# *Fixing Aromaticity, Charges, and Bonding*

You should have knowledge of the structure of your hetero compound from some source such as a textbook, internet, or journal article. Most particularly, you need to be aware of the presence of aromatic rings or double bonds such as those between two carbon atoms or between a carbon and oxygen (carbonyl group). Aromatic (or at least delocalized sextets) can occur in 5-membered rings such as pyrrole and thiophene. Pyridine-type molecules are also aromatic (benzene with a N replacing a CH in the ring). Also, some atoms, such as the oxygens in carboxylates or phosphates, and the nitrogen of aminium ions, are charged. If you have a carboxylic acid it is most likely in the form of the resonance-delocalized carboxylate anion under physiological conditions.

Double bonds, delocalized, and aromatic bonds sometimes are not interpreted correctly when the molecule is opened in DSVisualizer and so you will have to define them. Sometimes, compounds that should be charged are not, and they too must be fixed.

Open a molecule file in DSV that potentially needs to be fixed (or draw one resembling the examples shown here). Open a Hierarchy window. Next, you need to check to see if features need to be fixed. ***Make no changes to the molecule other than those described here.***
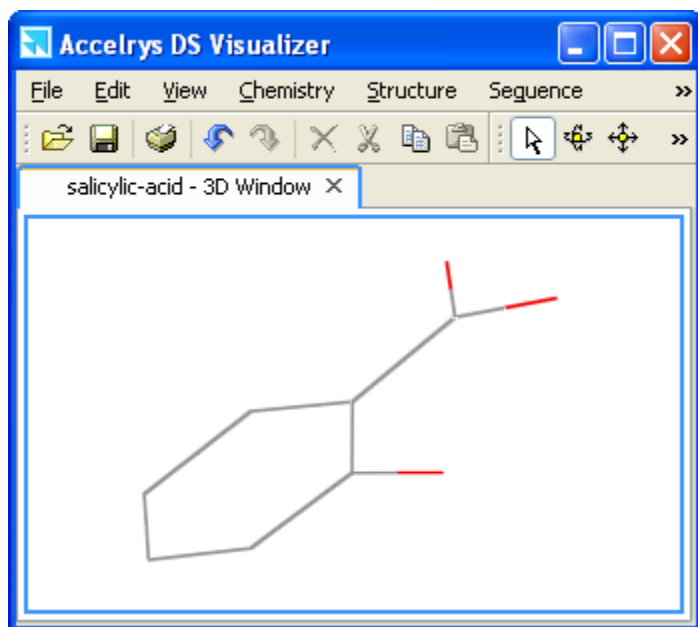

Here is salicylate, the conjugate base of salicylic acid. Although the ring is planar, as an aromatic ring should be, DSV may add too many hydrogens to the ring carbons. DSV might also treat the C=O of the carboxyl group as an alcohol (CHOH). Finally, if the C=O is intact, the carboxylic acid might not be deprotonated as the carboxylate anion.

The benzene ring must have its aromatic bonds defined and the C-O bonds in the CO_2 unit must be shown as negatively charged.

If the aromaticity is intact, you will see the delocalized broken lines within the hexagon and you do not need to fix it. Then, choose **Chemistry** | **Hydrogens** | **Add**. Inspect the molecule to determine if the carboxyl is protonated or not (and if the aromaticity is not intact, you will see too many H's on the ring). **Remove** the hydrogens. Finally, as a double check, choose **Structure** | **Labels** | **Add…** Choose "Atom" for the "Object" and "Formal Charge" for the "Attribute". If

the carboxyl is protonated, all its atoms will have a 0 charge. If the carboxylate is properly designated, the O of the C-O will have a -1 charge and the O of C=O will have a 0 charge.

