

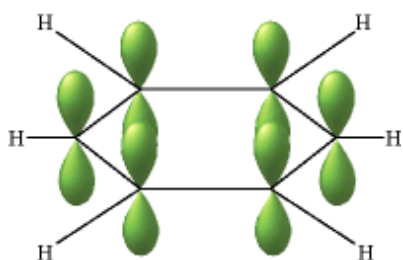
## A Second Year blog on Acids and Bases: 23rd March 2019

Resonance/Delocalisation/Stability/Conjugation and Hyperconjugation/the Inductive and Mesomeric Effects/Activation and Deactivation all involve the **sharing** of electrons. Sometimes electron density is **increased** (e.g. '+M' or '+I') and at other times electron density (e.g. '-M' or '-I') is **decreased**. The phrases "electron donating" and "electron withdrawing" are technically incorrect. In **molecular** species electrons are neither donated nor withdrawn, they are **SHARED** and **ELECTRON DENSITY** is thereby altered.

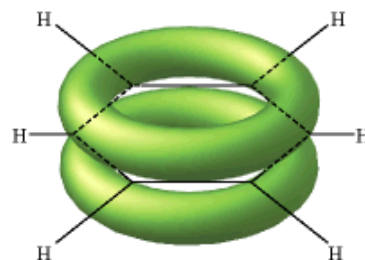
- The Inductive and Mesomeric effects are all about the **INCREASE** (+I or +M effects) or the **DECREASE** (-I or -M effects) in electron density – and now this next bit is vitally important. *In the Mesomeric Effect, it is not just the adjacent atom that is important. The electronegativity of the atom adjoining the adjacent atom is CRUCIAL*, and **that** is why there is a difference in the M effect between the species " $\text{NH}_2^-$ " and " $\text{NO}_2^+$ ".
- When we get to talking about Benzene and its derivatives in this book (and please do read last year's blogs on Benzene), I will go into it in much greater detail but, for the moment, let me tell you that Benzene ( $\text{C}_6\text{H}_6$ ) consists of six C atoms joined together in a ring with each C atom also joined to an H atom. By convention, the skeletal diagram below shows neither the six C atoms nor the six H atoms at each corner/vertex/apex of the Benzene ring.



- The way in which this configuration exists is that the electrons in the unhybridised 'p' orbitals of each of the six C atoms become **delocalised** amongst the six unhybridised 'p' orbitals, and **the six C atoms then share all the six delocalised electrons**. The following representations of Benzene are attempts to show what is happening.
- The representation **on the left** emphasises the fact that the unhybridised 'p' orbitals are all in the same vertical plane (at right angles to the horizontal plane of the six C atoms) and there will be an overlap of the unhybridised 'p' orbitals which allows for the mutual sharing of their electrons. The representation **on the right** below emphasises the *delocalisation* of all the electrons in the unhybridised 'p' orbitals in the planes above and below the horizontal plane of the benzene ring. **All the electrons in the unhybridised 'p' orbitals are SHARED. They are not confined to just one spot between any two bonding electrons. All six participating electrons are shared. They are DELOCALISED. The electrons can be found ANYWHERE in the circles above and below the Benzene ring.**



unhybridised 'p' orbitals perpendicular to the plane of the Benzene ring



delocalisation of the electrons in the unhybridised 'p' orbitals

**NB** These are **not** alternative configurations. Both are the same configuration of electrons (but with one not showing the overlap of delocalised electrons and the other showing the overlap).

