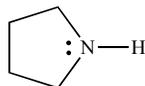


Where Is My Lone Pair?

Goal: In this tutorial we'll learn how to determine which orbital contains a lone pair. This is important for resonance, conjugation, and aromaticity. To master this subject you'll need a strong background in hybrid orbitals, so this would be a good time to review the Assigning Hybridization tutorial if necessary. You'll also need to be able to figure out how many lone pairs are present, even if they are not specifically drawn. Review the Formal Charge tutorial to work on this skill, if necessary. Finally, it will be easier to visualize the lone pair/orbital/three-dimensional structure relationship if you build a model of the molecule in each of the examples below. If you and your model kit still aren't on speaking terms, now's the time to review the model kit tutorials as well.

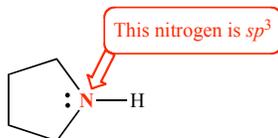
There is a general misconception that a lone pair can always be delocalized in resonance, conjugation, or aromaticity. The truth is that only a lone pair in a p orbital can be involved in these phenomena. (Exceptions exist, but they are very rare.) Therefore we need to know how to determine which orbital holds a particular lone pair. The process starts by determining the appropriate hybridization for the atom that hosts the lone pair. Then we can figure out what each of the hybrid orbitals is used for (σ bond, π bond, lone pair, or empty). We'll learn the process by example.

Example 1: What Orbital Hosts The Lone Pair in Pyrrolidine?



Pyrrolidine

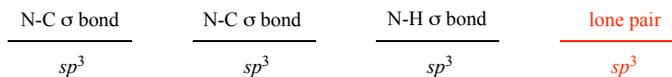
Answer: We start by assigning hybridization. The molecule does not benefit from increases resonance, conjugation, or aromaticity if the nitrogen atom has a p orbital, so we assign hybridization based only on the number of attachments. The nitrogen atom has four attachments: two carbon groups, one hydrogen atom, and one lone pair. The best way to arrange four attachments around a central atom to minimize electron repulsion is tetrahedral geometry. Nitrogen uses sp^3 orbitals to achieve this geometry.



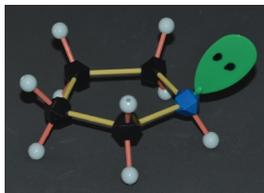
sp^3 hybridization gives four sp^3 orbitals and no p orbitals. The four sp^3 orbitals are used to contain the four attachments (electron pairs): three bonding electron pairs (C–N and N–H σ bonds) and one lone pair. *When assigning electron pairs to orbitals, start by assigning the σ bond electrons to hybrid orbitals:*



The remaining electron pairs are then assigned to the remaining orbitals. In this case, the lone pair is assigned to the unused sp^3 orbital:



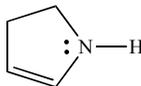
Therefore the nitrogen lone pair of pyrrolidine occupies an sp^3 orbital. Build a molecular model with the nitrogen lone pair orbital to visualize the molecule's three-dimensional structure.



Molecular model of pyrrolidine, showing the sp^3 orbital containing the nitrogen lone pair.

An atom having four σ bonds must use sp^3 hybridization to accommodate these bonds. This atom does not have a p orbital, and cannot participate in resonance (except the very rare case involving σ bonds), conjugation, or aromaticity.

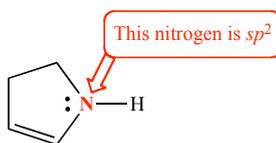
Example 2: What Orbital Hosts The Lone Pair in 2,3-Dihydropyrrole?



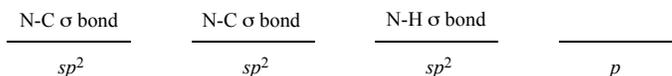
2,3-Dihydropyrrole

Answer: We start by assigning hybridization, and asking the question: "Does the molecule benefit with increased resonance, conjugation, or aromaticity if the nitrogen atom has a p orbital?" In this case the answer is yes. When the nitrogen has a p orbital there is conjugation and resonance between the nitrogen lone pair and the adjacent carbon-carbon π bond. Aromaticity is not possible in this case because there cannot be a closed loop of p orbitals.

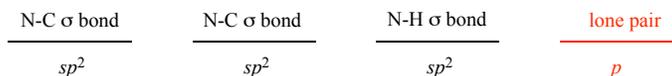
For the nitrogen atom to have a p orbital its hybridization must be either sp^2 or sp . Because the nitrogen is in a ring whose preferred C–N–C bond angle is much closer to 120° (for sp^2) versus 180° (for sp), we choose sp^2 hybridization. (A ring has to be rather large -- at least eight atoms -- before it can accommodate a 180° bond angle. So when an atom that is part of a ring needs a p orbital, this atom will most commonly be sp^2 .)



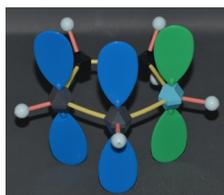
An sp^2 hybridized nitrogen atom has three sp^2 orbitals and one p orbital. The sp^2 orbitals are coplanar, and the p orbital is perpendicular to the sp^2 orbital plane. As we learned in example 1, we start the electrons-to-orbitals assignments by using the sp^2 orbitals to construct the σ bonds:



This leaves only the lone pair, and only one place to put it:

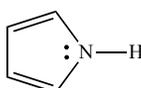


Therefore the nitrogen lone pair in dihydropyrrole is in a p orbital, and is part of the conjugated system. Build a molecular model with all p orbitals included to visualize the three-dimensional structure.



