

# Investigating Hydrocarbon Structure with Molecular Models and C-13 NMR Spectroscopy

## Materials Needed

- Molecular model set for organic chemistry
- Data table
- Exercises for your assigned role, student 1, 2, 3, or 4.

(This packet is for student 2)

## Overview

This exercise is designed to help you understand structure and bonding in hydrocarbons. It also introduces you to your molecular model kit, as well as spectroscopic data for the models that you build. You will build approximately ten models as you complete this activity. Each of your lab group partners will also build a related set of 10 models. After you have finished your model building and data analysis your group will meet to discuss all your results. If you get stuck along the way you can ask your partners what models they are building and what they are thinking. You or your group can also ask your instructor for guidance.

One of the resources you will use in this laboratory is the carbon-13 (C-13) Nuclear Magnetic Resonance (NMR) spectra of various compounds. Just as doctors and physical therapists use Magnetic Resonance Imaging to diagnose medical conditions, organic chemists can use the related NMR process to deduce the bonding patterns of atoms in organic molecules. NMR experiments study nuclei of specific elements in compounds. The isotopes and elements most useful to organic chemists are hydrogen (with a mass of 1) and carbon (with a mass of 13). The details of obtaining NMR spectra are not appropriate for one of your first experiences in organic chemistry, but the results of carbon-13 NMR can be very powerful to help you understand the structures of organic compounds. Don't worry that you won't get enough of this fun, later in this course you will also learn how to interpret the information from hydrogen (proton) NMR.

Besides the number of observed absorptions in a C-13 NMR, the position on the X-axis where the absorption occurs is important. This value is called the chemical shift. You will tabulate the value of the chemical shifts observed for hydrocarbons throughout this activity and look for patterns. Both the number of absorptions in the C-13 NMR and their chemical shift is useful to organic chemists in their understanding of the structure of organic compounds.

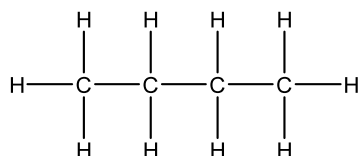
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## Exercises for Student 2

### Exercise 2-1

Record your responses on the provided data sheet.

- 1 a. Build a plastic model of butane,  $C_4H_{10}$ . If butane were typed onto a page it might be represented as



- 1 b. From the model you constructed, what is the approximate H—C—H or H—C—C bond angles?

A:  $60^\circ$

B:  $90^\circ$

C:  $109^\circ$

D:  $120^\circ$

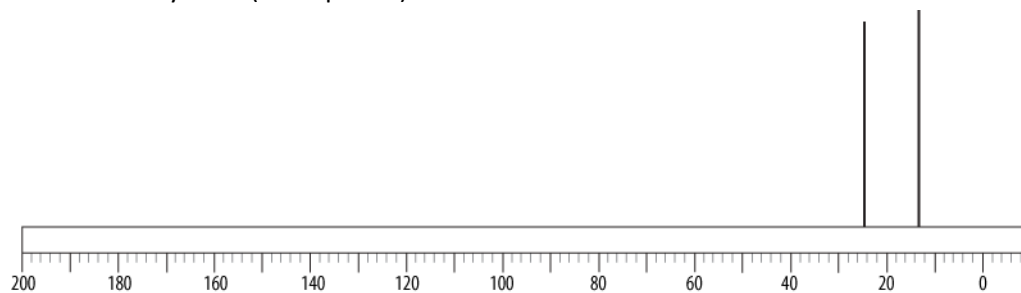
E:  $180^\circ$

- 1 c. What is the hybridization of the carbon atoms in butane? Briefly explain how you arrive at your answer.

- 1 d. Without breaking any bonds, what motion(s) is/are allowed that may change the position of any of the atoms in butane?

*Hint: if you hold one carbon atom in one hand, describe the motion observed if you turn the other carbon atom with your other hand as if you were turning on a water faucet.*

- 1 e. How many lines (absorptions) are seen the C-13 NMR of butane?



