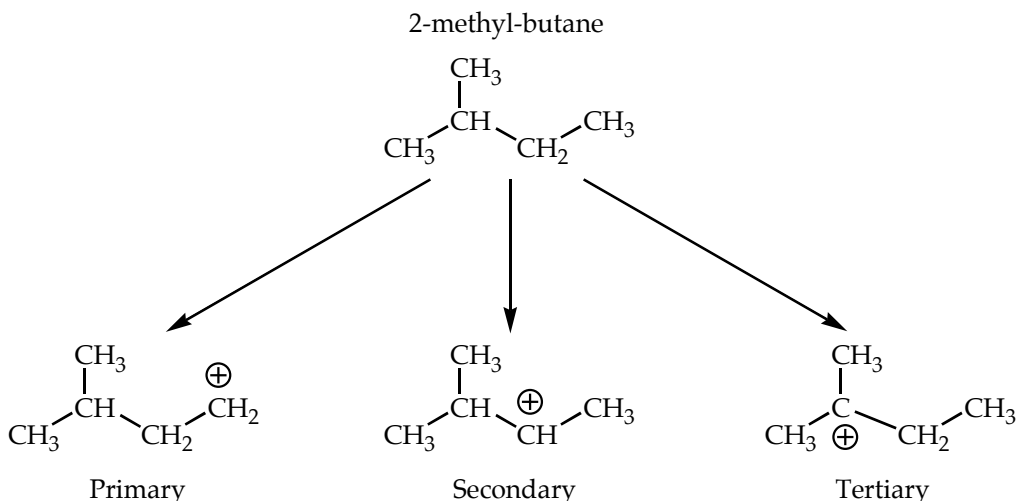# Carbocations

The goal of this exercise is to compare the stability of isomeric carbocations. In part A we are going to examine primary, secondary and tertiary carbocations based on 2-methyl butane.

2-methyl-butane

Because these three structures are isomeric we will be able to directly compare their heats of formation and determine their relative stabilities. We will start the exercise by building 2-methyl-butane and conducting a geometry optimization. Once we have optimized the geometry of 2-methyl-butane we will use the optimized geometry as a starting point to construct models of each of the carbocations.

In part B of this exercise we will look at the effects of resonance (delocalization) on carbocation stability. Here we will compare two isomeric carbocations based on 1-pentene, a secondary carbocation located on C4 and the secondary carbocation located on C3 (the allylic position).
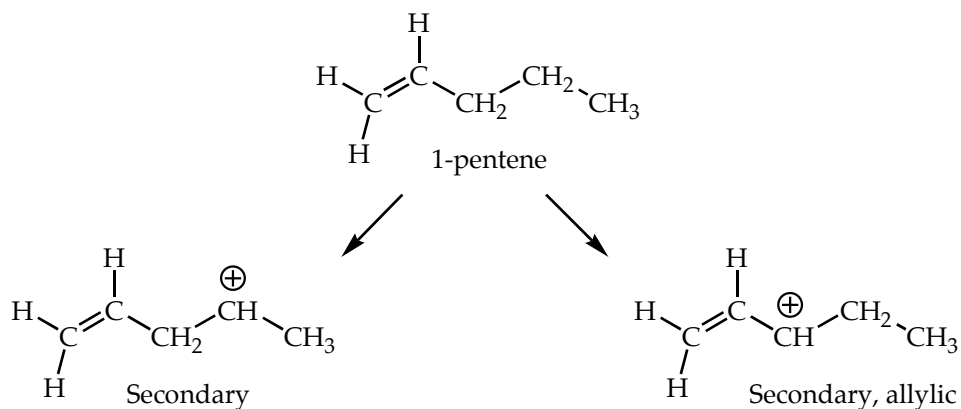
Once again, because the structures are isomeric we will be able to directly compare their heats of formation and determine their relative stabilities. Exercise B will begin by optimizing the geometry of 1-pentene as a starting point.