## THE “I” EFFECT

### ‘+I’ EFFECT : ALL alkyl groups exert a positive inductive (+I) effect

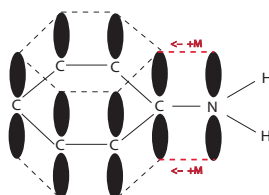
- Some sources give the electronegativity values of C as “2.55” and H as “2.20”. When therefore, a Carbon atom has Hydrogen atoms bonded to it, as in an Alkyl group (e.g.  $-\text{CH}_3$ , or  $-\text{C}_2\text{H}_5$ , or  $-\text{C}_n\text{H}_{2n+1}$ ), then the electron distribution pattern is denser around the Carbon atoms because they have drawn some of the electron density from the H atoms towards themselves. The Alkyl groups<sup>1</sup> then PUSH electron density away from themselves out along their fourth bonds, and *all Alkyl groups are thus electron “pushing” groups viz.  $\leftarrow-\text{CH}_3$  /  $\leftarrow-\text{C}_2\text{H}_5$  /  $\leftarrow-\text{C}_3\text{H}_7$  /  $\leftarrow-\text{C}_4\text{H}_9$  /  $\leftarrow-\text{C}_n\text{H}_{2n+1}$ .* (The arrow heads are just my way of trying to indicate that the alkyl group is pushing electron density along the fourth bond).

### ‘-I’ EFFECT: where the electron cloud is drawn towards the more electronegative atom

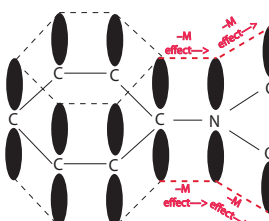
- Many elements are more electronegative than Carbon therefore, when bonded to a C atom, they all exert a **negative inductive (-I) effect** *along a sigma bond*.
- However, if there is also a  $\pi$  bond or a delocalised  $\pi$  bond (or ring) present, then although there will still be a -I effect **even so it will be overridden by a ‘+M’ effect (if there happens to be a ‘+M’ effect)**.

## THE “M” (Mesomeric) EFFECT

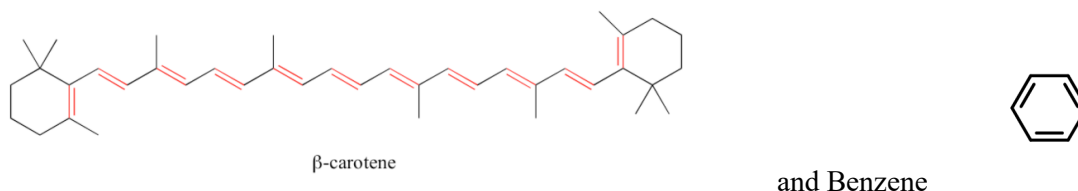
- In the ‘+M’ effect, the electron density of the  $\pi$  ring INCREASES.** In  $\text{C}_6\text{H}_5\text{NH}_2$  below, the unhybridised ‘p’ orbital on the N atom is so close to the unhybridised ‘p’ orbital of the C atom to which it is bonded that the electron in its unhybridised orbital gets locked into the  $\pi$  ring on the Benzene molecule and thus **INCREASES** the electron density of the  $\pi$  ring. **THAT is what the ‘+M’ effect is all about.** The electronegative N atom has pulled electron density off the H atoms and thereby **increased the electron density of the whole  $\pi$  ring**.



- In the ‘-M’ effect, the electron density of the  $\pi$  ring DECREASES.** Oxygen is more electronegative than Nitrogen, and if bonded together, an O atom will pull electron density off an N atom. In  $\text{C}_6\text{H}_5\text{NO}_2$  the O atom is pulling electron density off the N atom which in turn pulls electron density off the  $\pi$  ring. If a species that possesses an unhybridised ‘p’ orbital joins onto a pair of  $\pi$  bonded atoms and **DECREASES** the electron density in the existing overlap of the unhybridised ‘p’ orbitals (as the O atom is doing to the N atom below), then the Mesomeric effect is said to be a negative Mesomeric effect. **The ‘-M’ effect of the  $\text{NO}_2$  species reduces the electron density of the whole  $\pi$  ring.**



- When a species replaces one of the H atoms on Benzene (and it will then be called a “**substituent**”), it can have either an **Inductive effect** (along a  $\sigma$  bond) or a **Mesomeric effect** (along a  $\pi$  bond) on the Benzene molecule.
- You also need to know that any system where there is a series of alternating double and single bonds is called a “conjugated” system/a conjugated series, and  $\beta$ -carotene is an example of a conjugated system/series, and Benzene is another example of a conjugated system.