- 1 f. If the number of absorptions observed in the C-13 NMR of butane are not equal to the number of carbon atoms in butane, why not?

*Hint: Label one carbon atom #1, the second carbon atom #2, etc and then list the atoms each carbon (C#1 through C#4) is connected to. What do you notice about these connections?*

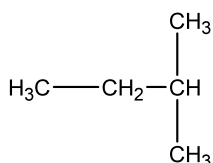
- 1 g. What property is apparent from the model of butane that also predicts the number of C-13 absorptions observed for butane?

- 1 h. What is the C-13 NMR chemical shift (X-axis value) of the C-13 absorptions of butane?

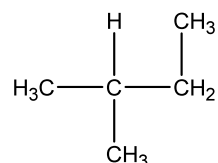
**Exercise 2-2**

2 a. Build the following two structures

Structure 2-2.1



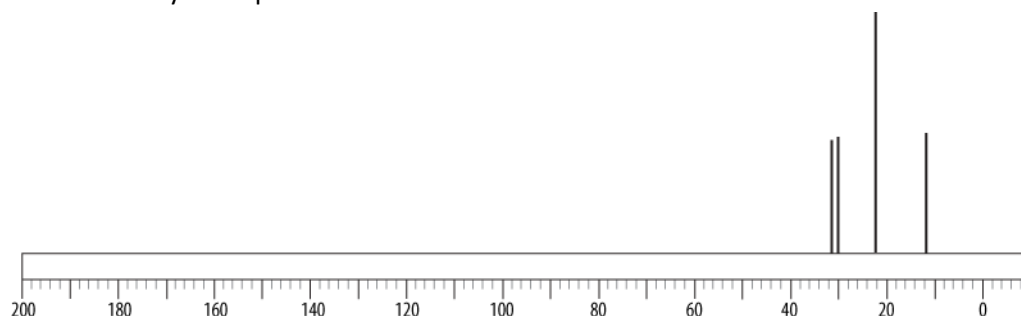
Structure 2-2.2



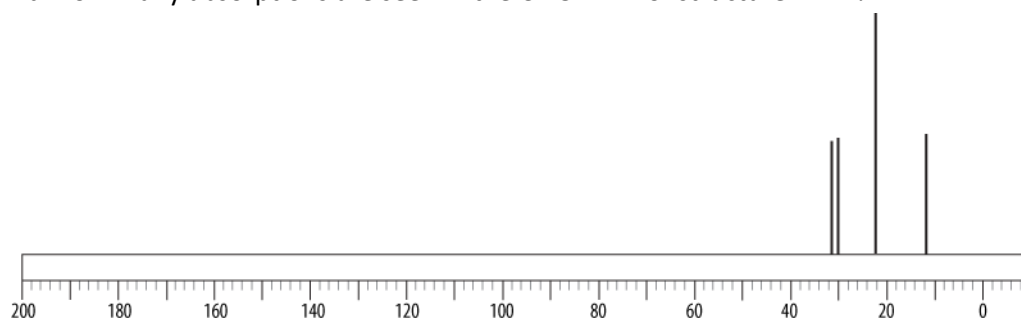
2 b. What is the relationship between these two structures?

*Consider these questions to help you decide: Are structures 2-2.1 and 2-2.2 the identical molecule, just presented or drawn differently? Are these structures isomers? (Different compounds with the same molecular formula.) If these structures are isomers what type of isomers are they?*

2 c. How many absorptions are seen in the C-13 NMR of structure 2-2.1?



2 d. How many absorptions are seen in the C-13 NMR of structure 2-2.2?

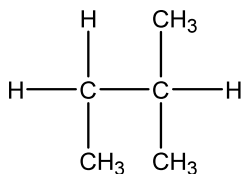
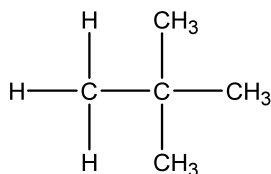


2 e. Based on the C-13 NMR of structures 2-2.1 and 2-2.2, what is the evidence that 2-2.1 and 2-2.2 are the same or different compounds? Explain your answer.

