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# The “Big Dog–Puppy Dog” Analogy for Resonance

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When introducing covalent bonding, teachers often start with the concepts of valence electrons, Lewis dot structures, and the octet rule. We conveniently characterize the covalent bonds within a molecule or polyatomic ion in terms of certain bond properties, namely, **bond order**, **bond length**, **bond energy**, and **formal charge**.<sup>1</sup> For instance, the cyanide anion ( $\text{CN}^-$ ) has a total of  $4 + 5 + 1 = 10$  valence electrons, so its Lewis dot structure would be  $:\text{C}\equiv\text{N}^-$ , with a C–N bond order of 3 and a formal charge of  $-1$  on the C atom.

Further discussion, usually within the context of valence bond theory, allows students to distinguish between  $\sigma$  and  $\pi$  **bonding pairs** of electrons shared between two nuclei, and **lone pairs** of electrons, which circulate in the region near a single nucleus and thus “belong” to that atom. Three-dimensional models and pictures showing hybridized orbitals help students to “see” the difference between lone pairs,  $\sigma$  bonds, and  $\pi$  bonds. It is relatively easy to see how a single pair of electrons shared between two atoms in a  $\sigma$ -bonding orbital represents a single bond with a bond order of one, whereas two pairs of electrons shared between two atoms in a  $\sigma$  bonding orbital and a  $\pi$  bonding orbital represents a double bond with a bond order of two.

The going gets rougher for most students, however, when they try to explain resonance structures,  $\pi$  bond delocalization, and fractional bond order. Consider the stalwart benzene molecule,  $\text{C}_6\text{H}_6$ . Figure 1 shows that two equally correct iso-energetic Lewis dot structures, otherwise known as **resonance structures**, may be drawn for this molecule. But resonance structures **1a** and **1b** represent extremes, in a sense, and they assume that  $\pi$ -bonding pairs of electrons are **localized** to specific C–C bonding positions. Considering that the average C–C bond order is 1.5 in benzene (9 bonding pairs/6 bonding positions),<sup>1</sup> structure **1c** is a more realistic view of what the bonding in benzene really looks like. In this last structure, the three  $\pi$ -bonding pairs of electrons have been “smeared” around the ring; that is, they have been **delocalized** equally over all six C–C bonding positions. In summary then, the individual resonance structures **1a** and **1b** (with three C–C single bonds and three C=C double bonds) are less realistic than the averaged or “hybrid” structure **1c** (with six C–C “1.5” bonds). Measurements of C–C bond energy and bond length do in fact support this conclusion.

The famous “dragon + unicorn = rhinoceros” analogy has been used in organic chemistry texts since the early 1960s to illustrate the relationship between localized individual resonance structures like **1a** and **1b** on the one hand, and delocalized hybrid structures like **1c** on the other. Rhinoceroses, like dragons, have thick scaly skin and are easily aroused to anger; they also, like unicorns, have a single horn in the middle of their forehead. Hence one might consider the dragon and the unicorn to be individual resonance structures that when combined in a resonance hybrid yield a rhinoceros.

This analogy stresses the important notion that individual resonance structures do not really exist. Just as dragons and unicorns exist only in fairy tales, individual resonance structures exist only on paper; they represent extreme forms that are never found in real life. On the contrary, a rhinoceros is a real live animal. The resonance hybrid (structure **1c** in Fig. 1) with its delocalized  $\pi$  bonds is our best representation of the benzene molecule as it exists in the real world.

## The Problem

Although introductory chemistry students can readily be taught how to draw individual resonance structures and how to calculate fractional bond orders and formal charges, they often fail to grasp the significance of these results. On a molecular level, what does resonance really mean?

Consider the nitrite anion ( $\text{NO}_2^-$ ) depicted in Figure 2. One can draw resonance structures showing that three pairs of electrons (two  $\sigma$ -bonding pairs and one  $\pi$ -bonding pair) are distributed over two bonding positions, giving an average bond order of 1.5. But what does this mean? Mathematically, students can perform the bond order calculation, and they can even grasp that a “1.5” bond should lie somewhere between a single and a double bond in terms of bond strength and length. But why are  $\sigma$  bonds always localized, whereas  $\pi$  bonds may be delocalized? What does a resonance hybrid really look like? What is the significance of the fact that the average formal charge on each oxygen atom in  $\text{NO}_2^-$  is  $-1/2$ ?

