

# MOLECULES DIFFERENT CASES

## Electron structures without molecules

Although there are many violations of the octet rule, most electron dot structures that one can write down in accordance with this rule and its general scope of validity correspond to molecules that actually exist. Sometimes, however, we are surprised to find that the molecules corresponding to an apparently reasonable Lewis formula are not known.

In some cases, this has been shown to be a consequence of the very high chemical reactivity of the molecules. Thus hypofluorous acid, HOF, has never been isolated, although its chlorine analog is well known. It was not until 1967 that its short-lived presence was detected spectroscopically. It is now believed that the molecule is stable, but that the products obtained when it reacts with itself are so much more stable that it decomposes almost as fast as it is formed:



Other molecules having proper Lewis structures but no apparent existence may be stable only at very low temperatures; examples are O<sub>4</sub> and H<sub>2</sub>O<sub>4</sub>.

*The fluorate ion,  $\text{FO}_3^-$ , has also never been detected, even though analogs containing the other halogen elements are well known. The problem here may well lie with the very small fluorine atom, which would allow the oxygens to approach so closely that they would repel each other.*

Small size is also suggested as the reason for the non-existence of the nitrogen analogs of the sulfate and sulfite ions. These would have the formulas  $\text{NO}_4^{3-}$  and  $\text{NO}_3^{2-}$ . Here, the problem is believed to be the high charge density: it costs a lot of energy to squeeze this much electric charge in such a small volume. Sulfur, having a larger radius, forms larger ions having lower charge densities, and the total charge would also be only  $-2$  instead of  $-3$ .

### **Molecules without electron structures**

There are also examples of molecules whose existence is beyond question, but for which no satisfactory Lewis structures can be written. Two examples are the triiodide ion  $\text{I}_3^-$ , and the bifluoride ion  $\text{HF}_2^-$ . The triiodide ion is a well known species found in aqueous solutions containing iodine and iodide ions:

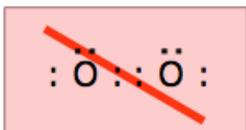
The bifluoride ion is formed in a rather similar way in hydrofluoric acid solutions containing fluoride ion:

Try writing electron-dot structures for these two species, and you will see the problem!

## Paramagnetic molecules

As you know, electrons tend to pair up in atoms and molecules so that their spins cancel out. If this does not happen— either because there is an uneven number of electrons or it is energetically unfavorable, then the species is said to be paramagnetic. Paramagnetic substances are attracted to a magnetic field, but unlike ferromagnetic materials such as iron, they do not retain their magnetic properties (act as magnets) in the absence of an applied field. Most molecules possess an even number of electrons and are diamagnetic.

### Dioxygen



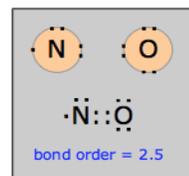
The most abundant paramagnetic molecule in our world is the

ordinary oxygen molecule which has twelve electrons. It is easy to write a proper Lewis structure for O<sub>2</sub> that places an octet around each oxygen atom and a double bond between them. However, it takes only a simple experiment to show that the electrons in dioxygen cannot all be arranged in pairs: if you place a magnet near some liquid oxygen, the liquid will be drawn to the magnet. This can only mean one thing: there are at least two unpaired electrons in the O<sub>2</sub> molecule. A more careful experiment shows that this number is exactly two. Are they in the bond or are they non-bonding electrons? You can decide this by sketching out a few possible structures.

The paramagnetism of oxygen is an anomaly in terms of the Lewis theory, although it is predicted by a more comprehensive theory that we will look at later. There are, however, a few other molecules that we would expect to be paramagnetic simply because they contain an odd number of valence electrons.

## Nitric oxide and nitrogen dioxide

Nitrogen, having five valence electrons, forms two well-known odd-electron molecules with oxygen. Nitric oxide, NO, a colorless, odorless, paramagnetic gas, is the simplest stable odd-electron molecule known. It is clear that no structure conforming to the octet rule is



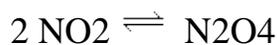
possible. The Lewis structure shown here is somewhat misleading; chemical and physical evidence suggest that the unpaired electron is not localized on the nitrogen atom, but extends over the entire molecule.

For example, if the structure were really  $\cdot\text{NO}$ , then we would expect the molecule to readily form a dimer  $\text{ON}:\text{NO}$ , but this is not observed. Bond-length measurements indicate that the N–O bond order is 2.5.

Nitric oxide has a remarkably rich chemistry. Until recently, its most famous role was as a precursor to photochemical smog. (The oxide is formed when fuels such as gasoline are burned at high temperatures in the presence of air.)

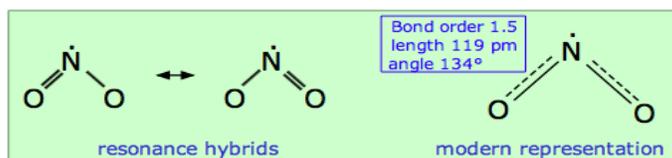
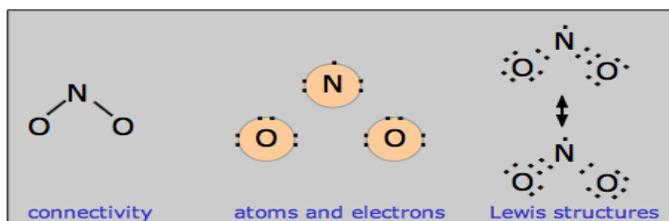
In the 1980s, to the surprise of almost everyone, NO was identified as an essential component of the signalling pathway of the mammalian cardiovascular system. As such, it provides a means by which cells communicate with one another. Other signalling molecules tend to be far more complicated, and no one would have expected a "free radical" molecule to have other than a damaging effect on the body.

**Nitrogen dioxide** is also an odd-electron molecule. In contrast to NO, the odd electron in NO<sub>2</sub> appears to be somewhat local to the nitrogen atom. As a consequence, the dimerization equilibrium



is so facile that neither gas can be retained in pure form at ordinary temperatures.

Because two equivalent Lewis structures can be written, NO<sub>2</sub> is a resonance hybrid in which the N–O bond order is 1.5.



## **More than one non-equivalent structure**

It sometimes happens that the octet rule can be satisfied by arranging the electrons in different ways. For example, there are three different ways of writing valid electron dot structures for the thiocyanate ion  $\text{SCN}^-$ . Some of these structures are more realistic than others; to decide among them, you need to know something about the concepts of formal charge and electronegativity. These topics are discussed in the lesson that follows this one, where examples of working out such structures are given.

Source: <http://www.chem1.com/acad/webtext/chembond/cb03.html>