- By **understanding** the Inductive and Mesomeric Effects, you learn about the “Stability” of different species in Chemistry and about the **Activation and Deactivation of the Benzene ring**.

### The Inductive and Mesomeric Effects

- A) **The Inductive effect which acts ONLY upon a sigma ( $\sigma$ ) bond, and**  
 B) **the Mesomeric effect which acts ONLY upon a pi ( $\pi$ ) bond.**

- Both the Inductive (I) and the Mesomeric (M) effects are concerned with either
  - the pushing of electron density onto a given species (this giving a positive effect), or
  - the pulling of electron density away from a given species (this giving a negative effect)
 therefore **both the Inductive and the Mesomeric effects will depend on the difference in electronegativity between the two atoms involved in any bond.**

#### A) The Inductive Effect

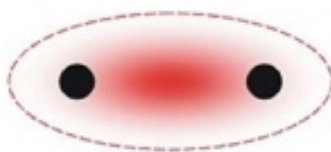
- The Inductive (I) effect is concerned with either
  - the pushing of electron density along a  $\sigma$  bond onto a given species (**the +I effect**), or
  - the pulling of electron density along a  $\sigma$  bond away from a given species (**the -I effect**).

#### Sigma ( $\sigma$ ) bonds<sup>1</sup>

- I would like you to be aware that we are talking about covalently bonded atoms (i.e. ones that are **sharing** one or more pairs of bonding electrons) and that it is the overlapping of orbitals and the sharing of the bonding electrons that causes the bond. When a pair of electrons (one from each of the pair of bonding atoms) is shared, **then a covalent bond is created**. The protons in the nuclei of the bonded atoms exert an electrostatic force of attraction on the pair of bonded electrons that lie

<sup>1</sup> Everything that I say in this Chapter is an ‘A’ Level explanation of what is happening. The real nature of what is happening is derived from wave mechanics (and that is not part of the ‘A’ Level Syllabus).

between the pair of bonded atoms. **The electrons are located between the two bonded atoms.** The  $\sigma$  bonded electrons cannot go anywhere in the sense that they cannot wander around and become “*delocalised*”. They are locked in the space between their parent nuclei.



Source: Prof Stephen Lower, Simon Fraser University

- When two atoms form a molecular bond, then the two atoms must be close enough together for there to be an overlap of orbitals. **When empty orbitals overlap, then in theory NOTHING happens.** A  $\sigma$  bond is a covalent **molecular bond**, and it can be formed **only** by either (i) the overlap of two half-filled orbitals (i.e. with each orbital having one electron in it) so that the two electrons are now shared by the two bonded atoms, or by (ii) the overlap of one orbital with two electrons in it and one orbital with no electrons in it, and where the two bonding electrons are donated by the first of the two bonding atoms (and a “dative” covalent bond is thus formed).
- The  $\sigma$  bond lies on the line connecting the **nuclei** of the two bonded atoms, and the strength of the bond will be determined by the electrostatic force of attraction of the two bonded nuclei on the bonded pair of electrons. The strength of the bond will also be determined by the size of the bonded atoms. The larger that the bonded atoms are, the farther apart will the two nuclei be from each other and thus *the longer will the bond be and the weaker will it be.* **The longer a  $\sigma$  bond is, the weaker it is – and the shorter it is, the stronger it is.** (In your First Year I explained this to you by using the analogy of a pencil. The shorter that a pencil is, the more difficult will it be to break.)
- Please note that **van der Waals’/London/Debye forces are NOT bonds<sup>2</sup>.** They are nothing more than weak forces of attraction. **Even Hydrogen bonds are not really ‘bonds’ either.** The force involved in Hydrogen bonds is only about  $50 \text{ kJ mol}^{-1}$  whereas the forces involved in covalent and ionic bonds are hundreds and sometimes even thousands of  $\text{kJ mol}^{-1}$ .