AROMATICITY
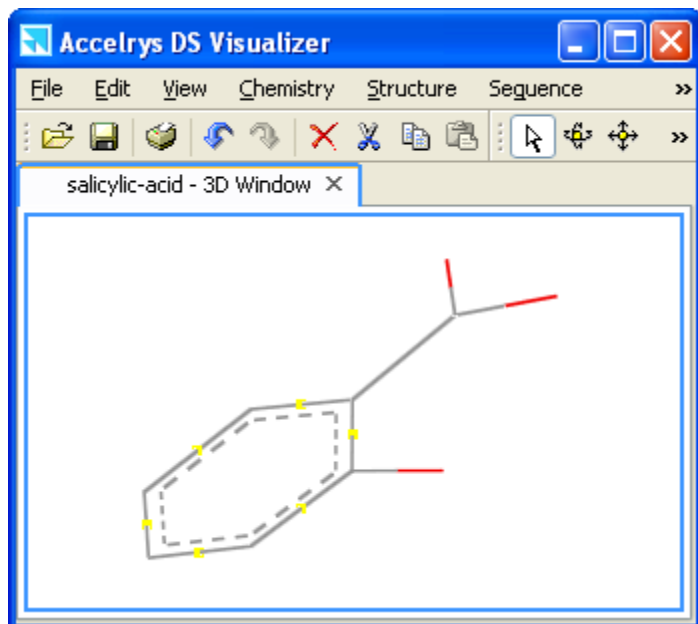
Select the six bonds in the ring.

From the menu choose **Chemistry** | **Bond** | **Aromatic**.

The dotted lines denoting partial double bonds appear.

If the model had hydrogens showing, choose **Chemistry** | **Hydrogens** | **Remove** and then **Chemistry** | **Hydrogens** | **Add** to finish the correction.

CHARGE

To fix a *carboxylate*, select one of the carbon-oxygen bonds. Then choose **Chemistry** | **Bond** | **Double**. Then select the other carboxyl oxygen and choose **Chemistry** | **Charge** | **-1.**

The carboxylate is thus overall $-(CO_2)^{-1}$. However, remember, the two O's are equivalent and so in reality, one is not double-bonded and the other single-bonded to the carbon.

The Figure shows that DSV will add a label when charges are defined. You can remove the labels.

To give an atom, such as nitrogen in aminium ions, a positive charge, repeat the instructions above using +1 as the charge.
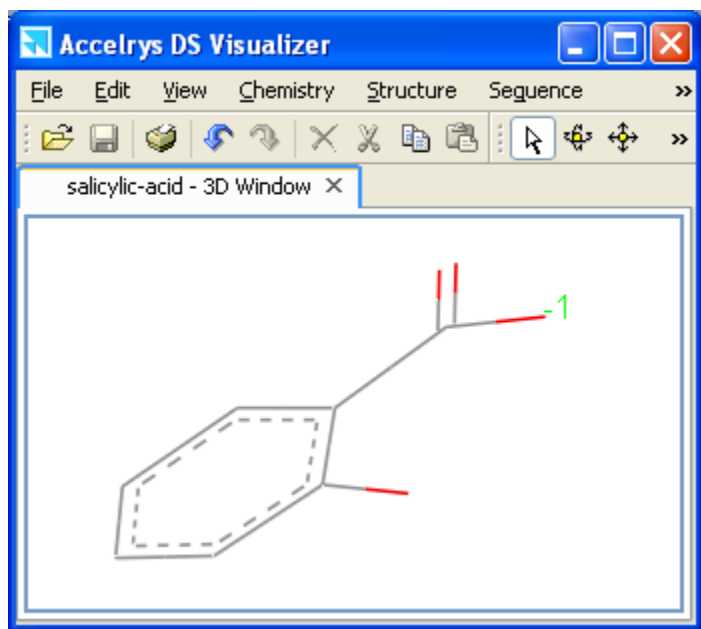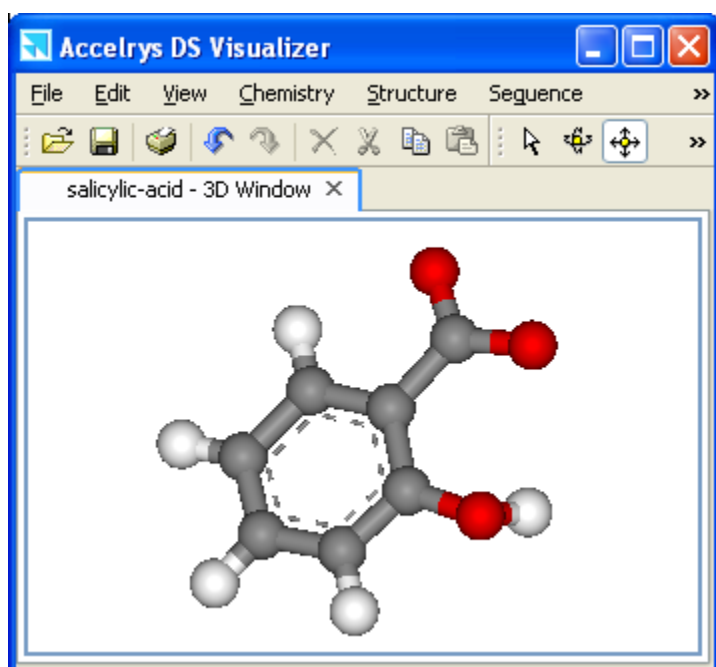
The Figure shows a ball-and-stick display of salicylate ion with the hydrogens added correctly.