Molecular model of dihydropyrrole, showing conjugation of the carbon-carbon π bond (p orbitals in blue) with the nitrogen lone pair in its p orbital (green).

Example 3: What Orbital Hosts The Lone Pair in Pyrrole?

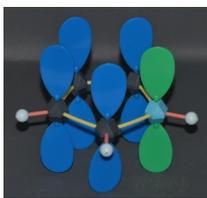


Pyrrole

Answer: Work through this one yourself; the logic is very similar to example 2 (except that pyrrole is aromatic). If you've worked the problem correctly your final answer should be:

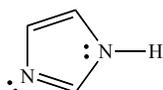


Therefore the nitrogen lone pair in pyrrole is in a p orbital, and is part of the aromatic p orbital loop. Build a molecular model with all p orbitals included to visualize the three-dimensional structure.



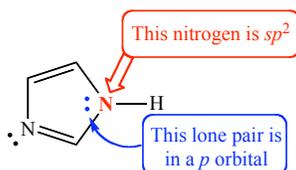
Molecular model of pyrrole, showing the four carbon p orbitals (in blue) and the nitrogen p orbital (green) that hosts the lone pair.

Example 4: What Orbitals Host The Lone Pairs in Imidazole?

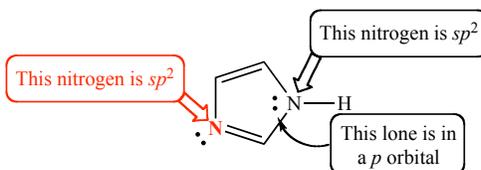


Imidazole

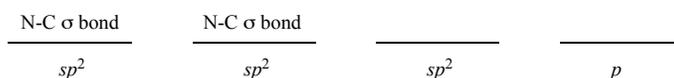
Answer: We analyze each lone pair using the same procedure as in the three previous examples. In examples 2 and 3 we observed that when a nitrogen lone pair is next to a π bond, the nitrogen lone pair is in a p orbital. So we can already assign one imidazole lone pair:



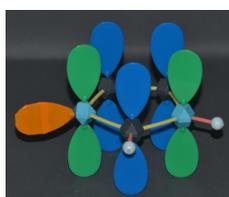
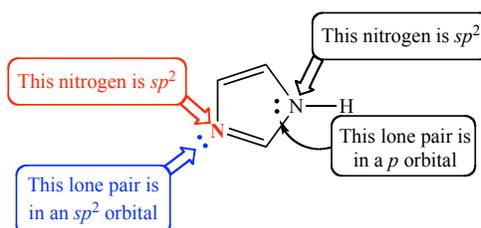
For the lone pair on the C=N nitrogen, we don't need to ask if we need a p orbital. The structure tells us that the nitrogen is part of a C=N double bond. Recall that the π bond of a double bond is formed by overlap of adjacent, parallel p orbitals, so therefore we already know the nitrogen must have a p orbital. The nitrogen's hybridization must be sp^2 or sp , and of these we pick sp^2 because the small ring cannot accommodate the linear bond angle required for sp hybridization.



To determine the orbital that hosts this nitrogen lone pair, we start by using the hybrid orbitals to build the σ bonds:

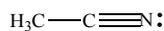


The nitrogen also has a π bond, which we know is formed by overlap of p orbitals. So we must assign the p orbital to the π bond. This leaves only one place for the lone pair to be: an sp^2 orbital.



Molecular model of imidazole. The carbon p orbitals are shown in blue, the nitrogen p orbitals are in green, and the nitrogen sp^2 orbital containing a lone pair is orange.

Example 5: What Orbital Hosts The Lone Pairs in Acetonitrile?



Acetonitrile

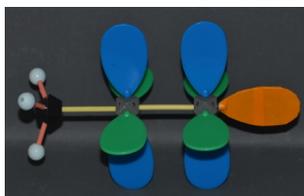
Answer: The nitrogen atom is part of a triple bond, so it needs two p orbitals (one p orbital for each of the two p bonds). Only sp hybridization provides two p orbitals. Before assigning electrons, the nitrogen orbitals look like this:



As before, we start by using the sp orbitals to construct the σ bond. The two π bonds use the two p orbitals. This leaves the remaining sp orbital to accommodate the lone pair:

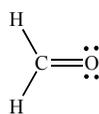


Once again, build the molecular model to help you visualize the three-dimensional relationship of the orbitals.



Molecular model of acetonitrile. One π bond is constructed by overlap of p_y orbitals from carbon and nitrogen (shown in green), and the other by overlap of p_z orbitals (blue). The lone pair is in a nitrogen sp orbital (orange).

Example 6: What Orbital Hosts The Lone Pairs in Formaldehyde?

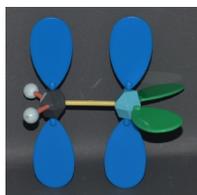


Formaldehyde

Answer: The oxygen atom must have either sp^2 or sp hybridization, because it needs a p orbital to participate in the C–O π bond. This oxygen atom has three attachments (the carbon and two lone pairs), so we use sp^2 hybridization. The unassigned orbitals look like this:



One sp^2 orbital is needed for the C–O σ bond, and the p orbital for the C–O π bond. This leaves two sp^2 orbitals to accommodate the lone pairs.



Molecular model of formaldehyde. The carbon p_z and oxygen p_z orbitals that overlap to form the π bond are in blue. The sp^2 orbitals that host the lone pairs are in green.

The same procedure we've learned here applies to lone pairs in most any situation you're likely to encounter in introductory organic chemistry.