### **The Inductive Effect along a SIGMA BOND**

- The inductive effect operates **only along a sigma bond** (which exists between *every* two covalently bonded atoms) e.g. as in the covalent bond,  $\text{C}^{\delta+} - \text{Br}^{\delta-}$  or as in the  $\text{H}^{\delta+} - \text{Br}^{\delta-}$  bond.
- If there is a difference in electronegativity between the two atoms, then the electron cloud/the distribution pattern of the bonding electrons will be denser around the atom that is more electronegative – and this is indicated by the insertion of the Greek symbols “ $\delta^+$ ” and “ $\delta^-$ ” as in  $\text{H}^{\delta+} - \text{Br}^{\delta-}$ .
- The greater the difference in electronegativity between the two bonding atoms, the more **POLAR** (or more polarised) will the bond be, and the easier will it be for the two atoms to separate/to split apart. For example, in  $\text{H}^{\delta+} - \text{Br}^{\delta-}$  the two atoms can split apart into two oppositely charged ions,  $\text{H}^+$  and  $\text{Br}^-$ , and it will be important to understand this when we come to understand reaction mechanisms.

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<sup>2</sup> If you go to the web and look at the photograph of the 1927 Solvay Conference, you will see Peter Debye at the extreme left of the centre row. Debye received his Nobel Prize in 1936. It is amazing how many intellectual giants Göttingen University produced in the period between the two World Wars.

### +I EFFECT : ALL alkyl groups exert a positive inductive (+I) effect

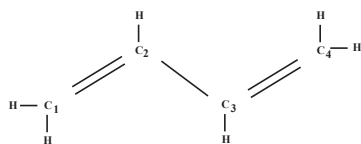
- Some sources give the electronegativity values of C as “2.55” and H as “2.20”. When therefore, a Carbon atom has Hydrogen atoms bonded to it, as in an Alkyl group (e.g.  $-\text{CH}_3$ , or  $-\text{C}_2\text{H}_5$ , or  $-\text{C}_n\text{H}_{2n+1}$ ), then the electron distribution pattern is denser around the Carbon atoms because they have drawn some of the electron density from the H atoms towards themselves. The Alkyl groups<sup>3</sup> then PUSH electron density away from themselves out along their fourth bonds, and *all Alkyl groups are thus electron “pushing” groups viz.  $\leftarrow\text{CH}_3 / \leftarrow\text{C}_2\text{H}_5 / \leftarrow\text{C}_3\text{H}_7 / \leftarrow\text{C}_4\text{H}_9 / \leftarrow\text{C}_n\text{H}_{2n+1}$* . (The arrow heads are just my way of trying to indicate that the alkyl group is pushing electron density along the fourth bond).

### -I EFFECT: where the electron cloud is drawn towards the more electronegative atom

- Many elements are more electronegative than Carbon therefore, when bonded to a C atom, they all exert a **negative inductive (-I) effect** *along a sigma bond*.
- However, if there is also a  $\pi$  bond or a delocalised  $\pi$  bond (or ring) present, then although there will still be a -I effect **even so it will be overridden by a + M effect (if there happens to be a +M effect)**.

