MOLECULAR SHAPES: STRUCTURAL ISOMERISM AND CONFORMATIONAL ANALYSIS

Molecular models are often used as visual aids to understanding the three-dimensional structures of organic molecules. The models used in this experiment show the correct angles between the various chemical bonds in a molecule, but do not accurately represent the relative sizes of atoms or their precise internuclear distances. Nevertheless, they do help one to appreciate the different possible arrangements of the atoms in a molecule, the different shapes that a molecule can assume, and the ways these shapes can be represented in two-dimensional formulas.

1. The Models

The molecular model set contains different colored wooden balls to represent the different kinds of atoms, such as carbon, hydrogen, and oxygen. They have holes bored in them to correspond to the number of covalent bonds that the various atoms can form in producing molecules. With atoms capable of forming more than one covalent bond, the holes are bored at angles to correspond to the normal bond angles of the atoms.

In the model kit manufactured by E. H. Sargent and Company,[1] the following colors are employed:

Carbon: black   Hydrogen: yellow   Chlorine: green

The small round sticks are used to represent bonds. Thus, by placing one end of a stick in a hole in one of the model atoms and the other in a hole of a second model atom, a covalent bond binding these two atoms together is represented.

The dimensions of the models are such that one inch represents approximately one Angstrom unit (1 Å = 10^{-8} cm). If the sticks in the model set come in two lengths, it is suggested that the shorter sticks be used for C-H bonds (1.09 Å) and the longer sticks for C-C bonds (1.54 Å).

2. The Carbon Atom

Procedure:

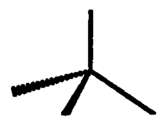
Insert a stick in each hole of a model carbon atom (black), and set the model on the desk top for observation. Mentally draw imaginary lines between the ends of the sticks.

[1] Other simple molecular model sets can be used in this experiment; the instructions may have to be altered slightly if the colors differ from those given here.

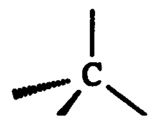
(1) What geometric figure is represented by these imaginary lines?

(2) What is the approximate angle between all possible pairs of covalent bonds in the model?

Note that if one imagines a plane to include the carbon atom and two of its bonds, the remaining two bonds are symmetrically disposed on either side of that plane. The plane is therefore called a *plane of symmetry*. The carbon atom can be represented by the figures shown below:



or



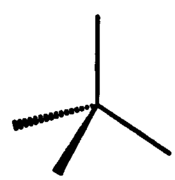
in which the solid bonds lie in the plane of the paper (the symmetry plane), the dashed bond extends away from the reader, and the wedge-shaped bond extends toward the reader.

(3) How many symmetry planes does the carbon atom model have?

The tetrahedral carbon atom also has a threefold *rotational axis of symmetry.*

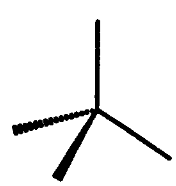
(4) What is meant by such an axis?

(5) By use of an arrow in the following figure, show the location of one such threefold axis in the carbon atom model.



(6) How many threefold rotational axes does the model have?

(7) The carbon atom model has an additional rotational axis of symmetry that is <u>not</u> threefold. Use an arrow in the following figure to show the location of one of these.



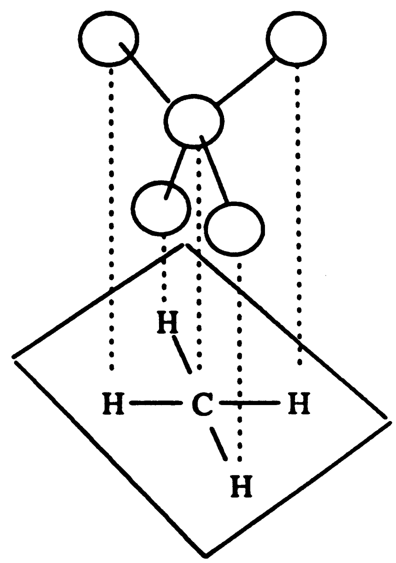
(8) How many-fold is the axis you drew in (7)?

