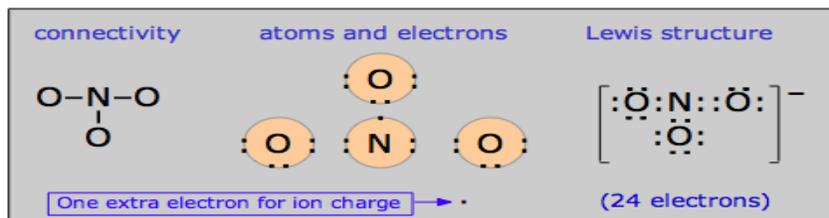# MULTIPLE EQUIVALENT STRUCTURES: RESONANCE

There is a rather large class of molecules for which one has no difficulty writing Lewis structures; in fact, we can write more than one valid structure for a given molecule! Consider, for example, the nitrate ion NO_3^-. We can develop a Lewis dot formula satisfying the octet rule as follows:

According to this structure, the ion contains two N–O single bonds and one N–O double bond. But there is no special reason to place the double bond where it is shown in the diagram above; it could equally well go in either of the other two locations. For this molecule, then, we can write three equally valid structures:
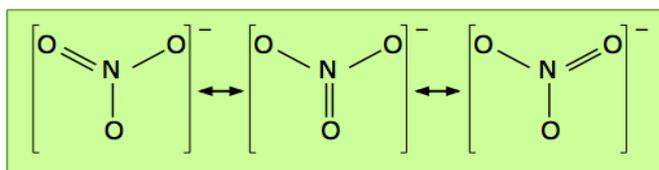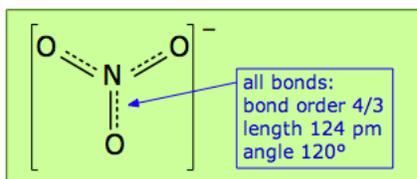

The double-ended arrows indicate that the nitrate ion is a superposition of all three structures, and this is supported by experimental evidence which shows that the three oxygen atoms are chemically identical, that all three bonds have the same

length, and that the molecule has trigonal symmetry (meaning that the three oxygens are geometrically equivalent.)

> *The term resonance was employed to describe this phenomenon in the 1930's, before chemical bonding became better understood; the three equivalent structures shown above are known as resonance hybrids. The choice of the word "resonance" was unfortunate because it connotes the existence of some kind of dynamic effect that has led to the mistaken idea that the structure is continually alternating between the three possibilities.*

In actual fact, the nitrate ion has only one structure in which the electrons spread themselves evenly so as to make all three N–O links into "1-1/3 bonds"; we describe them as having a bond order of 4/3. The preferred way of depicting a molecule that has more than one equivalent bonding structure is to use dashed lines to indicate the "fractional" bonds as shown here.

Very similar structures can be written for sulfur trioxide SO_3, and for the carbonate ion CO_3^{2-}.

> *In writing out resonance structures, it is important to bear in mind that only the electron pairs can be moved around; the atoms must retain the same connectivity. In some cases it is necessary to move electrons to locations that*

would produce a positive charge on one atom and a negative charge on the other. Since the separation of electric charge always costs energy, such resonance forms will tend to be less stabilizing and will not be as important contributors to the overall structure as those in where there is no charge separation.

Since electrons in molecules tend to arrange themselves into configurations that give the lowest possible energy, it is not surprising that the resonance hybrid represents a more stable (i.e., strongly bound) molecule than does any one of the contributing structures.

There is a good quantum-mechanical rationale for this; according to the Heisenberg uncertainty principle, the energy of the electron will be more uncertain as its position is more exactly specified. Since energies cannot be negative, the more "uncertain" the energy can be, the higher it can be. If an electron is spread out over two or three bonds in the hybrid instead of being confined to the space between only two atoms, its exact location is much less exactly known, and so its energy will be less uncertain, and therefore lower.

Carboxylic acids

This idea is embodied in the statement you will often see, particularly in the older literature, that a given structure "is stabilized by resonance".

This jargon has been used, for example, to explain the acidity of the -COOH group found in organic acids. Dissociation of a carboxylic acid such as formic acid yields a carboxylate ion –COO–which can be represented by two equivalent structures. These are more realistically interpreted as a single structure in which the C–O bond order is 1.5:
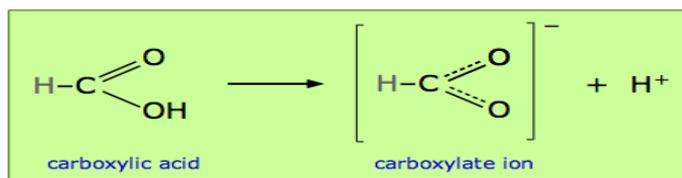

The idea is that resonance is only possible when the proton has been lost, and that the lower energy of the "resonating" structure provides the driving force for the loss of the proton, and thus is the source of the acidity carboxylic group. (By the way, this view of the cause of carboxylic acidity has been criticized; other factors that may well be more important are also involved.)

The Benzene ring

Perhaps the most well known molecule whose structure must be represented as a resonance hybrid is benzene, C6H6. The structure of this molecule had long been something of a mystery, in that it was difficult to understand how this formula could be consistent with the well-established tetravalence of carbon in organic compounds.

The breakthrough came in 1865 when the German chemist August Kekulé proposed that the molecule is based on a hexagonal ring of carbon atoms as shown at the left below.
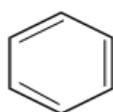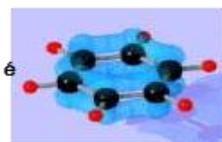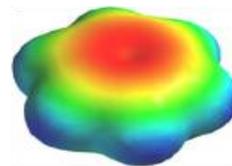

Kekulé
modern
(Hydrogen atoms at vertices are not conventionally shown)
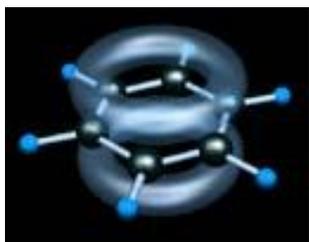
schematic showing π-orbitals (blue)

computer modeling of electron density

However, this structure is not consistent with the chemistry of benzene, which does not undergo the reactions that would be expected of a molecule containing carbon-carbon double bonds. Such compounds are normally quite reactive, while benzene, in contrast, tends to be rather inert to all but the most powerful reagents.

This apparent discrepancy disappeared after the resonance hybrid theory was developed; benzene is regarded as a hybrid of the two structures shown in the center above, and it is often depicted by the structure at the right, in which the circle represents a "half bond", so that the bond order of each C–C bond is 1.5. Bond length measurements are entirely consistent with this interpretation; they are almost exactly halfway between the values found in compounds known to contain single and double bonds.

A more realistic representation of the benzene molecule shows the two components of its bonds. The "sticks" joining adjacent carbons constitute "half" of the carbon-carbon bonding, while the circular charge clouds above and below the ring together make up the other "half". The details of this bonding arrangement are discussed in the section on the hybrid orbital model of bonding.