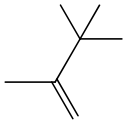
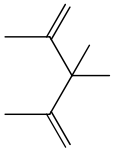
Lesson 4 For Organic Chemistry

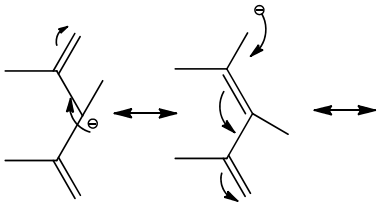
Review Question --- Acidity

Bear in mind that to answer questions about the comparison of acidity or basicity (or any other physical properties), you need to state the definition and hence the governing factors of the **property** being asked.

Qu 1: Arrange the following compounds in terms of **increasing acidity** (by considering the shown protons.)

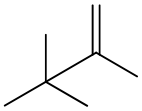
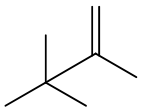
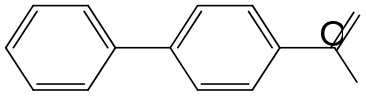
a.  b. 

→ The order should be ___ < ____. By considering the stability of their conjugate base i___, you should expect that more r_____ structures can be drawn for ___. It is because it bears two carbonyl groups. The negative charge can be dispersed more extensively as:



(Be careful : The charge is conserved.)

Qu 2: Arrange the following carboxylic acids in terms of **increasing acidity**. ***

a.  b.  c. 

→ The order should be: __< ___< ___. Obviously, we should adopt the definition 1 of acidity that we consider the s_____ of their conjugate base i____. Acid a is the _____ acid because the ion is **destabilized** by the p_____ inductive effect; Acid c is the _____ acid because the ion is **stabilized** by r_____ effect. Note that resonance effect is more powerful than n_____ inductive effect because resonance can lower the e_____ of the ion.

Qu 3: Explain the fact that the pKa of $(CH_3)_3C\mathbf{H}$ = 50 while that of $(CH_3)_2N\mathbf{H}$ = 36.

→ Actually, you should realise that when the **atom** linked with the acidic proton is more e_____, it should be a stronger acid because the negative _____ effect can stabilize the conjugate base ion.

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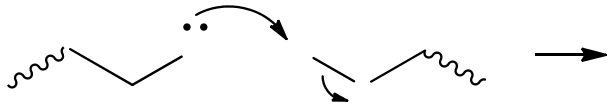
Acidity and Basicity

4. Basicity

In HKAL, the organic bases are usually amines. **Why** are amines basic? It is because the n_____ atom which always bears a _____ pair of electrons can **attack** to gain a proton. Note that a base is a proton a_____. Therefore, amines or any 'lone pair of electron carrying' species can act as a **base**.

In general, the basic **mechanism** for an acid-base reaction is shown as:

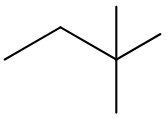
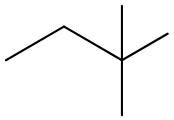
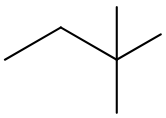


To do comparison of basicities of different bases, again, we first need to give a brief d_____ of what basicity is. For basicity, we **don't** focus on about the stability of the conjugate acid ion. Instead, we have:

Basicity is a measure of the **availability** of donating **a lone pair electron** from an **atom** to an acid.

Case 1 --- Inductive Effect

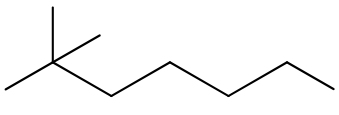
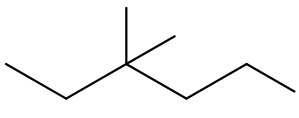
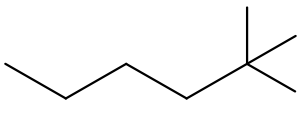
Qu 1 : Please arrange the following bases in the descending order of basicity.

a.  b.  c. 

→ The order should be: ___> ___> ___.

→ **Unlike** the case of acidity, positive inductive effect can **increase** the basicity of a base. It is because the effect can **increase** the electron density among the amine region (or N atom). Conversely, negative inductive effect will l_____ the basicity of a base since it will r_____ the electron d_____ on N atom. So, as alkyl groups are electron d_____ while fluorine atom is electron w_____ __ is the strongest base while __ is the weakest base.

Qu 2 : Please arrange the following bases in the descending order of basicity. ***

a.  b.  c. 

→ The order should be ___> ___> ___. It is because the degree of negative _____ effect depends on the relative position between the electron-w_____ F atoms. The farer the group, the lower will be the withdrawing effect.

→ Note that negative inductive effect will l_____ the basicity of the amines.

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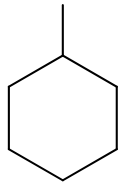
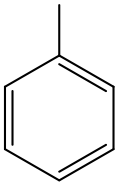
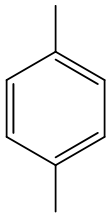
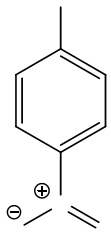
4. Basicity

Case 2 --- Resonance Effect

Qu 1 : Please arrange the following bases in the descending order of basicity.

a.  b.  c.  d. 

