing how O composition is determined by difference
- describing how combustion is achieved without O_2 supply; sample mixed with CuO / $KClO_3$.

Chupka's Carbon Sublimation Apparatus

3 points each for:
- recognizing that the apparatus measures heat of atomization
- use of tantalum as oven because it has a lower vapor pressure than graphite

Other details (3 pts each, max 9 total)
- optical pyrometer through quartz window for temperature measurement
- heating by electron impact on oven from wire at 500-1000V higher potential
- effusion hole small enough that gas effusion does not disturb equilibrium
- gas is ionized for MS analysis to distinguish C from C_2, C_3…
- heat of atomization determined by plot of log(K) vs 1/T

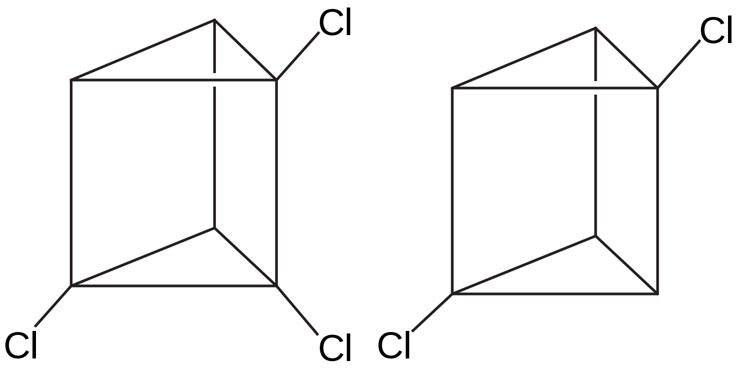
7. (8 minutes) One could easily imagine the existence of the following three isomers of "dichloroprismane". Suggest a set of chemical transformations the results of which might allow you to identify which is which of these isomers if they came in unlabelled bottles.



By substituting chlorine for an additional H atom, the first compound can give only the first product molecule (the only one with two Cl atoms on the same vertical edge of the prism. The second can give either the first or the second product (the only ones that have two Cl atoms on opposite corners of a square face). The third can give any of the three product molecules shown. Assuming the mono substitution can be achieved experimentally, this correspondence establishes which starting material is which, and which product is which.

[Note that the prism is supposed to have equilateral triangles top and bottom, and identical square side faces. Otherwise additional isomers are possible.]

[Obviously this analysis is based on Koerner's identification of the three isomers of disubstituted benzene. In fact, as we'll soon see, Ladenburg, a friend of Koerner's, had proposed this triangular prism structure for benzene. What Ladenburg had not thought (and you were not expected to see) is that more isomers are possible. These di- and trisubstituted structures are not strictly identical (superimposable after rotation) with any of the structures above.



Approximate scoring scheme:

4 points each for

- using monochlorination reaction
- list of tricholoroprismane isomers contained ALL possible isomers
- list of tricholoroprismane isomers contained no duplicate isomers
- describing a coherent method to distinguish the three which was consistent with the isomers drawn.