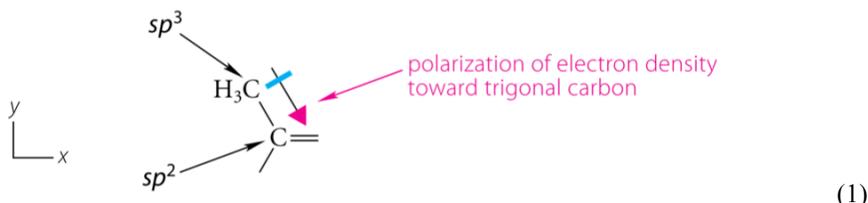


## Supplement 4.1: Electronegativity Effects of Hybridization. The Effect of Hybridization on Acidity and Basicity

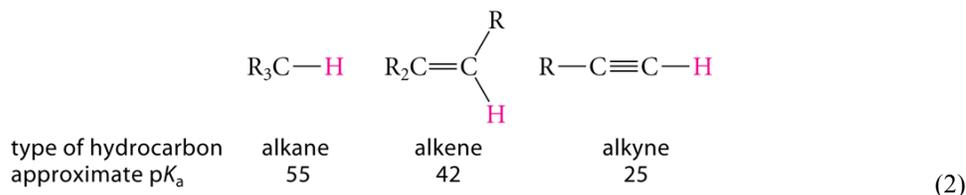
Table 1.1 in the text (p. 9) suggests that there is a single electronegativity for carbon. Actually, the electronegativity of carbon depends on its hybridization state. Carbons that are  $sp^2$ -hybridized are somewhat more electronegative (about 0.2 electronegativity units) than  $sp^3$ -hybridized carbons;  $sp$ -hybridized carbons are even more electronegative by another 0.2 units. This means that  $sp^3$ - $sp^2$  carbon-carbon bonds have a slight bond dipole.



Such bond dipoles explain the dipole moments of alkenes such as *cis*-2-butene. (See text p. 145.) The dipole moment of *cis*-2-butene is the vector sum of the  $H_3C-C$  and  $H-C$  bond dipoles. Although both types of bond dipole are oriented toward the alkene carbon, there is good evidence (Problem 4.63, p. 179) that the bond dipole of the  $H_3C-C$  bond is greater. This would be expected from the greater length of the  $C-C$  bond. (Remember that dipole moment for a given charge separation increases with length of the dipole; Eq. 1.4, p 11.) This is why *cis*-2-butene has a net dipole moment.

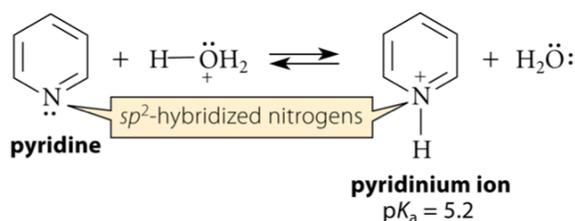
The reason for the greater electronegativity of an  $sp^2$ -hybridized carbon is that it has an electron in a  $2p$  orbital. Electron density in a  $2p$  orbital is not evenly distributed around the nucleus in all directions. That is, if a  $2p$  orbital is oriented along the  $z$ -axis, a  $2p$  electron does not screen the nucleus from other electrons situated in the  $xy$  plane, the plane of the page in diagram (1), above. Therefore, the relatively unscreened positive charge of the atomic nucleus in an  $sp^2$  carbon pulls the electrons in the  $sp^3$ - $sp^2$  carbon-carbon bond towards itself and creates a partial positive charge on the attached methyl groups and thus creates the bond dipole. (A similar effect occurs in  $C-H$  bonds; look at the EPM of ethylene on p. 130 of your text. Note the partial positive charge on the ethylene hydrogens.) In an  $sp^3$  carbon, in contrast, the  $2p$  electron density is equally distributed in the hybrid orbitals.

One of the most important aspects of hybridization is its effect on acidity. For example, the acidities of alkanes, alkenes, and alkynes differ significantly:

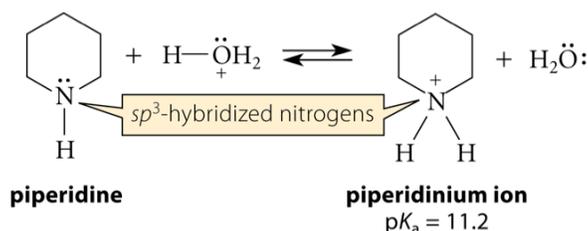


You learned in Sec. 3.6, p. 112, that acidities can be dissected into bond-strength effects and electronegativity effects. The order in (2) cannot be a bond-strength effect, because bond strengths increase with increasing  $s$  character. That is, the strength of a  $C(sp)-H$  bond is greater than that of a  $C(sp^2)-H$  bond, which is greater than that of a  $C(sp^3)-H$  bond. Therefore, this must be an electronegativity effect. This acidity order, then, is consistent with increasing electronegativity of carbons with increasing  $s$  character in their hybridizations.

The acidity of hydrocarbons has important applications in laboratory chemistry but is of peripheral significance in biology, because these  $pK_a$  values are so far from physiological pH. The effect of hybridization on acidity and basicity, however, becomes important in biology when we consider the hybridization of *nitrogen* atoms. Consider the following  $pK_a$  values:



(3a)



In the conjugate-acid cations, the proton attached to the  $sp^2$ -hybridized nitrogen is more acidic than the one attached to the  $sp^3$ -hybridized nitrogen. In other words, *amines with  $sp^2$ -hybridized nitrogens are less basic than those with  $sp^3$ -hybridized nitrogens*. The effect of hybridization on the basicity of amines is a reflection of the increased electronegativity of nitrogen atoms with more  $s$  character.

Let's now summarize the structural effects on acidity:

1. The element effect
2. The charge effect
3. The polar effect
4. The resonance effect
5. The hybridization effect.

### Problems (for Answers click [HERE](#))

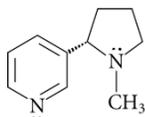
1. (a) What is the hybridization of the nitrogen in a nitrile?



**a nitrile**

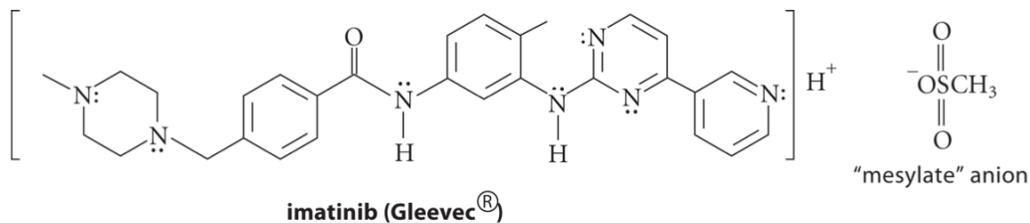
- (b) How would you expect the basicity of a nitrile to compare with that of an amine?

2. Nicotine is the addictive component of tobacco. Both nitrogens of nicotine are basic. Which nitrogen is more basic? Explain.



**nicotine**

3. The anticancer drug Gleevec® is available commercially as its mesylate salt.



This means that one of the nitrogens of Gleevec is protonated. Which nitrogen is protonated? Explain your reasoning.