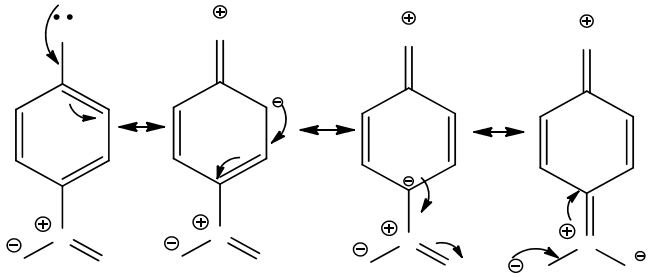
→ The order should be ___> ___> ___> ____.

→ **Unlike** the case of acidity, resonance effect will r_____ the basicity because the del_____ of the lone pair electron over the _____ ring means that the e_____ density on N **atom** is **lowered**. So, ___ is the strongest base since it has no benzene ring = no r_____. NH_2 NH_2

→ Note that the **nitro-group** ( ) on d is an electron-_____ group. It will further **reduce** the electron d_____ on the N atom. Hence, the availability of donating the lone pair electron will be the **lowest**.

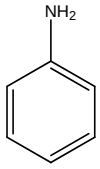
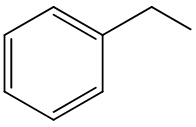
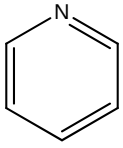
→ As **alkyl group** is an electron-_____ group, it will **increase** the electron density of the N **atom** of c. Hence, c has the second high basicity.

→ The drawing of resonance structures for d is shown as illustration: (***)



(Draw two more…)

Qu 2 : Please arrange the following bases in the descending order of basicity.

a.  b.  c. 

→ The order should be: ___> ___> ___.

→ The position of the benzene ring will affect the **possibility** and the **extent** of the de_____ of the lone pair electron on N atom. For b, there is ___ resonance. Instead, the benzene ring becomes an electron-_____ group. For c, the reduction of electron d_____ on N is the highest.

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Case 3 --- Formation of hydrogen bond (with solvent) ***

Qu: Please arrange the following ammonia derivatives in the descending order of basicity in the case:

a. NH_3 b. $(CH_3)NH_2$ c. $(CH_3)_2NH$ d. $(CH_3)_3N$

i) ***in the solvent of water*** ii) ***in their gaseous state***

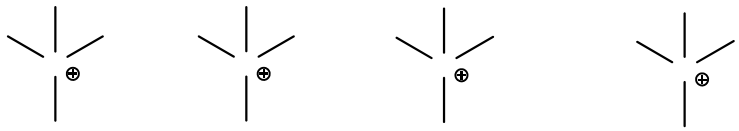
Case 3i) The 'resultant' order should be ___> ___> ___> ___.

→ Regarding the **definition 1**: **Bascity** depends on the a_____ of donating a lone pair electron.

→ The **more** the electron-d_____ methyl groups, the stronger the base is = d > c > b > a.

→ But, regarding the **definition 2** : **Basicity** depends on the stability of the conjugate acid ion.

→ By considering the structures of the conjugate acid ions, you should expect that hydrogen bonds can be formed between the ions and the **solvent** w_____ molecules.



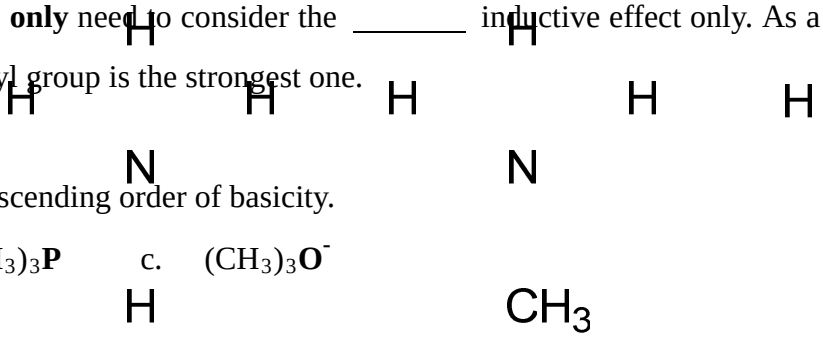
→ The **more** the hydrogen bonds that the ion can form with water, the more stable the ion will be. Hence, the more basic the respective base will be. So, we have the order : a > b > c > d.

→ As you should know that there is no electron-donating group of ___. The electron density on N atom of NH_3 is the least and hence, it is the weakest one.

→ To compare the basicity of the other three ammonia derivatives with methyl group(s), we should know that the 'formation of hydrogen bond'/ 'solvation effect' is a more important effect since it is an ___thermic process. So, we have the resultant order : a < d < b < c.

Case 3ii) The order shoud be :___> ___> ___> ___.

→ In **gaseous state**, there is **no** w_____ present in the system. Hence, the **solvation effect** is no longer exist since there is no solvent anymore. That means we **only** need to consider the _____ inductive effect only. As a result, the amine with the highest number of methyl group is the strongest one.



Further Thinking ***

Qu: Please arrange the following bases in the descending order of basicity.

a. $(CH_3)_3\mathbf{N}$ b. $(CH_3)_3\mathbf{P}$ c. $(CH_3)_3\mathbf{O}^-$

→ The order should be: __> __> __.

→ c is a negatively charged species. The c_____ density on the O atom is the highest among the three.

→ b is the weakest base because P has the lowest _____ density since P has the l_____ size.