HYBRIDIZATION

The hybridization is fixed by various methods. Choose the method according to the functional group that is being fixed. Before fixing, be sure that a fix is needed. **Add Hydrogens** to see if the valence is correct. Then **Remove** the hydrogens (not Hide).

Fix a *carbonyl* group by selecting the C-O bond and from the menu choosing **Double**. Carbonyl groups appear in aldehydes, ketones, amides, and esters.

If you have an *amide* functional group, the hybridization of the N should be sp^2. The carbonyl is a C=O. The final geometry should have the HN-C=O in the same plane as shown in the illustration below. You do not need to explicitly fix any other atom's hybridization.
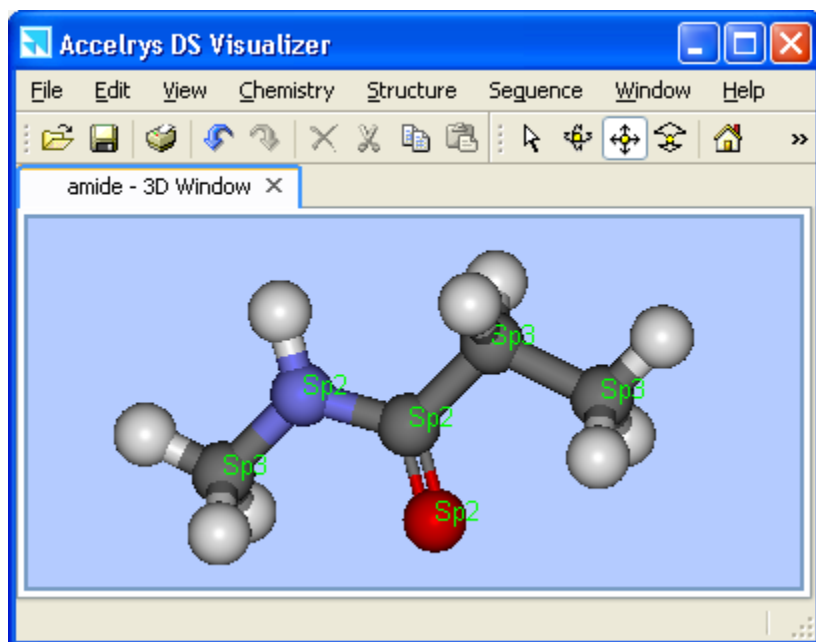
To check the hybridization, choose **Structure** | **Labels** | **Add**..Then choose **Atom** and **Hybridization** in the boxes.

If the hybridization is not sp^2 for the N, then choose **Chemistry** | **Hybridization** | **sp^2**.

Now that the bonds (and thus the hybridization) and/or charges are defined, you can **Add Hydrogens**.

Save the file as an MDL *mol* file.