

What's the shape of that molecule?

Part 2. Will that be a single, double or a triple bond?

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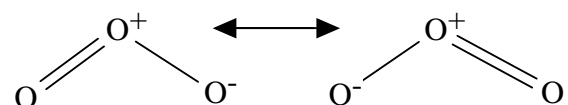
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Having correctly predicted the shape¹ of a molecule, cation, or anion, a problem arises when the student wants to know the actual structure of a molecule which contains O, N, or S atoms. In these situations, two (or more) structures, differing only in the position of the electrons, are often used when the properties of the compound cannot be rationalized through the use of single Lewis structure. Curved arrows can be used to progress systematically from one structure to another; however, the electrons do not truly shift but are delocalized between the atoms.

For example, two resonance forms may be drawn for ozone (a V shaped molecule via the method introduced in the previous paper):



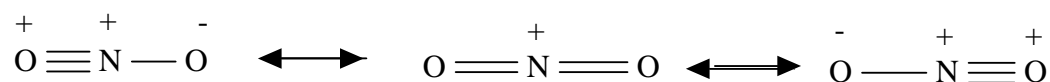
Neither one is a correct structure for O₃ as the experimentally determined bond lengths are the same, rather than the single and double bonds illustrated in the resonance structures. In this case we have a real molecule described in terms of two non-existent molecules. The important thing for the student to realize is that only the shape of the molecule is a measurable property, one cannot "see" whether there is a single, double, or a triple bond between any two atoms in the molecule. Thus we are uncertain about the exact location of all the electrons in the molecule (hardly surprising on the basis of Heisenberg's Uncertainty Principle).

We have found that stressing to the students that **the shape of the molecule is the same for all the various resonance forms** assists the students with some of the following.

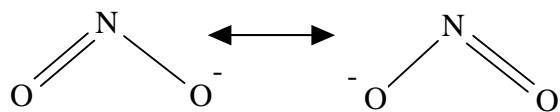
Example 1.

Which will have the longer N-O bond length: NO₂⁺ or NO₂⁻?

The nitrogen atom can accommodate only 8 electrons so that we can have several resonance forms based on the following molecular shapes:



NO₂⁺ - a linear structure



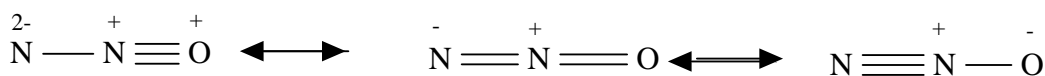
NO_2^- - a V-shaped structure

As with O_3 , there is a single N-O distance in each of NO_2^+ and NO_2^- ; however, in NO_2^- the N-O bond order in each resonance structure is 1.5 (3 pairs of bonding electrons shared by two oxygen atoms) while in NO_2^+ it is 2.0 (4 pairs of bonding electrons shared by two oxygen atoms). NO_2^- does indeed have the longer N-O distance² - 124 pm versus 110 pm for NO_2^+ . We cannot draw the true structure of either ion, but we can make use of the resonance structures to describe differences between the two ions.

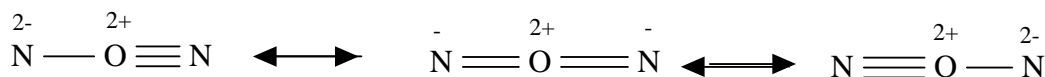
Example 2.

The molecule N_2O could have two possible molecular arrangements: N-N-O or N-O-N. Using resonance structures, suggest which one is more likely.

Both molecular arrangements will have a linear shape (AX_2), and we can draw several resonance structures for each one:



N-N-O structure



N-O-N structure

If one considers the formal charges, one molecular arrangement appears more likely: N-O-N always has a 2^+ formal charge on O, while N-N-O has resonance structures in which a smaller charge separation is present. This would lead one to predict that N-N-O is the correct molecular arrangement of atoms.