3. The Methane Molecule

Procedure:

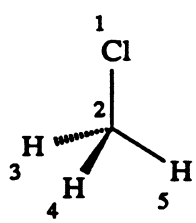
Use a black ball (carbon) and four yellow balls (hydrogen) to construct a model of the methane molecule, CH_4. Place the model on the desk top and observe it by looking directly down on top of it. Rotate the model to place two hydrogen atoms to the right and one to the left. Take hold of the top hydrogen atom and tip the model to the right about 45° so that the methane model is resting on only two hydrogen atoms. Note that these two hydrogen atoms, which are now at the top and bottom of the carbon atom, lie in a plane beneath the carbon atom, whereas the two remaining hydrogen atoms to the left and right of the carbon atom lie in a plane above the carbon atom. Now imagine the methane model to be pressed down flat on the desk top. This imaginary flat model, which is the projection of the methane model on a plane surface, is the conventional structural formula for methane.

projection formula of methane



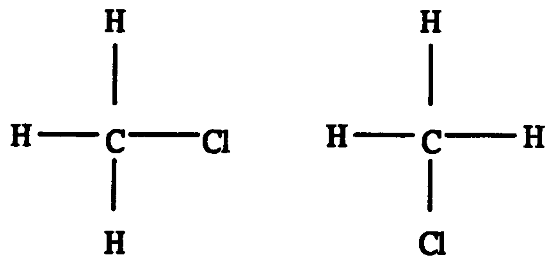
Replace one of the hydrogen atoms by a chlorine atom (green). The resulting molecule is called chloromethane, or methyl chloride.

(9) Use the numbering system in the following figure to describe all the symmetry planes in chloromethane.



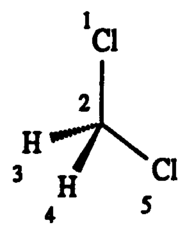
(10) Use the above figure and arrows to show any axes of symmetry in chloromethane. (Also state how many-fold.)

Satisfy yourself that the plane projection formulas represent the same three-dimensional structure.



Replace a second hydrogen atom by a chlorine atom, to give methylene chloride, CH_2Cl_2.

(11) Use the numbering system in the following figure to describe all the symmetry planes in methylene chloride.



(12) Use the above figure and arrows to show any symmetry axes in methylene chloride. (Also state how many-fold.)

Satisfy yourself that the plane projection formulas:

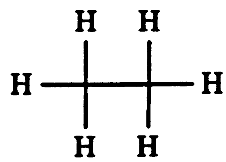
represent the same three-dimensional structure.

(13) Of what significance, with regard to the geometry of the four bonds of tetravalent carbon, is the fact that one and only one substance is known which has the formula CH_2Cl_2?

4. The Conformations of Ethane

Procedure:

Join two carbon atoms with a bond, then attach six hydrogens to the remaining valences to construct a model of ethane, C_2H_6.

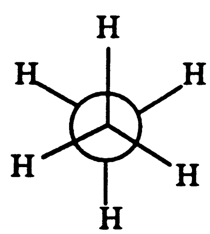


$CH_3—CH_3$

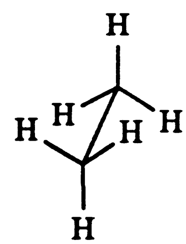
projection formula | condensed formula

ethane

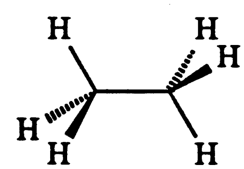
Sight down the carbon-carbon bond, and slowly rotate one carbon atom with respect to the other until a C—H bond on one carbon atom bisects the H—C—H angle on the other carbon atom. This is called the *staggered conformation* of the molecule, which can be represented by several conventions (Newman, "sawhorse," dashed line-wedge), as shown.



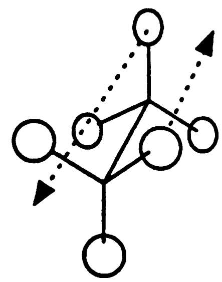
Newman projection



"sawhorse" formula



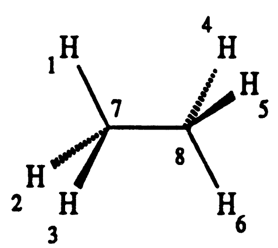
dashed line-wedge formula



staggered conformation of ethane

(14) Use the numbering system in the following figure to describe all the symmetry planes in the staggered conformation of ethane.

* If necessary to define points in space between atoms, do so as in the following example: 1-midpoint-4 (Remember that it only takes 3 points to define a plane).



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(15) Use the above figure and arrows to show any rotational symmetry axes in the staggered conformation of ethane. (Also state how-many fold.) ______________

This conformation of ethane also has a *center of symmetry*.