### B) The M Effect / When does an M effect come into play?

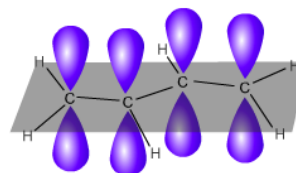
- The M effect** is somewhat more complicated to describe in words than was the I effect, *but it is all about unhybridised ‘p’ orbitals being so close to each other that this then allows the electrons therein to leach into/to swim over into and wander freely through each other’s ‘p’ orbitals*. It becomes a bit easier to understand when it is seen in diagrams!
- The M effect is triggered when two species A and B are bound together and where
  - one of them (let’s call it species A) has either a double bond or else has an alternating-double-and-single-bond system such as that which exists in butadiene (shown below)



and

- where species B (which joins onto species A) has a half-filled unhybridised ‘p’ orbital that comes so close to one of the unhybridised ‘p’ orbitals in species A, that the electrons in B’s ‘p’ orbital leach into/swim over into A’s unhybridised ‘p’ orbitals.

Delocalisation in Butadiene



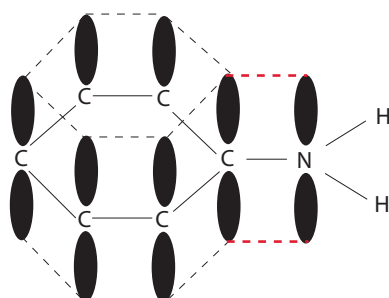
<sup>3</sup> I did not say “alkanes”. I said “alkyl groups”.

- For example, in the diagram below a chlorine atom has joined onto buta-1,3-diene to create 4-chlorobuta-1,3-diene<sup>4</sup> and there is now a –M effect. The diagrams below are of the same molecule.



- Let me use Benzene as an example – and here I am going to use C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> as my molecule. Let us regard Benzene as the designated ‘*species A*’ and it can be thought of as having an alternating double and single bond system. NH<sub>2</sub> will then be the designated ‘*species B*’ that has bonded onto one of the C atoms in the –C<sub>6</sub>H<sub>5</sub> species. The N atom in NH<sub>2</sub> will then have an unhybridised ‘p’ orbital so close to the unhybridised ‘p’ orbital in the delocalised π ring in Benzene, that the electron in N’s unhybridised ‘p’ orbital will leach into/swim over into Benzene’s delocalised π ring.

An M effect has now been established



- I have used a red dotted line to indicate that the unhybridised ‘p’ orbital in N is **so** close to the unhybridised ‘p’ orbital in the C atom to which it has bonded that **the electron in N’s unhybridised ‘p’ orbital thinks that it belongs to Benzene’s delocalised π ring so it starts swimming in the delocalised π ring as though it owns it.**