A.1 2-Methylbutane

1. Login to WebMO.

2. At the top of the WebMO Job Manager Page, click on the New Job button. This will bring up the Build Molecule page.

3. To build 2-methylbutane: It is essential to get the starting geometry as close to the global minimum as possible. The WebMO editor is a very crude tool with which to build complex molecules. For the best possible results you must follow these directions very closely. Start by clicking the mouse near the top of the screen to place a carbon atom. Click on the Carbon atom and hold the mouse button down. Now drag the mouse vertically away from the first carbon towards the bottom of the screen, all the while holding down the mouse button. Release the mouse button when the curser resides where you would like to place the second carbon atom. Do not put the atoms too close together, or too far apart (about two to three atom diameters is about right). Click and drag to place the other three carbons so that your carbon frame looks like the image below.
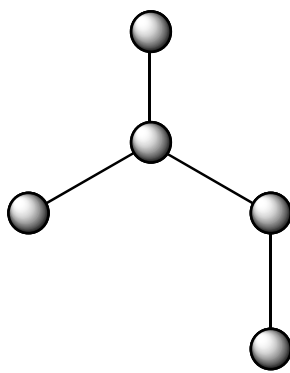
4. From the "Clean-Up" menu select "Comprehensive - Mechanics," or click on the wrench icon (comprehensive clean-up tool shortcut) on the left of the window to add the remainder of the hydrogens.

5. The Comprehensive - Mechanics Clean-Up should not only add hydrogens to each carbon, it should add them in a staggered conformation. Confirm that your structure contains staggered conformations by first selecting the curved arrow icon (rotate tool) at the left of the window and then rotating your molecule to view the conformations.

6. Click on the Job Options link to the left of the model window or the arrow to the right on the bottom of the screen..

7. On the Configure Mopac Job Options page,

Job Name   Give your molecule its standard IUPAC name, followed by an underscore and an identifier of your choice, such as 2-methylbutane_geometry_opt. Use any identifier you find useful, as long as the molecule name begins with the IUPAC name and an underscore.

Calculation   **Select Geometry Optimization from the *Calculation* drop-down menu**. This will calculate the local minimum energy conformation and the corresponding heat of formation for your compound.

Theory   Select AM1 from the *Theory* drop-down menu.

Charge   Leave the charge at 0

Multiplicity   Leave the multiplicity at Singlet.

Leave *Preview Input File* unchecked. Do not select Advanced Options.

Click on the Submit Job link.

8. This will return you to the Job Manager Page, where you will see your job listed. In the status column you will see *Running* in red. Click on the Refresh button at the top-left corner of the screen.

9. Your job's status should now say *Complete* in green. Click on the View link to the right of the job's status to see the results of the calculation.

10. Verify that your heat of formation is close to -35.39 kcal/mol under calculated quantities.

11. Click on the New Job Using This Geometry button just below the model window. This will start a new calculation using the old geometry as a starting point. Continue with section A.2.

A.2 2-Methylbutyl Primary Carbocation

1. You should be looking at the Build Molecule window which contains your geometry optimized 2-methyl butane.

2. We need to select one of the hydrogens to delete on C4 (see below).
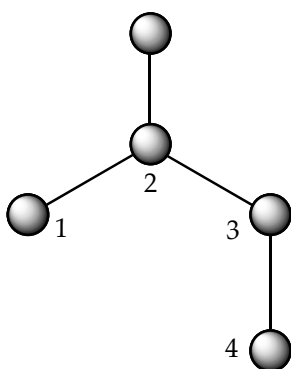
It does not matter which hydrogen you choose on C4 as they are all equivalent. Begin by using the "Tools" menu and selecting "Adjust," or click on the straight arrow icon (Adjust tool shortcut) to the left of the screen. With the "Adjust" tool selected, click on **one** of the hydrogen atoms on C4. The selected hydrogen atom will remain boldly colored while items not selected will be faded gray. If you make a mistake click the mouse to the side of the molecule, this will remove all selections and the molecule will again appear bold in color (no selection).