2 f. List the chemical shifts (X-axis values) of each of the absorptions in compounds 2-2.1 and 2-2.2.

**Exercise 2-3**

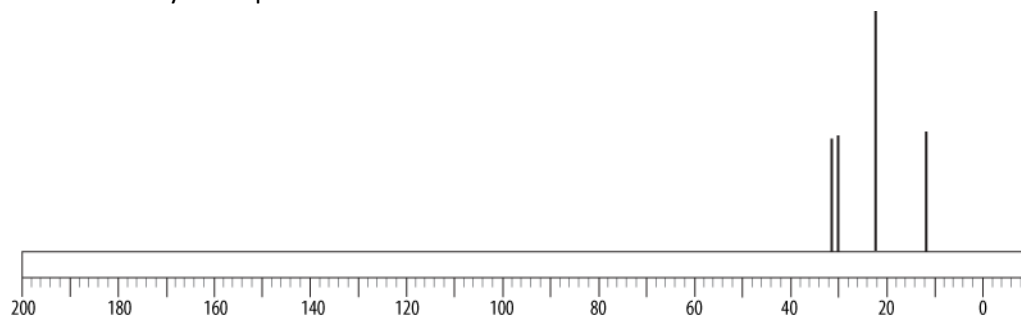
3 a. Build the following C<sub>5</sub>H<sub>12</sub> structures

*Structure 2-3.1**Structure 2-3.2*

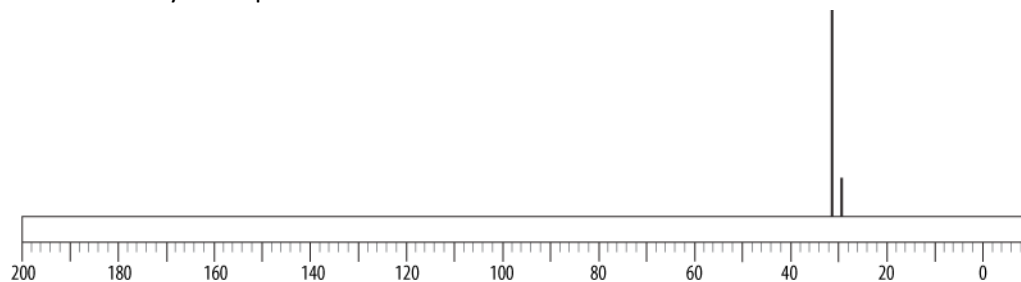
3 b. What is the relationship between these two structures?

*Consider these questions to help you decide: Are structures 2-3.1 and 2-3.2 the identical molecule, just presented or drawn differently? Are these structures isomers? If these structures are isomers what type of isomers are they?*

3 c. How many absorptions are seen in the C-13 NMR of structure 2-3.1?



3 d. How many absorptions are seen in the C-13 NMR of structure 2-3.2?

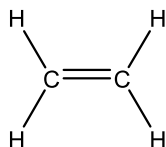


3 e. Based on the C-13 NMR of structures 2-3.1 and 2-3.2, what is the evidence that 2-3.1 and 2-3.2 are the same or different compounds? Explain your answer.

3 f. List the chemical shifts (X-axis values) of each of the absorptions in compounds 2-3.1 and 2-3.2.

**Exercise 2-4**

4 a. Build ethene  $C_2H_4$ . Be sure to check that you have constructed the double bond correctly!



4 b. What is the approximate H—C—H or H—C—C bond angle?