(16) A center of symmetry is defined as a point within an object such that a straight line drawn from any part or element of the object to the center and exended an equal distance on the other side encounters an equal part or element. Where is the center of symmetry located in the staggered conformation of ethane?

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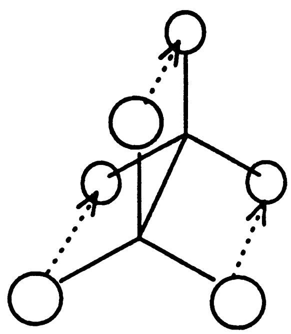
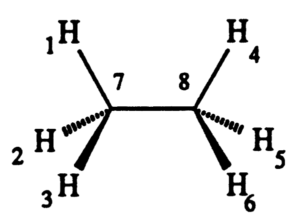
Rotate one carbon atom 60° with respect to the other, to construct the *eclipsed conformation* of ethane, as shown in the figure.



eclipsed conformation of ethane

(17) Draw the eclipsed conformation of ethane according to the Newman, "Sawhorse," and dashed line-wedge notations.

(18) Use the numbering system in the following figure to describe all the symmetry planes in the eclipsed conformation of ethane.



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(19) Use the above figure and arrows to show any rotational symmetry axes in the eclipsed conformation of ethane. (Also state how-many fold.) ____________

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(20) Does the eclipsed conformation of ethane have a center of symmetry? If so, where is it?

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(21) In which conformation, staggered or eclipsed, does a hydrogen atom on one carbon atom come closer to a hydrogen atom on the other carbon atom?

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(22) If nonbonded, like atoms repel each other when they come close to one another, which conformation of ethane would you expect to be the less stable?

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(23) What type of motion converts this conformation to the more stable conformation?

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(24) Give a definition of the term "conformation." ______________________________

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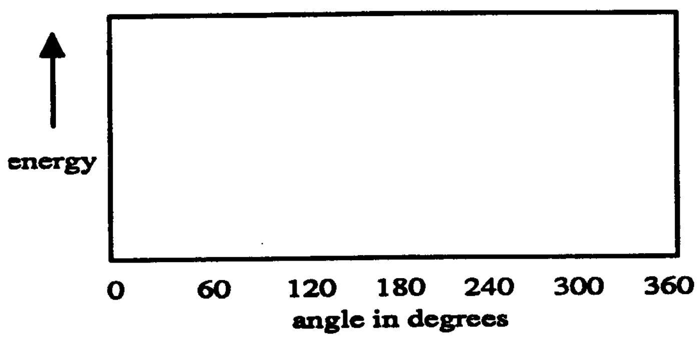
(25) Plot the energy of the ethane molecule (vertical axis) against the angle of rotation of the C—C bond (horizontal axis), starting in the staggered conformation as 0°. Go through one full revolution (360°).



5. The butanes. Isomerism and Conformations

Procedure:

Join four carbon atoms in a consecutive chain, and attach the appropriate number of hydrogen atoms to each carbon.

(26) What is the molecular formula of the hydrocarbon? ______________

(27) Write its structural formula.

The compound is called butane (or sometimes *n*-butane, *n* for normal). Now join three carbon atoms by bonds, and attach a fourth carbon atom to the central carbon in the chain. Add the appropriate number of hydrogen atoms to each carbon.

(28) Is the molecular formula of this hydrocarbon the same as or different from that of *n*-butane? ______________________________

(29) Write its structural formula. Is it the same as that of *n*-butane? The compound is called isobutane, or 2-methylpropane. Compounds that have the same molecular formula but different structural formulas are said to be *structural isomers.*

(30) Describe how the process that would interconvert the two butanes differs from the process that interconverts the staggered and eclipsed forms of ethane?

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Sight down the bond which connects carbon atoms 2 and 3 in the model of *n*-butane.

(31) Draw two different staggered conformations of *n*-butane, using the Newman Projections. Letter the one that you think would be more stable as A, the other as B.