3. With the hydrogen selected choose the "Adjust" menu and select "Delete Selection." The selected hydrogen and bond will be deleted.

4. Now click on C4 still using the adjust tool. With the carbon selected choose the "Adjust" menu and select "Charge." A pop-up widow will appear allowing you to change the charge on the carbon atom. In the pop-up window type 1 for a +1 charge and hit the "OK" button. The carbon should now be labeled with a "+1" charge.

5. Click on the <u>Job Options</u> link to the left of the model window or the arrow to the right on the bottom of the screen.

6. On the Configure Mopac Job Options page,

Job Name   Give your molecule its standard IUPAC name, followed by an underscore and an identifier of your choice, such as 2-methylbutyl_primary_cation_geom_opt. Use any identifier you find useful, as long as the molecule name begins with the IUPAC name and an underscore.

Calculation   **Select <u>Geometry Optimization</u> from the *Calculation* drop-down menu**. This will calculate the local minimum energy conformation and the corresponding heat of formation for your compound.

Theory   Select <u>AM1</u> from the *Theory* drop-down menu.

Charge   **Should display a "1" for +1 charge. If displaying "0" you need to change it to "1".**

Multiplicity   Leave the multiplicity at Singlet.

Leave *Preview Input File* unchecked. Do not select Advanced Options.

Click on the <u>Submit Job</u> link or click on the arrow to the right at the bottom of the screen.

7. This will return you to the Job Manager Page, where you will see your job listed. In the status column you will see *Running* in red. Click on the Refresh button at the top-left corner of the screen.

8. Your job's status should now say *Complete* in green. Click on the <u>View</u> link to the right of the job's status to see the results of the calculation.

9. Several types of information are available from the completed job page.

Job Number & Name   The Job number and name are at the top of the page. Job numbers are in order of all of the jobs run on the server, each job has a unique number.

Calculate Geometry   The molecule is displayed with the optimized geometry

Keywords (Route)   The keywords the computational engine used to optimize the molecule are displayed

Symmetry   The symmetry point group to which the molecule belongs is displayed

Heat of Formation   The calculated Heat of Formation for the molecule is displayed in kcal/mol

Dipole Moment   The calculated Dipole Moment of the molecule is displayed in Debye and can be visualized by clicking the *adjacent* magnifying glass button.

Partial Charges   The calculated partial charge on each element of the molecule is given in table format. The partial charges can be visualized by clicking the *adjacent* magnifying glass button.

Bond Orders   The calculated bond orders (strength of bonding interaction) are displayed. Values less than one indicate no existing bond. Values approximately one indicate a single bond interaction between the two atoms. Values approximately two and three indicate a double or triple bond interaction, respectively.

Other Information   It is possible to rotate, translate, and enlarge or decrease (zoom) the size of the model in the window using the tool bar in the upper left hand corner. The white bar (information bar) directly below the gray model window conveys information regarding each tool name as the curser rolls over the tool. Once the tool is selected by clicking once on the icon, the information bar provides instructions on the use of each tool.

      Curved Arrow – Rotate   Default tool, used to rotate the molecule by clicking and holding the mouse button down while moving the mouse.

      Crossed Arrows – Translate   Used to move the molecule to a different position on the screen.

      Magnifying Glass – Zoom   Used to enlarge or decrease the size of the molecule in the window

      Straight Arrow – Selection   This tool has many uses. Clicking once on an atom will provide the hybridization of the atom in the information bar. Clicking beside the molecule (not on an atom) will remove the selection. Two atoms can be selected at the same time to provide a bond length (or simple distance between two non-bonded atoms). To select two atoms, click on the first atom to select it, then holding the shift key select the second atom. Bond angles and dihedral angles can be obtained by select three and four atoms, respectively.

10. Click on the Job Manager button to return to the Job Manager screen.

A.3 2-Methylbutyl Secondary Carbocation

1. From the Job Manager page, find the geometry optimized model of 2-methyl-butane that you constructed in step A.1. Click on the <u>View</u> link to the right of the job's status.

