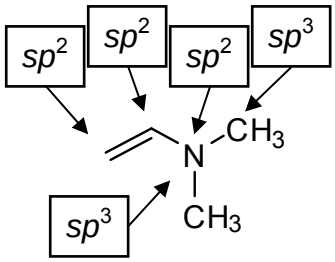
Chemistry 2302

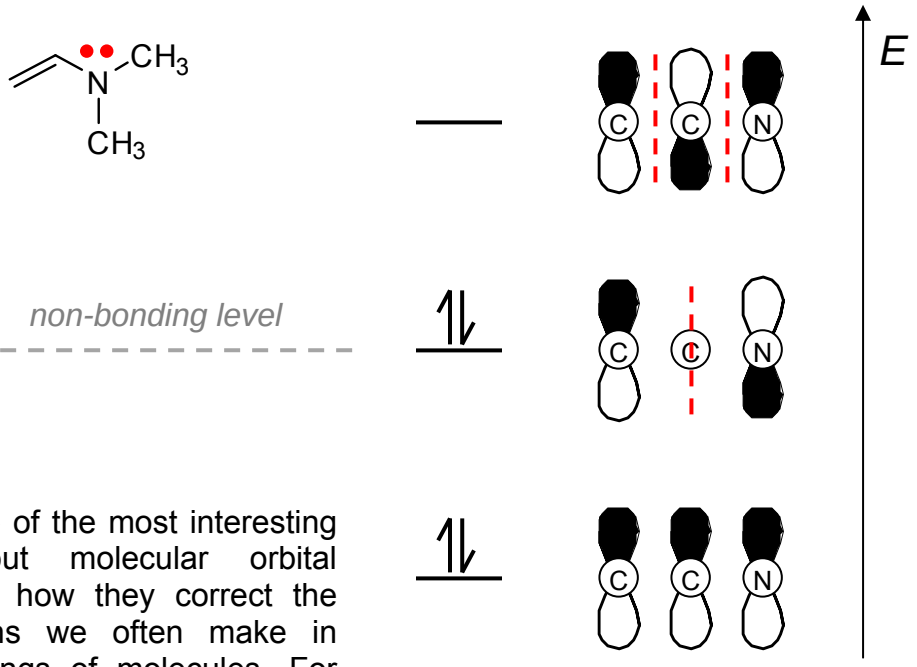
Workshop 2 Solutions
Molecular Orbitals and Reactivity

1. As you remember from CHEM 2301, hybridization is usually determined by the number of σ bonds and lone pairs on an atom. However, there is an exception: if an atom would ordinarily be identified as sp^3, but (a) has at least one lone pair, and (b) is adjacent to a multiple bond, then it re-hybridizes sp^2. (This only happens from sp^3 to sp^2; it does not transform sp^2 centers to *sp* ones.) In this molecule, the nitrogen atom has three σ bonds and one lone pair, and that might lead you to assign sp^3 hybridization to the nitrogen. But the nitrogen is adjacent to a double bond, so it re-hybridizes sp^2.



2. So, **three** atoms (two C's and an N) contribute to the conjugated π system. The carbons contribute one electron each, and the nitrogen contributes a lone pair, so the total number of electrons in the system is **four**.

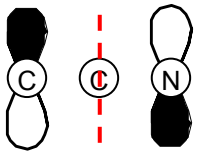
3.



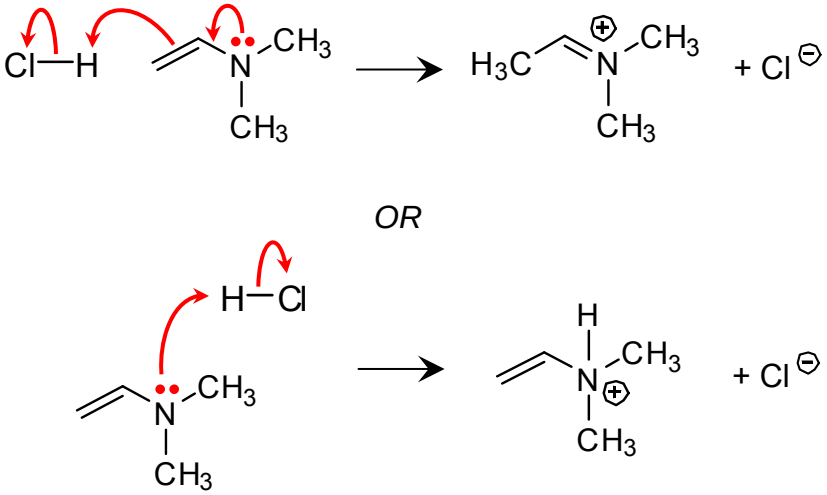
For me, one of the most interesting things about molecular orbital diagrams is how they correct the simplifications we often make in Lewis drawings of molecules. For example, the Lewis drawing above says that our molecule has two electrons in a π bond between two carbons, and another two electrons that sit exclusively on N as a lone pair. But the MO diagram says that two electrons wander over the entire C-C-N set of atoms, and the other

two—our “lone pair”—spends half of its time on nitrogen, half of its time on the end carbon, and none of its time in the middle.

4. The HOMO (highest occupied molecular orbital) has orbital density at the two ends, but none in the middle.

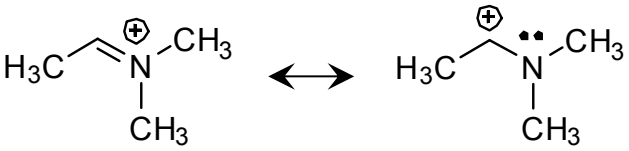


5.

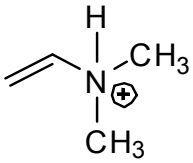


Most importantly, the proton does not add to the center carbon; both electron pushing and the orbital diagram say it shouldn’t.

6.



has resonance structures that redistribute and stabilize charge, while



does not. So resonance effects would suggest that protonation occurs preferentially at carbon to produce the conjugate acid above, not at nitrogen. However, the positive charge is accommodated better at an sp^3-hybridized nitrogen (which acts less electronegative due to its lower *s*-character) than an sp^2-hybridized nitrogen.