

Introduction to Molecular Modeling with SpartanModel and Spartan 04

Molecular models provide another way to look at and play with molecules. You will use several kinds of models in this class because each has its own advantages for play.¹

This activity uses a computer modeling tool: SpartanModel (or SpModel).² Future activities will also use Spartan 04 for Windows (or Sp04).³ The two programs are similar in many respects, so I hope that you will use SpModel often because it is good preparation for Sp04.

You may not realize it, but many kinds of computer models can be built. SpModel and Sp04 are like Swiss Army knives in this respect; they contain tools for building several kinds of models. Different modeling techniques might yield different “views” of a molecule, so please pay attention carefully to my modeling instructions. (Note: I have not provided instructions for the use of SpModel. Brief instructions are provided in your textbook and more detailed instructions are provided in the PDF tutorial that comes with the software.)

Purpose

A Lewis structure shows that neutral N makes three bonds and holds one lone pair. If the bonds are all single bonds, nitrogen adopts a pyramidal (or pseudo-tetrahedral) geometry.

If the lone pair is partially delocalized into a neighboring bond, the geometry of N might change and so might its ability to share the lone pair with other molecules:

\[
\begin{align*}
\text{NH}_2 & \quad \text{vs.} \quad \text{NZH} \\
\text{H} & \quad \text{N} & \quad \text{Z} & \quad \text{H}
\end{align*}
\]

Consequences:
- Shortened NZ bond
- More planar N
- Less e-rich N

This activity explores possible consequences of N lone pair delocalization. At the most basic level, it will provide practice making and using models, drawing resonance forms, and thinking about resonance. I hope, though, that you will also learn which functional groups contain a delocalized N lone pair because this knowledge will be useful throughout the year (and, if you mull over these delocalized molecules, you can also discover a general rule for lone pair delocalization).

Activities presented here:

1. Retrieve/build models with SpModel. Measure distances, angles, and charges. Examine potential maps and reset color scale.

¹ Play means any activity that allows you to adjust or manipulate something and see the consequences of your actions without incurring any significant cost to yourself or others. Play can be serious (examples: molecular modeling, climate modeling, etc.)
² Download from the Learning by Modeling CD.
³ Located on the computers in the chemistry computer lab, Rm. 203.
SpartanModel activity #1

✓ Preliminaries: Whenever you use SpModel or Sp04, always maximize the model window so that it occupies the full-screen (on a PC, click the Maximize button in the upper right corner). This is more than a convenience issue; it also guarantees that all SpModel data will appear on the screen.

Data collection for normal amines

✓ Retrieve the following models: cyclohexylamine, dimethylamine, quinuclidine, benzylamine, and serine.

✓ Measure CN bond distance(s) and record them on the worksheet (see last page). Use the same units for all distances (pm or Å) and record this on the worksheet too.

✓ Measure X-N-Y bond angles and record the angles and the X/Y atoms on the worksheet.
  
  ○ Optional: Bond angles vary for different X/Y combinations. Another way to determine whether N is closer to pyramidal (all angles 109.5°) to trigonal planar (all angles 120°) is to calculate and report the mean X-N-Y bond angle. Or, you might calculate the sum of X-N-Y angles, which varies from 328.5° (= 3 x 109.5°) to 360° (= 3 x 120°).

✓ Measure the atomic charge on N and record this on the worksheet.

✓ Examine the potential map, particularly the portion of the map surrounding N.
  
  ○ First, note the relative positions of the electron-rich (lone pair) region and the three N-C(H) bonds. What does this suggest to you about the shape of the lone pair orbital? (Does most of the orbital lie on one side of N?)

  ○ Second, note whether the lone pair region is consistently red or red-orange. The maps all use the standard color scale (-40 → +40 kcal/mol), so what does the color tell you about the potential near the N lone pair?

  ○ Third, display the map’s properties and reset the potential range to its default value. Determine the actual potential near the N lone pair and record this on the worksheet.