2. Click on the New Job Using This Geometry button just below the model window. This will start a new calculation using the old geometry as a starting point.

3. We need to select one of the hydrogens to delete on C3 (see below).
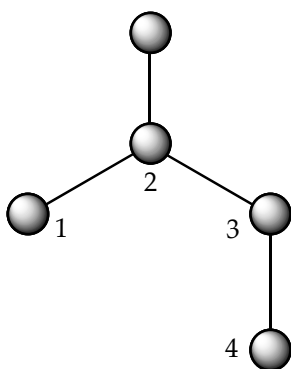
It does not matter which hydrogen on C3 you choose as they are equivalent. Begin by using the "Tools" menu and selecting "Adjust," or click on the straight arrow icon (Adjust tool shortcut) to the left of the screen. With the "Adjust" tool selected, click on one of the hydrogen atoms. The selected hydrogen atom will remain boldly colored while items not selected will be faded gray. If you make a mistake click the mouse to the side of the molecule, this will remove all selections and the molecule will again appear bold in color (no selection).

4. With the hydrogen selected choose the "Adjust" menu and select "Delete Selection." The selected hydrogen and bond will be deleted.

5. Now click on C3 still using the adjust tool. With the carbon selected choose the "Adjust" menu and select "Charge." A pop-up widow will appear allowing you to change the charge on the carbon atom. In the pop-up window type 1 for a +1 charge and hit the "OK" button. The carbon should now be labeled with a "+1" charge.

6. Click on the <u>Job Options</u> link to the left of the model window or the arrow to the right on the bottom of the screen.

7. On the Configure Mopac Job Options page,

Job Name   Give your molecule its standard IUPAC name, followed by an underscore and an identifier of your choice, such as 2-methylbutyl_secondary_cation_geom_opt. Use any identifier you find useful, as long as the molecule name begins with the IUPAC name and an underscore.

Calculation   **Select <u>Geometry Optimization</u> from the *Calculation* drop-down menu**. This will calculate the local minimum energy conformation and the corresponding heat of formation for your compound.

Theory   Select <u>AM1</u> from the *Theory* drop-down menu.

Charge   **Should display a "1" for +1 charge. If displaying "0" you need to change it to "1".**

Multiplicity   Leave the multiplicity at Singlet.

Leave *Preview Input File* unchecked. Do not select Advanced Options.

Click on the <u>Submit Job</u> link or click on the arrow to the right at the bottom of the screen.

8. This will return you to the Job Manager Page, where you will see your job listed. In the status column you will see *Running* in red. Click on the Refresh button at the top-left corner of the screen.

9. Your job's status should now say *Complete* in green. Click on the <u>View</u> link to the right of the job's status to see the results of the calculation.

10. Click on the Job Manager button to return to the Job Manager screen.

A.4 2-Methylbutyl Tertiary Carbocation

1. From the Job Manager page, find the geometry optimized model of 2-methyl-butane that you constructed in step A.1. Click on the <u>View</u> link to the right of the job's status.

2. Click on the New Job Using This Geometry button just below the model window. This will start a new calculation using the old geometry as a starting point.

3. We need to select the hydrogen to delete on C2 (see below).
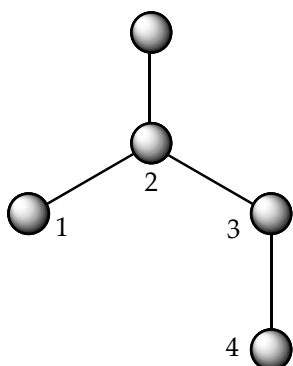
4. With the hydrogen on C2 selected choose the "Adjust" menu and select "Delete Selection." The selected hydrogen and bond will be deleted.

5. Now click on C2 still using the adjust tool. With the carbon selected choose the "Adjust" menu and select "Charge." A pop-up widow will appear allowing you to change the charge on the carbon atom. In the pop-up window type 1 for a +1 charge and hit the "OK" button. The carbon should now be labeled with a "+1" charge.