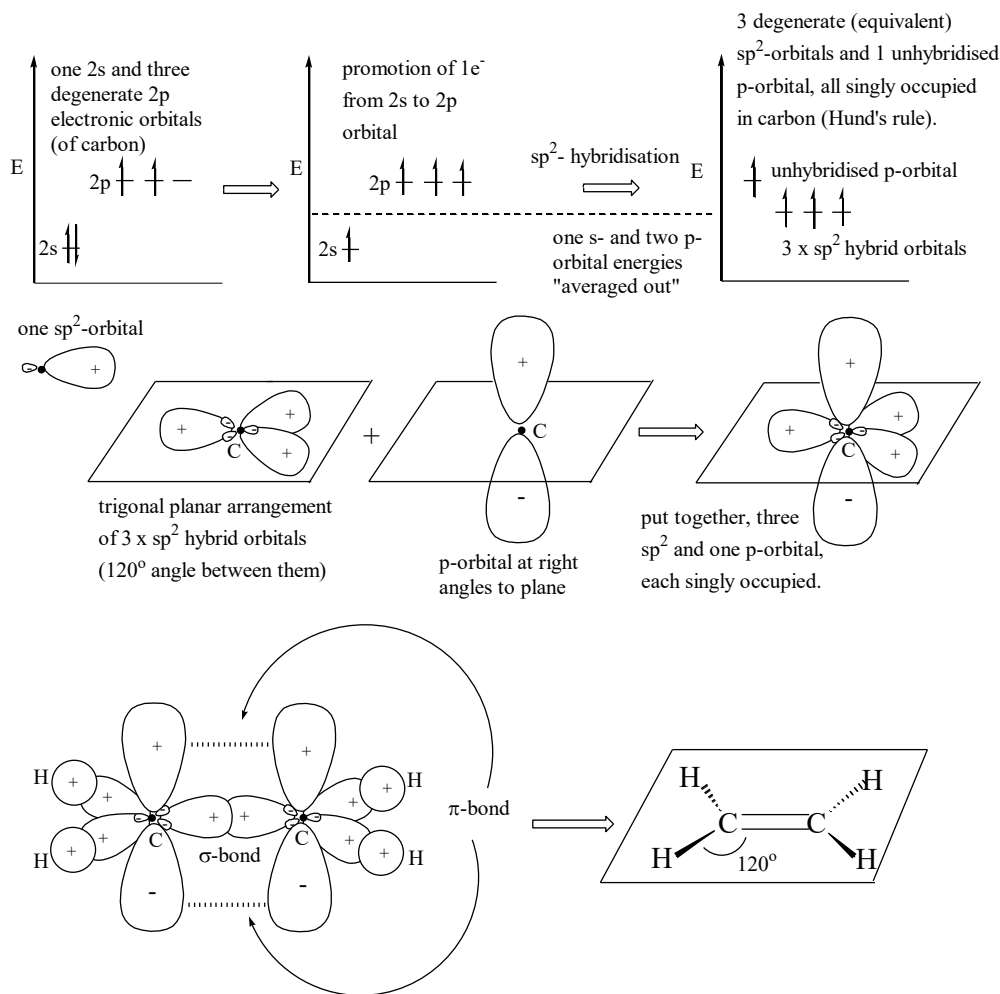
NB There **CANNOT** be a double bond between the N and the C atoms because N is in Group 5 and it already has three bonds. **There is NO double bond between the N and the C atoms – and yet the electron in N’s unhybridised ‘p’ orbital is behaving as though there were one.**

- OK, we have established how an M effect occurs, and now we have to see when it will be a +M effect and when it will be a –M effect.**

<sup>4</sup> Strictly speaking, it is better/advisable to state the orientation of the Cl and name it “(1E)-1-chlorobuta-1,3-diene”. The “E” comes from the “Zusammen” / “Entgegen” location Nomenclature.

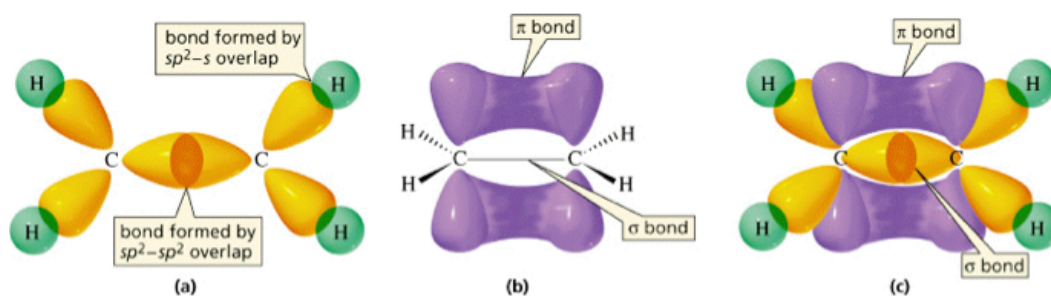
## The M effect can work only through a $\pi$ bond

- You may not have done much (or indeed any) Chemistry in the summer hols, therefore let me remind you that Benzene's alternating double and single bond/delocalised  $\pi$  ring system makes it behave a bit like an Alkene – so please therefore re-read Chapter 5 on Alkenes in my First Year Organic book.
- The diagram below is the one from Dr N Chatterton of London Metropolitan University, and it shows the shape of the three ' $sp^2$ ' hybridised atomic orbitals that a Carbon atom needs to form when it forms an Ethene molecule. (Do not worry about the word "degenerate" – it just means "possesses the same amount of energy".)