Data analysis for normal amines

✓ You have collected four types of data. How uniform are the numerical values? Which data might be useful indicators of a localized lone pair? (To put it another way, do any data ever wander off without a corresponding change in the other data?) Are there any outlier compounds in this set? (Note: you do not have to give me your answers, but you should decide on your answers before looking at the compounds in the next set.)

---

4 I have tried to spell each name exactly as it appears in the SpModel database.
5 Select Properties from the Display menu to open the Properties window. Click on the map to make the map properties dis/appear. Click Reset to restore the default color scale. Or, type -40 and +40 in the From: and To: boxes to restore the standard color scale (press Enter on the keyboard after typing each number).
Data collection for (possibly) unusual amines

- **Build** models of the 4 molecules drawn below (building tips are provided for each). After you finish each one, you should find that you have a “hit” in the SpModel database (“hits” appear at the bottom of the SpModel window). Retrieve the database model so that you can work with a more polished and detailed model (only retrieved models contain potential maps and computer-optimized geometries). Record the name of your retrieved molecule on the worksheet.

1. **NHN** building tips:
   - Rings: cyclopentane
   - Make bond 2x

2. **NH2 O** building tips:
   - Rings: benzene
   - Groups: amide

3. **NH2 NH2 O** building tips:
   - Groups: amide
   - See 1st model

4. **NH2 NH2 O** building tips:
   - Groups: alkene
   - Make bond

- **After you build (and retrieve) each model, perform the data collection steps (distance, angle, charge, potential) for the designated N only.**
Data collection for (possibly) unusual amines

✓ According to your data, which molecules contain N with a delocalized lone pair? (Note: some ideas about possible consequences of lone pair delocalization are listed on p. 1.) Indicate on your worksheet whether your decision is supported by distances, angles, charges, and/or potentials.

  o Note: single bond distances may shrink for other reasons than lone pair delocalization. To get a feel for this, retrieve the following models: ethane, acetone, and toluene. Measure and record the CC single bond distance between CH₃ and its neighboring C on the worksheet. If this bond is always a pure single bond, how much of a decrease in bond distance can be assigned to factors other than lone pair delocalization? Record your answer on the worksheet.

✓ For each molecule that contains a delocalized lone pair, draw three formulas on your worksheet:

  o the major resonance form (essentially identical to the “building” formulas given above, but includes lone pairs)
  o the most important minor resonance form (the one that moves the lone pair to a bonding position)
  o a dashed line formula that shows the superposition of these resonance forms

Analysis of poly-N molecules

✓ Retrieve the following molecules: serotonin, zidovudine (AZT)

✓ Draw the major resonance form of each molecule on your worksheet.

✓ Using the model's properties, label each N lone pair in your formula as localized or delocalized
Name _______________________________________

**Normal amines**

<table>
<thead>
<tr>
<th>Amine</th>
<th>NC bond distance (pm or Å)</th>
<th>X-N-Y bond angle (°)</th>
<th>N atomic charge</th>
<th>N lone pair potential (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C–C bond distances (pm or Å) in:

Ethane ________ Acetone ________ Toluene ________

Bond distance shrinkage in a single bond *not* due to lone pair delocalization (pm or Å) ________

(continues on next side)

---

6 Scratch out the units that are not being used.

7 List the angle and X and Y. For example, for cyclohexylamine “113.35 H C”

8 This is the default energy unit for electrostatic potential in *SpModel* (and *Sp04*)
## (Possibly) Oddball amines

<table>
<thead>
<tr>
<th>Amine⁹</th>
<th>NC bond distance (pm or Å)</th>
<th>X-N-Y bond angle (°)</th>
<th>N atomic charge</th>
<th>N lone pair potential (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Molecules with delocalized N lone pairs and data that supports lone pair delocalization (circle each):

1. Name __________________ distance angle charge potential
2. Name __________________ distance angle charge potential
3. Name __________________ distance angle charge potential
4. Name __________________ distance angle charge potential

Formulas of molecules with delocalized N lone pairs

---

⁹ Enter the name of the compound that you retrieved from the SpModel database

(STAPLE additional sheets if needed and write your name on these sheets):