6. Click on the <u>Job Options</u> link to the left of the model window or the arrow to the right on the bottom of the screen.

7. On the Configure Mopac Job Options page,

Job Name   Give your molecule its standard IUPAC name, followed by an underscore and an identifier of your choice, such as 2-methylbutyl_tertiary_cation_geom_opt. Use any identifier you find useful, as long as the molecule name begins with the IUPAC name and an underscore.

Calculation   **Select <u>Geometry Optimization</u> from the *Calculation* drop-down menu**. This will calculate the local minimum energy conformation and the corresponding heat of formation for your compound.

Theory   Select <u>AM1</u> from the *Theory* drop-down menu.

Charge   **Should display a "1" for +1 charge. If displaying "0" you need to change it to "1".**

Multiplicity   Leave the multiplicity at Singlet.

Leave *Preview Input File* unchecked. Do not select Advanced Options.

Click on the <u>Submit Job</u> link or click on the arrow to the right at the bottom of the screen.

8. This will return you to the Job Manager Page, where you will see your job listed. In the status column you will see *Running* in red. Click on the Refresh button at the top-left corner of the screen.

9. Your job's status should now say *Complete* in green. Click on the <u>View</u> link to the right of the job's status to see the results of the calculation.

10. Click on the Job Manager button to return to the Job Manager screen.

B.1 1-Pentene

1. Login to WebMO.

2. At the top of the WebMO Job Manager Page, click on the New Job button. This will bring up the Build Molecule page.

3. To draw 1-Pentene: Start by clicking the mouse near the left side middle screen to place a carbon atom. Click on the Carbon atom and hold the mouse button down. Now drag the mouse diagonally up and toward the right away from the first carbon all the while holding down the mouse button. Release the mouse button when the curser resides where you would like to place the second carbon atom. Do not put the atoms too close together, or too far apart (about two to three atom diameters is about right). Click and drag to place the other three carbons so that your carbon frame looks like the image below. To create the double bond, click on the first atom, hold the mouse button down, and drag to the second carbon atom. Release the mouse button while over the second carbon atom. A double bond should now reside between carbon one and carbon two.
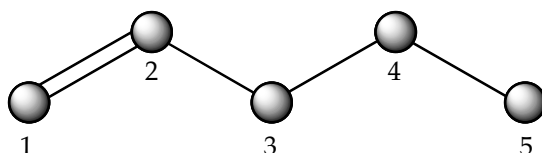
4. From the "Clean-Up" menu select "Comprehensive – Mechanics," or click on the wrench icon (comprehensive - mechanics clean-up tool shortcut) on the left of the to add the remainder of the hydrogens.

5. The Comprehensive Clean-Up should not only add hydrogens to each carbon, it should add them in a staggered conformation. Confirm that your structure contains staggered conformations by first selecting the curved arrow icon (rotate tool) at the left of the window and then rotating your molecule to view the conformations. Carbon five may be in an eclipsed conformation, this is O.K., proceed to step six.

6. Click on the Job Options link to the left of the model window or the arrow to the right on the bottom of the screen.

7. On the Configure Mopac Job Options page,

Job Name   Give your molecule its standard IUPAC name, followed by an underscore and an identifier of your choice, such as 1-pentene_geometry_opt. Use any identifier you find useful, as long as the molecule name begins with the IUPAC name and an underscore.

Calculation   **Select Geometry Optimization from the *Calculation* drop-down menu**. This will calculate the local minimum energy conformation and the corresponding heat of formation for your compound.

Theory   Select AM1 from the *Theory* drop-down menu.

Charge   Leave the charge at 0

Multiplicity   Leave the multiplicity at Singlet.

Leave *Preview Input File* unchecked. Do not select Advanced Options.

Click on the Submit Job link or click the right arrow at the bottom of the screen.

8. This will return you to the Job Manager Page, where you will see your job listed. In the status column you will see *Running* in red. Click on the Refresh button at the top-left corner of the screen.