A:  $60^\circ$

B:  $90^\circ$

C:  $109^\circ$

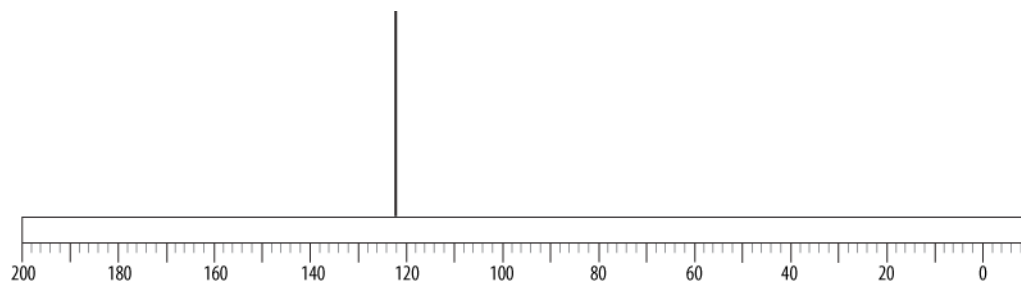
D:  $120^\circ$

E:  $180^\circ$

4 c. What is the hybridization of the carbon atoms in ethene? Briefly explain how you arrived at your answer.

4 d. How does the C—C double bond in ethene compare to the C—C single bond in ethane?

4 e. How many absorptions are observed in the C-13 NMR of ethene?



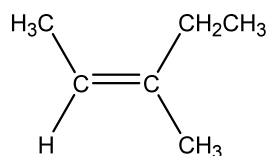
4 f. Explain the number of absorptions observed. (See hint in Exercise 2-1, question 1f.)

4 g. What is the chemical shift (X axis value) of the observed absorption of ethene?

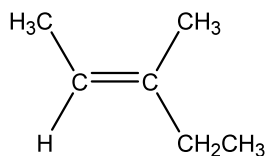
**Exercise 2-5**

5 a. Build the following  $C_6H_{12}$  structures

Structure 2-5.1



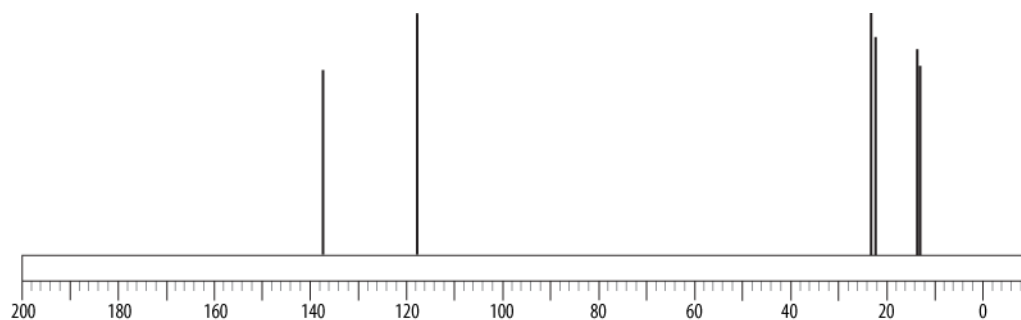
Structure 2-5.2



5 b. What is the relationship between these two structures?

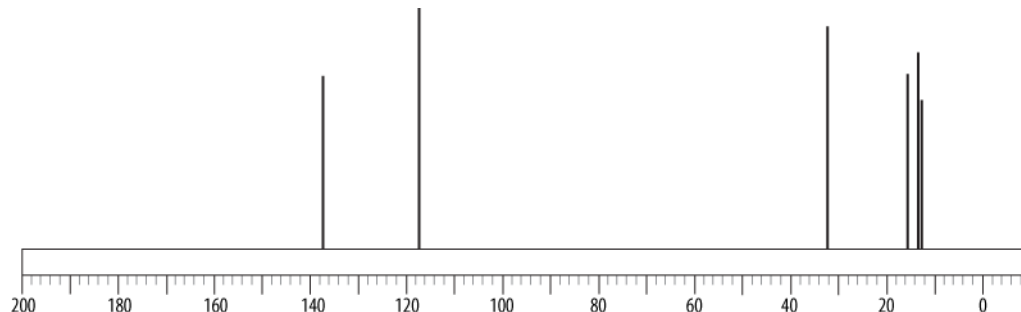
*To help you answer this, if the two structures (and physical models of the structures) can be interconverted (without breaking bonds) they could be identical molecules just presented or drawn differently. To also help you in your decision look at the C-13 NMR spectra of Compounds 2-5.1 and 2-5.2 presented below.*

5 c. How many absorptions are observed in the C-13 NMR of structure 2-5.1?