Simply showing overhead transparencies of overlapping  $p_z$  orbitals forming delocalized  $\pi$  bonding orbitals is just not enough to fix in students’ minds the nature of delocalized  $\pi$  bonds. Such drawings tend to be too complex and confusing. Most students do not get from these pictures a clear notion of the dynamic nature of delocalized  $\pi$ -bonding electrons.

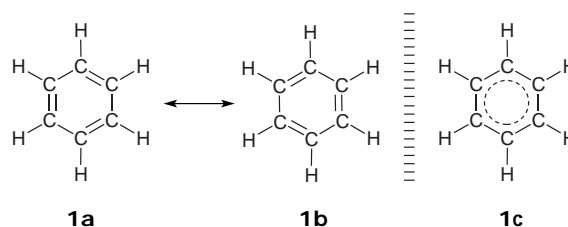


Figure 1. Benzene resonance structures.

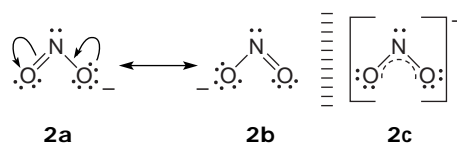


Figure 2. Nitrite anion ( $\text{NO}_2^-$ ) resonance structures.

## The Analogy

To better visualize  $\pi$  bond delocalization and to explain fractional bond order and formal charge in hybrid resonance structures, I have devised the “big dog–puppy dog” analogy (see Fig. 3). This analogy depicts the resonance structures of  $\text{NO}_2^-$  by envisioning a dog run with three fixed points (O, N, and O nuclei), connected by two wires. A puppy dog is bound to each O–N run by a small-ringed chain; owing to the large diameter of the fixed points and the small ring attached to the wire, each puppy dog is localized to a specific O–N run. One puppy dog thus occupies the left hand O–N run, the other one occupies the right; these dogs represent  $\sigma$ -bonding electrons. They move freely in the space between the “N” and their respective “O” fixed points.

A single big dog is bound to the run by a large-ringed chain; owing to the large diameter of the ring, this big dog has access to *both* O–N runs. He can run all the way from the left-hand O fixed point, across the middle N, to the right-hand O fixed point. He therefore represents  $\pi$ -bonding electrons. Furthermore, we can imagine that the big dog chases a bunny rabbit; the rabbit represents the “extra” electron that is responsible for the formal  $-1$  charge on the singly bonded N–O oxygen atom (see Fig. 2, structures **2a** and **2b**). The rabbit “feeds” at either the left- or the right-hand O fixed point and can run between these points through her underground burrow. Rabbits’ self-preservation instincts being what they are, the scared bunny will always be found on the side of the run opposite the big dog. Similarly, the extra electron and the formal  $-1$  charge is always found on the single-bonded  $\text{O}^-$ ; on the side opposite the neutral double-bonded  $=\text{O}$ .

This analogy has several advantages. First of all, it is graphic, humorous, and not overly complex. Students are entertained as they come to understand on a gut level the meaning of localized  $\sigma$ -bonding electrons (puppy dogs) and delocalized  $\pi$ -bonding electrons (big dog). I should add that rarely, a student will point out a problem with the analogy: Why don't the puppies chase the rabbit? In other words, why does only the  $\pi$  bond determine on which side the single bond N–O $^-$  resides? My answer to this semi-serious criticism is that we must assume that the rabbit is too big and the puppies are too small for them to take up the chase.

The analogy also gives a good feeling for the dynamic nature of chemical bonds: electrons move! Individual resonance structures represent static snapshots of a molecule, with the electrons (dogs) momentarily frozen as if in a strobe light. In Figures 1 and 2, individual resonance structures **a** and **b** are the static snapshots. The true nature of the molecule is represented more realistically by the resonance hybrid, form **c**. Here we see that pairs of  $\pi$ -bonding electrons may actually be spread evenly over more than one bonding position. Furthermore, for the polyatomic nitrite anion, the “extra” electron and its accompanying  $-1$  charge are shared equally by the two oxygen atoms, as depicted in the resonance hybrid form **2c** in Figure 2.