9. Your job's status should now say *Complete* in green. Click on the <u>View</u> link to the right of the job's status to see the results of the calculation.

10. Verify that your heat of formation is close to –6.69 kcal/mol under calculated quantities.

11. Click on the New Job Using This Geometry button just below the model window. This will start a new calculation using the old geometry as a starting point. Continue with section B.2.

B.2 1-Pentenyl Secondary Carbocation

1. You should be looking at the Build Molecule window which contains your geometry optimized 1-pentene.

2. We need to select one of the hydrogens to delete on C4 (see below).
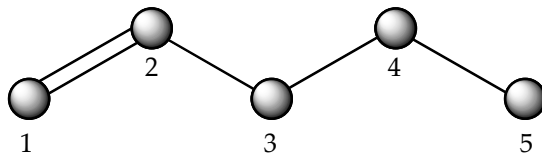
It does not matter which hydrogen you choose on C4 as they are equivalent. Begin by using the "Tools" menu and selecting "Adjust," or click on the straight arrow icon (Adjust tool shortcut) to the left of the screen. With the "Adjust" tool selected, click on one of the hydrogen atoms. The selected hydrogen atom will remain boldly colored while items not selected will be faded gray. If you make a mistake click the mouse to the side of the molecule, this will remove all selections and the molecule will again appear bold in color (no selection).

3. With the hydrogen selected choose the "Adjust" menu and select "Delete Selection." The selected hydrogen and bond will be deleted.

4. Now click on C4 still using the adjust tool. With the carbon selected choose the "Adjust" menu and select "Charge." A pop-up widow will appear allowing you to change the charge on the carbon atom. In the pop-up window type 1 for a +1 charge and hit the "OK" button. The carbon should now be labeled with a "+1" charge.

5. Click on the Job Options link to the left of the model window or the arrow to the right on the bottom of the screen.

6. On the Configure Mopac Job Options page,

Job Name   Give your molecule its standard IUPAC name, followed by an underscore and an identifier of your choice, such as 1-pentenyl_secondary_cation_geom_opt. Use any identifier you find useful, as long as the molecule name begins with the IUPAC name and an underscore.

Calculation   **Select Geometry Optimization from the *Calculation* drop-down menu**. This will calculate the local minimum energy conformation and the corresponding heat of formation for your compound.

Theory   Select AM1 from the *Theory* drop-down menu.

Charge   **Should display a "1" for +1 charge. If displaying "0" you need to change it to "1".**

Multiplicity   Leave the multiplicity at Singlet.

Leave *Preview Input File* unchecked. Do not select Advanced Options.

Click on the Submit Job link or click on the arrow to the right at the bottom of the screen.

7. This will return you to the Job Manager Page, where you will see your job listed. In the status column you will see *Running* in red. Click on the Refresh button at the top-left corner of the screen.

8. Your job's status should now say *Complete* in green. Click on the View link to the right of the job's status to see the results of the calculation.

9. Click on the Job Manager button to return to the Job Manager screen.

B.3 1-Pentenyl Secondary Allylic Carbocation

1. From the Job Manager page, find the geometry optimized model of 1-pentene that you constructed in step B.1. Click on the <u>View</u> link to the right of the job's status.

2. Click on the New Job Using This Geometry button just below the model window. This will start a new calculation using the old geometry as a starting point.

3. We need to select one of the hydrogens to delete on C3 (see below).
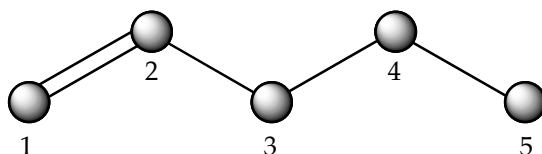
It does not matter which hydrogen you choose on C3 as they are equivalent.

4. With the hydrogen selected choose the "Adjust" menu and select "Delete Selection." The selected hydrogen and bond will be deleted.