5 d. What are the observed chemical shifts (x-axis value) for these absorptions?

5 e. How many absorptions are observed in the C-13 NMR of structure 2-5.2?



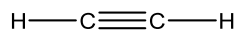
5 f. What are the observed chemical shifts (x-axis value) for these absorptions?

5 g. Explain the number of absorptions observed and the number of carbon atoms in the molecular formula of both structures 2-5.1 and 2-5.2. (See hint in Exercise 2-1, question 1f.)

5 h. What does the C-13 NMR data for structures 2-5.1 and 2-5.2 tell you about structures 2-5.1 and 2-5.2 being identical or different compounds?

**Exercise 2-6**

6 a. Build ethyne, which is also known as acetylene,  $C_2H_2$ . (Be sure to check that you have constructed the triple bond correctly!)



6 b. What are the  $H-C-C$  bond angles in ethyne?

A:  $60^\circ$

B:  $90^\circ$

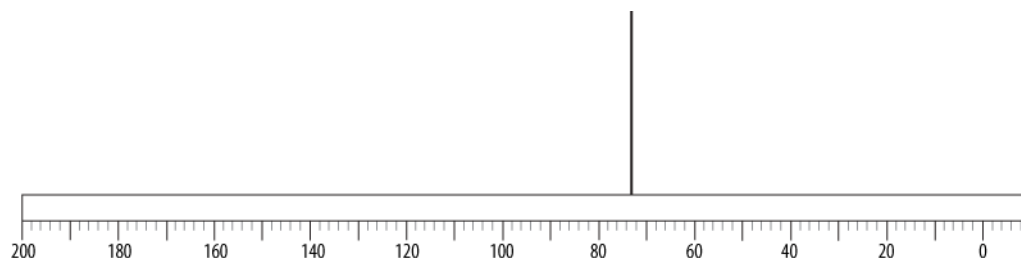
C:  $109^\circ$

D:  $120^\circ$

E:  $180^\circ$

6 c. What is the hybridization of the carbon atoms in ethyne? Briefly explain how you arrived at your answer.

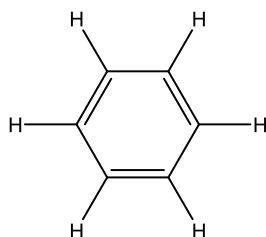
6 d. How many absorptions are observed in the C-13 NMR of ethyne?



6 e. What is/are the chemical shift (x axis value) of the observed C-13 NMR absorption(s) of ethyne?

**Exercise 2-7**

7 a. Build benzene,  $C_6H_6$ .



7 b. What is most striking about the position of all the atoms in the benzene molecule?

7 c. What are the  $H-C-C$  or  $C-C-C$  bond angles in benzene?

A:  $60^\circ$

B:  $90^\circ$

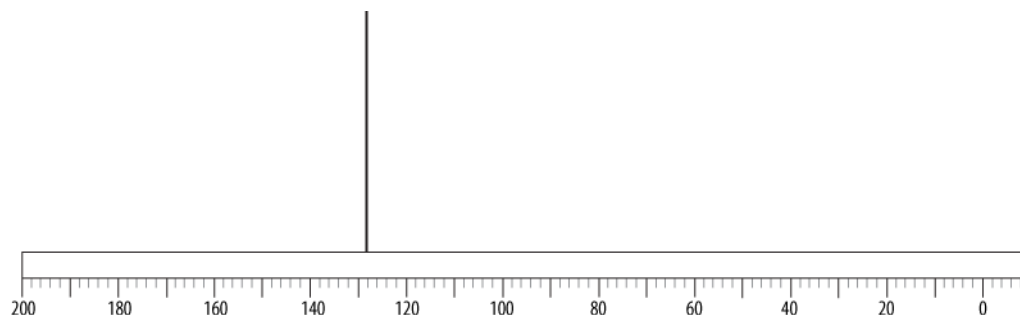
C:  $109^\circ$

D:  $120^\circ$

E:  $180^\circ$

7 d. What is the hybridization of the carbon atoms in benzene? Briefly explain how you arrived at your answer.