Source, Dr N Chatterton, London Metropolitan University

- The  $\pi$  bond is in Ethene, and as you can see in the diagram, the bond between each C atom and each H atom is formed by the overlap of two atomic orbitals viz. an 's' orbital from the H atom and an hybridised ' $sp^2$ ' orbital from the C atom thus forming a molecular  $\sigma$  orbital which forms the **molecular  $\sigma$  bond**.
- The diagram overleaf is from Prof Stephen Lower's (Simon Fraser University) excellent virtual Chemistry textbook <http://www.chem1.com/acad/webtext/virtualtextbook.html> and it attempts to show the Ethene molecule in three dimensions.



- Benzene is slightly different from Ethene, and in your shoes I would start by looking at Dr Wayne Breslyn's drawing of the Lewis structure for Benzene ( $C_6H_6$ ) on [https://www.youtube.com/watch?v=2kXg\\_jncMpM](https://www.youtube.com/watch?v=2kXg_jncMpM).

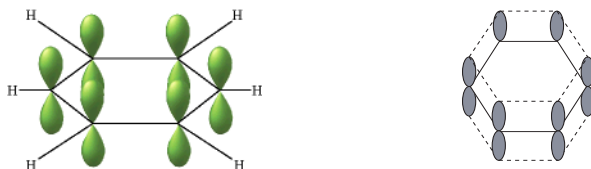
### The Mesomeric effect acting along a $\pi$ bond

- In telling you about the Inductive effect, I stressed the fact that the 'I' effect acts only along a  $\sigma$  bond – and now I will stress the fact that **the Mesomeric effect will act only along a  $\pi$  bond**.
- The Mesomeric effect will work along **any**  $\pi$  bonded system (alkene/poly-alkene/benzene/poly-benzene system)! However, the atom which is exerting the M effect on the atom to which it is bonded is **not double-bonded to that atom**. The M effect works merely by increasing the electron density in the  $\pi$  bonded system.<sup>5</sup>
- In the diagrams of Ethene, two C atoms have bonded together and formed a double bond (i.e. a  $\sigma$  bond and a  $\pi$  bond) – but as yet there is no Mesomeric effect involved. However, if a third atom (which possesses an unhybridised 'p' orbital *that lies in the same plane as the unhybridised 'p' orbitals of the two atoms that already have a double bond between them*) now bonds onto one of the double bonded atoms, **then the third atom will get locked into the overlap of the existing  $\pi$  bond and increase the electron density of this bond even though it is NOT double bonded to its neighbouring atom**.
- **Please do read that last sentence again. It is SO important, and I am going to bash home this message to you.**
- Let me draw the situation for you, and then you will see what I am talking about, and I shall again use the benzene compound called "phenylamine" / "aniline" ( $C_6H_5NH_2$ ) to illustrate what I am saying.
- **Again, please note that there is NO DOUBLE BOND between the N atom and the C atom to which it is bonded.**
- The first two representations below are those of Benzene ( $C_6H_6$ ). Would you take my word for it that in the hexagon overleaf, there is a C atom at each of the six corners of Benzene, and that each of those C atoms is attached to an H atom. That is what Benzene is,  $C_6H_6$ . (The first representation is that of Prof Stephen Lower of Simon Fraser University. The second is mine.) Carbon atoms

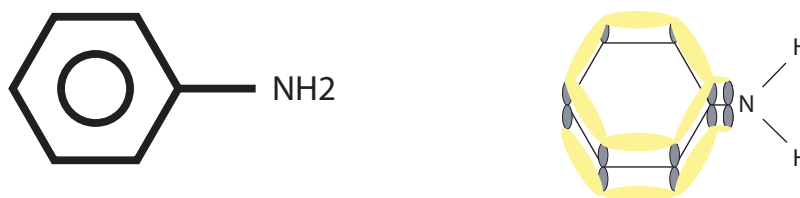
<sup>5</sup> As we shall see in a few weeks' time, the Mesomeric effect on an Arene is of extraordinary importance in the synthesis of Carbon compounds in medicine.



