

## SpartanModel Modeling Activity #2: Is BCG a Resonance Hybrid?

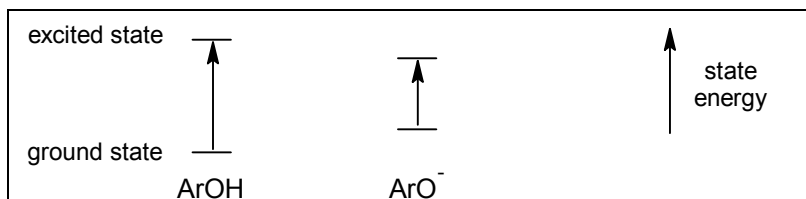
### Overview

This activity illustrates some of the ways in which molecular models can be used to detect resonance hybrids, i.e., molecules that cannot be described adequately by a single Lewis structure. Some of the work that you do here should be included in your lab report (see below). Full instructions for writing your lab report can be found in the online lab manual.

### Background

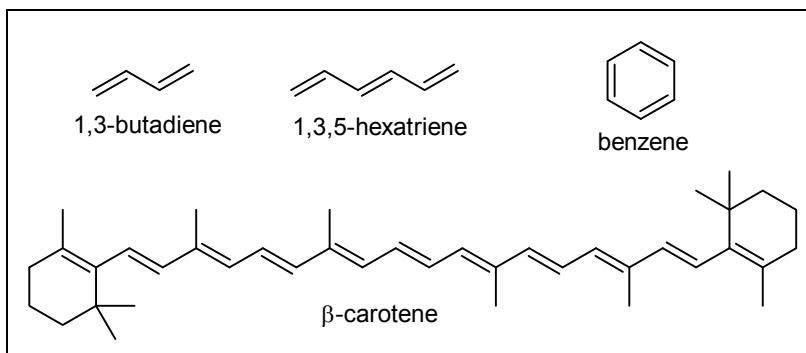
In the lab we noticed that the color of our BCG solutions depends on pH. The conclusion we drew was (de)protonating a specific functional group in BCG affects the molecule's UV-vis spectrum.

In most molecules, the absorption of UV-visible light triggers electronic excitations. The molecule, which normally exists in its lowest energy form or "ground state," absorbs light energy and gets promoted to an "excited state". The excitation is called "electronic" because the electrons are moving in a new, more energetic way.

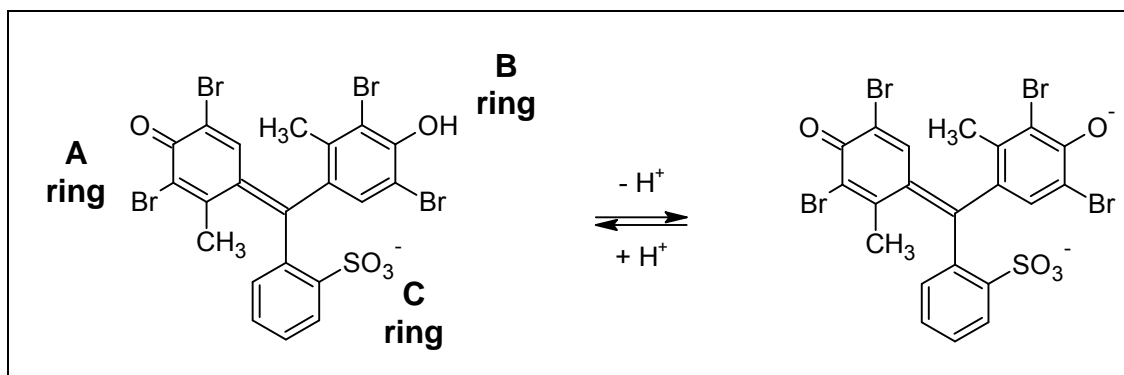


There is a close connection between molecular structure and excitation energy. Removing a single proton can influence a molecule's electron pattern (ground state energy) and also the way electrons move in the excited state (excited state energy). This will change the energy gap between these states, the UV-vis spectrum, and the molecule's color.

Loudon 15.2C provides a useful rule-of-thumb for connecting structure and excitation energy: "*The longer the conjugated  $\pi$ -system (that is, the more consecutive conjugated multiple bonds), the higher the wavelength of the absorption.*" To make sense of this, you need to know that a conjugated  $\pi$ -system is simply an alternating chain of double and single bonds. The smallest conjugated  $\pi$ -system is 1,3-butadiene. 1,3,5-Hexatriene, benzene, and  $\beta$ -carotene contain longer extensions of this theme.