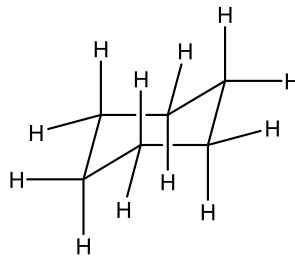
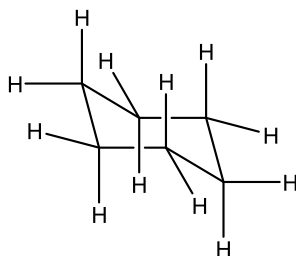
- 7 e. How many absorptions are observed in the C-13 NMR of benzene? What does this imply about the carbon atoms and carbon—carbon bonds in benzene?



- 7 f. What is the chemical shift (x axis value) of the observed absorptions in benzene?

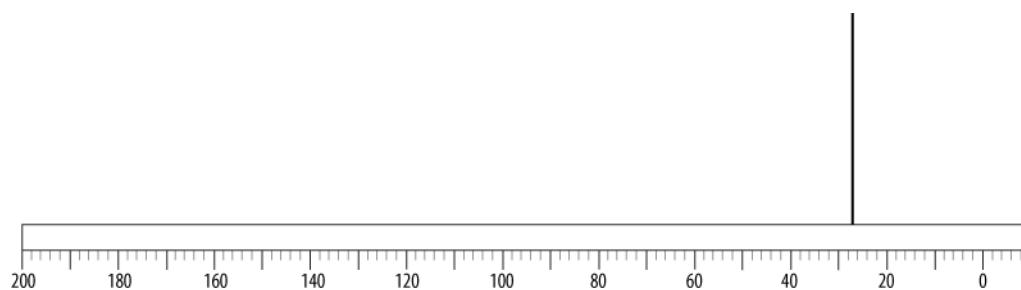
### Exercise 2-8

- 8 a. Build cyclohexane,  $C_6H_{12}$ .

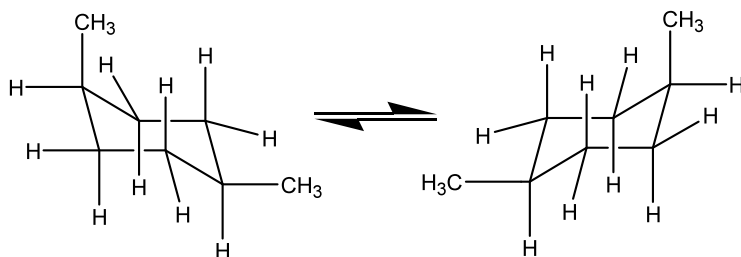


- 8 b. Do all of the atoms lay in one plane in cyclohexane as in benzene?
- 8 c. The puckered conformation above is called the chair conformation. Through twisting and turning (without breaking bonds) form your model of cyclohexane into one of these shapes? Why do you think cyclohexane adopts this shape?
- 8 d. The hydrogens that stick straight up or down are called “axial,” those that angle off to the sides are “equatorial.” Each carbon atom in the chair conformation of cyclohexane has one axial and one equatorial hydrogen. Using the chair conformation of cyclohexane shown in step 7a, draw circles around all axial hydrogens and squares around all equatorial hydrogens. How many axial hydrogens are in cyclohexane? How many equatorial hydrogens are in cyclohexane?
- 8 e. How many absorptions occur in the C-13 NMR of cyclohexane? What is the chemical shift (x axis value) of the absorptions of cyclohexane?