(32) Give a reason for your choice. ______________________________

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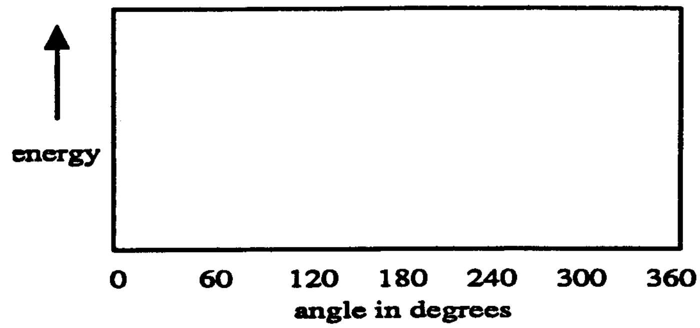
Use the same convention to draw two different eclipsed conformations of n-butane. Letter the one that you think would be less stable as D, the other as C.

(33) Give a reason for your choice. ____

(34) Construct an energy diagram for the various conformers of n-butane, starting at 0° with the more stable staggered conformation, and proceeding through one full revolution of the C2-C3 bond.



Use the models to determine how many pentanes (hydrocarbons with the formula C_5H_{12} are possible.

(35) Draw their structural formulas.

6. Rings of Carbon Atoms. Cyclohexane Conformations

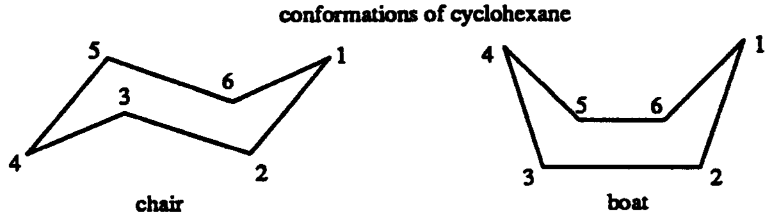
Procedure:

Connect six carbon atoms by means of five valence sticks. Insert sticks in all the unused holes in the carbon atom models. Note the zigzag nature of the chain when extended. Remove one valence stick from one of the terminal carbon atoms and, by twisting the atoms about their bonds, connect atom 1 to atom 6 to form a six-membered (cyclohexane) ring.

(36) Is the ring planar? ____________________

Note that the ring can be arranged in either a chair or a boat form.

conformations of cyclohexane



With the model in the chair form, sight along any carbon-carbon bond.

(37) Are the H-bonds to the carbon atoms staggered or eclipsed?

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Check this for each set of adjacent carbon atoms. Note that the bonds attached to the carbon atoms fall into two sets, those roughly in the mean plane of the carbon atoms (called *equatorial bonds*), and those perpendicular to the mean molecular plane (called *axial bonds*).

(38) Draw a model of the chair form, and clearly label the equatorial bonds *e* and the axial bonds *a*.

Now arrange the model in the boat conformation. Sight along the C2-C3 and C5-C6 bonds (see the formula above, for the numbering.)

(39) Are the H-bonds to these carbon atoms staggered or eclipsed?

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Note that two of the bonds, one each on carbons 1 and 4, point in toward one another. These are called *bowsprit bonds.*

(40) Draw a model of the boat form of cyclohexane, and label the "bowsprit" hydrogens.

(41) Which form of cyclohexane do you expect to be more stable, the chair or the boat? Why?

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Note that the interconversion of chair and boat forms proceeds through an intermediate flexible structure, called the *twist* form of cyclohexane.

(42) Draw a model of the twist form.

Add a green ball to one of the cyclohexane bonds, to make a model of chlorocyclohexane in a chair conformation.

(43) Did you place the chlorine in an axial, or an equatorial position?

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(44) Draw the model.

Now flip the chlorine-bearing carbon (carbon 1) so that the model assumes a boat conformation. Next, flip carbon 4 so that the model once again is in a chair conformation.

(45) Is the chlorine in an axial or equatorial position?

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(46) Draw the model.

(47) Which conformation is more stable, the one with chlorine axial or equatorial? Explain the reason for your answer. ______________________________

Remove the chlorine, remove one carbon atom from the ring, and construct a model of cyclopentane.

(48) Is the ring more or less planar than the cyclohexane ring? ______________

(49) Are the bonds on adjacent carbons more or less staggered than they were in the chair form of cyclohexane?

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(50) Can the ring twist in any way to minimize the eclipsing that is observed?

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(51) Draw a model of such a twisted conformation of cyclopentane.

Remove one more carbon atom from the ring, and attempt to make a model of cyclobutane.

(52) Can this be done with the present model set? ______________________

(53) Cyclobutanes and cyclopropanes are known. What can you say about the C-C-C bond angles in cyclobutanes and cyclopropanes, relative to those in larger rings?

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