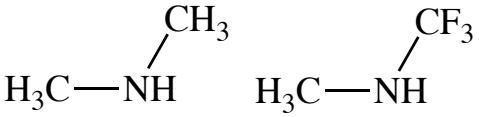
Ex 39A - Basicity

Question One

For each of the following groups of molecules, rank them by their basicity. Is the difference due to size, inductive effects, resonance effects or electronegativity?

i) 

The conjugate acid of the second amine will be destabilized by the inductive electron withdrawing effect of the trifluoromethyl group making the first molecule more basic.

ii) Ph_2As^-

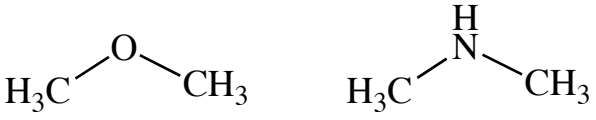
Ph_2P^-

The phosphide anion is more basic. This anion has the negative charge dispersed over a smaller volume than the arsenide making it less stable.

iii) $H_2C{=}NH$

$H_3C{-}NH_2$

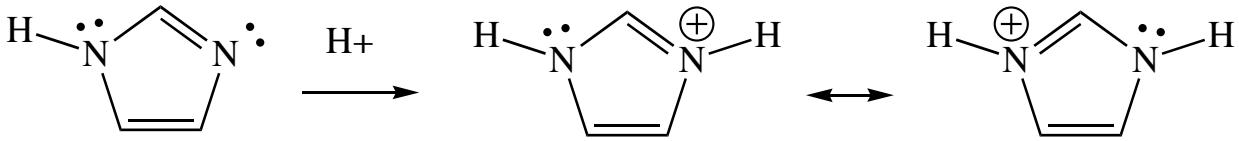
For the same atom, the one with greater s character (top here) will be less basic since this atom is effectively more electronegative.

iv) 

In basicity, the least electronegative atom is the most basic, the amine in this example.

Question Two

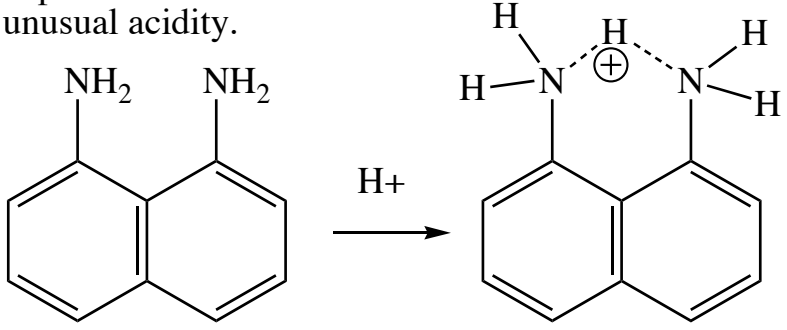
Histidine is unusually basic because it forms a resonance stabilized conjugate acid. Which N atom is protonated? Give the structure of the conjugate acid.



Note that protonation of the other N atom will not offer resonance stabilization.

Question Three

The molecule below is known as "Proton Sponge". It is far more basic than would be expected of an amino arene. Draw the structure of the conjugate base and rationalize its unusual acidity.



The proton is stabilized by the very proximal lone pair on the neighbouring amino group so that the charge is significantly dispersed.