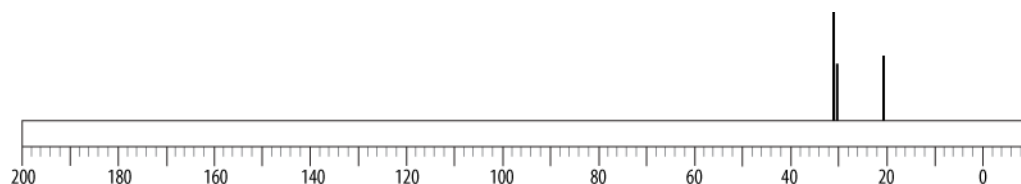
**Exercise 2-9**

9 a. Build *cis*-1,4-dimethylcyclohexane.



*Note that the two structures shown can be interconverted by simply bending or twisting the C—C bonds of the ring. This motion allows axial methyl groups to become equatorial and vice versa.*

9 b. How many absorptions are in the C-13 NMR of *cis*-1,4-dimethylcyclohexane?



9 c. Explain the number of absorptions observed.

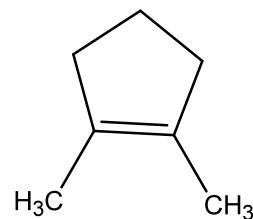
9 d. What are the chemical shifts (x axis value) of the observed absorptions?

9 e. What does the chemical shift (x axis value) indicate about the hybridization of the carbon atoms of *cis*-1,4-dimethylcyclohexane?

## Discussion Questions

Answer the questions below, discussing them with your group. Continue on another sheet if needed.

1. What claims can you make about the hybridization of carbon atoms, the number and type of bonds to those carbon atoms, and the geometric arrangement of atoms around those carbon atoms?
2. What claims can you make about the hybridization of a carbon atom and the C-13 chemical shift of the carbon atom?
3. What property of an organic compound causes the number of C -13 signals to be less than the number of carbon atoms in the molecular formula?
4. How can the C-13 NMR spectra of two compounds be used to tell if the compounds are isomers or the same compound just drawn differently?
5. With your group members, draw what you predict for the C-13 NMR of 1,2-dimethylcyclopentene. (See structure below.) Your NMR drawing needs to show the number of absorptions and approximate chemical shift (X-axis position) you predict.



6. Draw another isomer of  $C_7H_{12}$ . Draw the C-13 NMR spectrum you predict for this isomer. Label this spectrum "Isomer of 1,2-dimethylcyclopentene."

Student 2 Data Table

exercise	compounds	Bond angles	Number of C-13 absorptions	Hybridization on carbon	Relationship between two compounds (include evidence for your answer)	Chemical shifts (x-axis value) of C-13 absorptions	Comments on compound or C-13 absorptions
2-1	C <sub>4</sub> H <sub>10</sub> butane	1b	1e	1c		1h	
2-2	C <sub>5</sub> H <sub>12</sub> Structure 2-2.1		2c		2e	2f	
2-2	C <sub>5</sub> H <sub>12</sub> Structure 2-2.2		2d			2f	
2-3	C <sub>5</sub> H <sub>12</sub> Structure 2-3.1		3c		3e	3f	
2-3	C <sub>5</sub> H <sub>12</sub> Structure 2-3.2		3d			3f	
2-4	C <sub>2</sub> H <sub>4</sub> ethene	4b	4e	4c		4g	
2-5	C <sub>6</sub> H <sub>12</sub> Structure 2-5.1		5c		5h	5d	
2-5	C <sub>6</sub> H <sub>12</sub> Structure 2-5.2		5e			5f	
2-6	C <sub>2</sub> H <sub>2</sub> ethyne	6b	6d	6c		6e	
2-7	C <sub>6</sub> H <sub>6</sub> benzene	7c	7e	7d		7f	
2-8	C <sub>6</sub> H <sub>12</sub> cyclohexane		8e			8e	
2-9	<i>cis</i> -1,4-dimethylcyclohexane		9b			9d	