One must be careful that students understand the differences between facts and theories when dealing with these types of questions. Purser³ has recently described the debate in the literature concerning the structure of SO_2 . There are six different sets of possible resonance structures (all with the same V-shape) for this molecule; ranging from two sulfur-oxygen single bonds to two sulfur-oxygen triple bonds. The true structure, he concluded, was best represented by having two sulfur-oxygen double bonds.

Rather than wasting time drawing multiple Lewis structures, it would be more useful to provide the students with the experimentally determined bond lengths of a series of compounds and allow them to suggest the most likely structure for the compound under consideration.

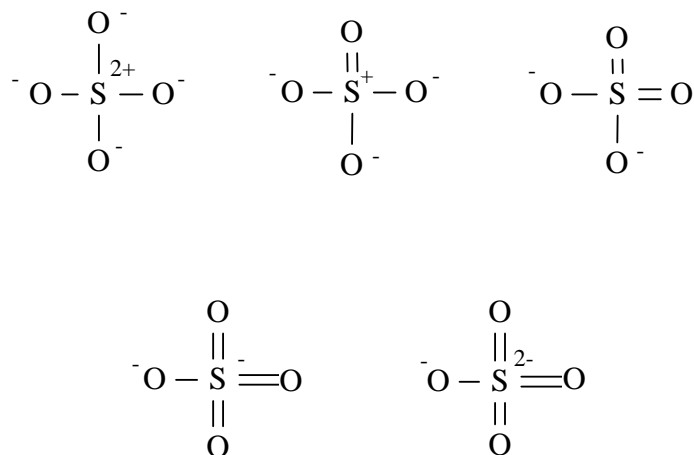
Example 3.

Construct resonance structures for the sulfate ion (SO_4^{2-}) and use the listed bond lengths⁴ to suggest the most likely structure of H_2SO_4 .

S-O in SO_4^{2-} 149 pm (all the same)

S-O in SOF ₂	141 pm
S-O in SO ₂ F ₂	141 pm (all the same)
S-O in SO ₂	143 pm (all the same)
S-O in SO ₃	143 pm (all the same)
S-O in H ₂ SO ₄	157 pm and 142 pm

Five sets of resonance structures (all with the same tetrahedral shape but differing number of single and double bonds) are possible, with some sets less likely than others from a consideration of the formal charges present in some of the structures.



It is important for the students to remember that individual electrons cannot be recognized in molecules and that Lewis structures are only approximations of electron distributions. Those structures in which formal charge separations are kept to a minimum appear to more closely represent the actual electron distribution, and are generally the ones used. In this case the sulfate anion could be best described as having a S-O bond order of 1.5, corresponding to the set of resonance structures having two single and two double bonds. On this basis, H₂SO₄ would best be described as having two sulfur-oxygen single bonds and two sulfur-oxygen double bonds. The results for all the compounds are listed below.

Structure	Bond Length	Bond Order
SO ₂	143 pm	2.00 (S=O)
SO ₃	143 pm	2.00 (S=O)
SOF ₂	141 pm	2.00 (S=O)
SO ₂ F ₂	141 pm	2.00 (S=O)
SO ₄ ²⁻	149 pm	1.50
H ₂ SO ₄	157 pm	1.00 (S-O-H)
H ₂ SO ₄	142 pm	2.00 (S=O)

The end result is that the student hopefully realizes that although Lewis structures are widely used, one must be aware of their limitations. In many regards, a delocalized structure is probably a better representation as we don't have to state the exact position of the electrons. The shape of a molecule predicted using VSEPR considerations is independent of whether one proposes single, double, or triple bonds. If one is interested in whether a molecule is polar or not, then Lewis structures are not really necessary, only the molecular shape is required.

References

1. R. Perkins and C. Lassigne, CHEM 13 NEWS, December 1992, pages 4-5.
2. J. Kotz and K. Purcell, *Chemistry and Chemical Reactivity*, 1st edition, 338 (1987).
3. G. Purser, *Journal of Chemical Education*, **66**, 710 (1989).
4. R.J. Gillespie, CHEM 13 NEWS, March 1988, pages 8-9.