5. Now click on C3 still using the adjust tool. With the carbon selected choose the "Adjust" menu and select "Charge." A pop-up widow will appear allowing you to change the charge on the carbon atom. In the pop-up window type 1 for a +1 charge and hit the "OK" button. The carbon should now be labeled with a "+1" charge.

6. Click on the <u>Job Options</u> link to the left of the model window or the arrow to the right on the bottom of the screen.

7. On the Configure Mopac Job Options page,

Job Name Give your molecule its standard IUPAC name, followed by an underscore and an identifier of your choice, such as 1-pentenyl_secondary_allylic_cation_geom. Use any identifier you find useful, as long as the molecule name begins with the IUPAC name and an underscore.

Calculation **Select <u>Geometry Optimization</u> from the *Calculation* drop-down menu**. This will calculate the local minimum energy conformation and the corresponding heat of formation for your compound.

Theory Select <u>AM1</u> from the *Theory* drop-down menu.

Charge **Should display a "1" for +1 charge. If displaying "0" you need to change it to "1".**

Multiplicity Leave the multiplicity at Singlet.

Leave *Preview Input File* unchecked. Do not select Advanced Options.

Click on the <u>Submit Job</u> link or click on the arrow to the right at the bottom of the screen.

8. This will return you to the Job Manager Page, where you will see your job listed. In the status column you will see *Running* in red. Click on the Refresh button at the top-left corner of the screen.
9. Your job's status should now say *Complete* in green. Click on the <u>View</u> link to the right of the job's status to see the results of the calculation.

10. Click on the Job Manager button to return to the Job Manager screen.

Questions for Analysis

Part A
1. Draw structures of the three carbocations from part A and list their heats of formation under each structure.

2. Use the "View" button located next to the partial charges on the results page of each model to explore the partial charges on the carbons. Is there a correlation between the partial charge on each carbocation and the heat of formation of the ions. Explain.

3. What is happening to the partial charge on the neighboring carbons (the carbons connected to the carbocations) as compared to carbons not directly connected to carbocations?

4. Do you see evidence of inductive effects that would explain the greater stability of tertiary carbocations over secondary and primary carbocations. Explain.

5. Reset the viewer using the "Reset" button below the model. Use the selection tool (the straight arrow icon) to select a carbon atom in the model. Hold down the shift key and select an adjacent carbon. The bond length between the two atoms will be displayed. Click off the model to deselect all items. Explore the effect the carbocations have on the carbon-carbon bond lengths. Again draw structures of the three isomers and include the carbon-carbon bond lengths. Do you notice a trend in the carbon-carbon bond length as you move away from the carbocation center? Explain.

6. Is there a similar trend with the carbon-hydrogen bond lengths?

7. By using the selection tool and the shift key you can select three atoms. With three atoms selected the model window displays the bond angle between the three. What bond angles do you find around the carbocations? Is this what you expected to find? What hybridization do these carbocations display?

Part B
1. Draw structures of the two carbocations from part B and list their heats of formation under each structure.

2. Use the "View" button located next to the partial charges on the results page of each model to explore the partial charges on the carbons. Is there a correlation between the partial charge on each carbocation and the heat of formation of the ions. Explain.

3. Focus on the partial charges on the allylic cation. Two of the carbons in this molecule bear partial positive charge rather than just one carbon, explain.

4. On paper, resonance theory seems to indicate that carbons 1 and 3 should have equal positive charge, but is this what we observe? Why does carbon 3 have a greater positive charge? Do the resonance contributor contribute equally?

5. Which carbon is more likely to be attacked by a nucleophile, carbon 1 or carbon 3 for the allylic carbocation. Explain your reasoning.

6. Would you expect more extensive conjugation to stabilize, destabilize or have little effect on the stability of an allylic carbocation. For example: would the difference in energy between 1,3,5-nonatriene with a cation in the allylic position of carbon 7 verse the secondary cation on carbon 8 to be greater than, less than, or about the same as the system we have explored? You have the tools to find out! What about the analogous benzyl system (propyl-benzene)?