In the dog–bunny analogy, both the big dog ( $\pi$ -bonding electrons) and the bunny (extra electron) are free to roam over the entire  $\text{NO}_2^-$  molecule; we imagine them constantly running back and forth. Any single snapshot will find the big dog on one side and the bunny on the other; out of 100 snapshots, 50 should find the big dog on the left and the bunny on the right, whereas the other 50 should have the

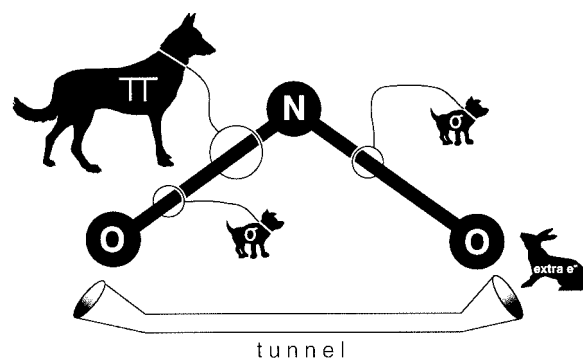


Figure 3. The Big Dog–Puppy Dog pictorial analogy for resonance. The molecule analogized in this diagram is  $\text{NO}_2^-$  (see Fig. 2 for the “traditional” resonance structures). In the pictorial analogy, the O–N–O circles represent fixed points on the dog run, or nuclei in the polyatomic ion. The two puppy dogs are restricted to individual dog runs; they represent localized  $\sigma$ -bonding pairs. The big dog can roam over both runs; he represents a delocalized  $\pi$ -bonding pair. The bunny rabbit may tunnel from one O to the other to escape the pursuing big dog; she represents the “extra” electron that gives  $\text{NO}_2^-$  its negative charge.

opposite configuration. Accordingly, on average, each O–N run can be said to have one puppy dog, half of a big dog, and half of a bunny rabbit; the average O–N bond order is thus 1.5, and the average charge on an O atom is  $-1/2$ . Although there is no such thing as half a dog, if every other family in the United States owns a dog, then the average American family does in fact own half a dog. Similarly, there is no such thing as half a bond (at least not according to valence bond theory), but the average N–O bond in  $\text{NO}_2^-$  does contain 1.5 bonding pairs of electrons.

In closing, it is important to point out that the Big Dog–Puppy Dog analogy for resonance is based in valence bond theory and does not attempt to capture the intricacies of quantum mechanics. Molecular orbital theory, which admittedly is a more accurate portrayal of covalent bonding, is notoriously awkward to visualize. Furthermore, MO theory is often taught after valence bond theory, in a separate chapter of the introductory chemistry textbook. The Big Dog–Puppy Dog analogy may provide students who have not yet encountered MO theory with a graphic visualization scheme that explains resonance structures and delocalized  $\pi$  electrons from the perspective of valence bond theory. The analogy is vivid and graspable and is therefore a good one for introductory chemistry students.

## Acknowledgment

I would like to thank Carla Beebe for her critical reading of the manuscript and her helpful suggestions.

## Note

### 1. Definitions:

**Bond order (BO):** The number of bonding pairs of electrons shared between two atoms at a single bonding position.

**Bond length:** The distance between the nuclei of two bonded atoms.

**Bond energy:** The amount of energy that must be supplied in order to break a specific bond.

*Formal charge (FC):* The charge on an atom in a molecule, calculated by assuming equal sharing of all bonding electrons.

$$FC = (\text{group \#}) - (\text{\# of lone pair } e^{-}\text{'s}) - 1/2(\text{\# of bonding } e^{-}\text{'s})$$

Discussions of bond order, length, energy, and formal charge can be found in any standard introductory chemistry text; see for example Kotz and Purcell's *Chemistry and Chemical Reactivity*, 2nd ed.; Saunders: Philadelphia, 1991; pp 374–389.