If Loudon's principle is correct, the blue form of BCG ( $\lambda_{\max} > 620 \text{ nm}$ )<sup>1</sup> must contain a longer conjugated  $\pi$ -system than the yellow form ( $\lambda_{\max} \sim 450 \text{ nm}$ ). Yellow BCG (left) and blue BCG (right) are shown below. Is it obvious that one contains a longer conjugated  $\pi$ -system?



Conjugated systems involving only carbon are easy to identify, but systems that involve heteroatoms and charged atoms are more difficult. Many of them are resonance hybrids, so this modeling activity focuses on this problem: how can you recognize a conjugated resonance hybrid?

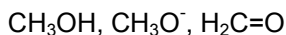
You will begin by building some anions and noticing whether the charge appears to be localized over a single atom or delocalized over multiple atoms. If the latter, you will draw two or more resonance structures to properly describe the anion.

Second, you will inspect the geometry of the delocalized anions by examining bond distances involving the charged atoms. These should support your designation of these anions as "delocalized."

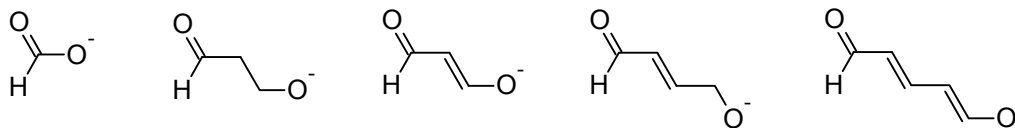
Finally, for each delocalized anion, you will build its neutral conjugate acid and examine the geometry again. You will be trying to establish whether the protonated atom is as tightly connected to the adjacent conjugated  $\pi$ -system as it was in the anion.

### Instructions

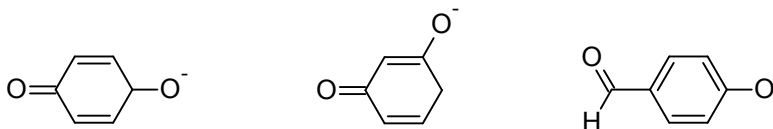
1. **Standard bond distances.** Build each of these molecules, optimize their geometries using the **Properties** button and record their CO bond distances. *For our purposes today*, these molecules should not be regarded as resonance hybrids.



2. **Anions – Charge.** Build each of these anions (list goes on to next page), optimize their geometries, and display their potential maps (do not delete any model; just keep making new ones). Circle each anion for which the charge appears to be delocalized roughly equally over both oxygens. Return to **Properties** and click on each oxygen atom to obtain its atomic charge. The charges should be consistent with the information obtained from the map, but note any map/charge discrepancies and show them to your instructor.



<sup>1</sup>  $\lambda$ , the Greek *lambda*, is commonly used to denote wavelength.  $\lambda_{\max}$  is the wavelength for which light absorption is a maximum. My values are based on the incomplete spectrum available from Wikipedia.



- Anions – Geometry/Resonance.** For each delocalized anion, measure the two CO bond distances and compare them to your standard distances from step 1. Assign a bond order to each CO bond (single, double, or partial double). In the table on the next page, draw two resonance structures that adequately describe your delocalized anion. Remember, the anion is a hybrid of these structures so “averaging” the patterns in your drawings should lead to your model’s charge distribution and bond distance patterns.
- Neutral conjugate acid.** For each delocalized anion, replace the  $O^-$  with an OH (you can either rebuild the model from scratch or try this shortcut: click the **Add Fragment** button, click  $-OH$ , and *double-click*  $O^-$ ). Optimize the model’s geometry and measure the two CO bond distances. Have they changed in a way that moves them closer to your standard distances? If they have, this suggests that the OH group is “disengaging” from the adjacent  $\pi$ -system, i.e., the  $\pi$ -system is getting shorter by one atom. Mark the table on the next page as to whether the  $\pi$ -system is shorter or not.

### (Extra) Instructions for Lab Report

In addition to the instructions in the online manual, attach your table (next page) and your answers to the following questions to your lab report.

- Re-draw blue BCG, then draw a second resonance structure that shows how the negative charge on B-ring  $O^-$  can be shifted to A-ring O. Remember, a resonance structure must be drawn according to the same rules as a Lewis structure, i.e., show all nonbonding electrons and formal charges. (For simplicity’s sake, replace the C-ring with ‘Ar’.)
- Choose two delocalized anions from the modeling activity and re-draw their resonance structures. Add curved arrows to each resonance structure showing how it can be converted to the other structure.
- All of the localized anions seem to share one common structural feature. See if you can find it. Then tell me what you think it is.

**Modeling Data Table** (complete; attach to your lab report)

<b>Delocalized Anion Resonance Structures</b>	<b>CO bond distances (Å)</b>	<b>Does OH disengage from <math>\pi</math>- system?</b>