have to have four bonds, and each C atom in Benzene has four bonds: one  $\sigma$  bond to each one of its neighbouring C atoms, one  $\sigma$  bond to its H atom, and (in a sense) half a  $\pi$  bond to each of its neighbouring C atoms (and those two half bonds together make a full  $\pi$  bond). **In actual fact, the  $\pi$  bond takes the form of a delocalised  $\pi$  ring (which I have shown as a dotted line above and below the plane of the six C atoms) that locks together ALL the 6 C atoms in Benzene.**



- The next two representations are those of phenylamine (or aniline as it is also called).

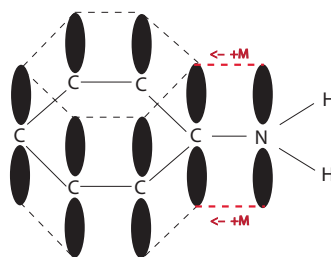


- There cannot be a double bond between the C atom (in Group IV) and the N atom because then the C atom would have **five** bonds and a C atom can have only four bonds. Moreover, there cannot be a double bond between the N atom (in Group V) and the C atom because the N atom would then have **four** bonds and an N atom can have only three bonds to complete its octet.
- There is no double bond between the C atom and the N atom** – but even though there is no double bond between the N and the C atoms, nevertheless the proximity of the two adjacent unhybridised ‘p’ orbitals causes the electron in the non-double-bonded atom to join in the delocalised  $\pi$  ring **without any double bond being formed**.
- It is purely the proximity of the unhybridised ‘p’ orbitals of the C and the N atoms that causes the M effect even though no double bond is formed.**
- Let me remind you that in the Mesomeric Effect, it is not just the adjacent atom that is important. The electronegativity of the atom adjoining the adjacent atom is **CRUCIAL** and **that** is why there is a difference in the M effect between the species “ $\text{NH}_2^-$ ” and “ $\text{NO}_2^+$ ”.

#### a) **The Positive (+M) Mesomeric effect acting along a $\pi$ bond**

- In the +M effect, the electron density of the  $\pi$  ring INCREASES.** In  $\text{C}_6\text{H}_5\text{NH}_2$  overleaf, the unhybridised ‘p’ orbital on the N atom is so close to the unhybridised ‘p’ orbital of the C atom to which it is bonded, that the electron in its unhybridised orbital gets locked into the  $\pi$  ring on the Benzene molecule and thus **INCREASES** the electron density of the  $\pi$  ring. **THAT is what the ‘+M’ effect is all about.** The electronegative N atom has pulled electron density off the H atoms and has thereby **increased the electron density of the whole  $\pi$  ring**.

- The M effect is created by the proximity of unhybridised 'p' orbitals which allows the delocalisation of the electrons in all the adjoining unhybridised 'p' orbitals. Whether the resulting M effect is positive or negative will depend on the atom which has joined onto the C atom.
- If a species that possesses an unhybridised 'p' orbital joins onto a pair of  $\pi$  bonded atoms and **increases the electron density in their existing overlapping unhybridised 'p' orbitals**, then the Mesomeric effect is said to be a positive Mesomeric effect. That is it! It is literally as simple as that. There is nothing more to it than that! **That is the positive Mesomeric effect.**
- In the example of  $C_6H_5NH_2$ , an " $-NH_2$ " species has replaced an H atom on a Benzene molecule and it is the proximity of the unhybridised 'p' orbital on the bonded N atom which is in the same plane as the unhybridised 'p' orbital on the C atom that allows the electron from the N atom to wander into/to "leach" into the delocalised  $\pi$  ring of the Benzene part of the phenylamine molecule and thereby increase the electron density in the  $\pi$  ring – thus creating a **+M effect**.
- Nitrogen is more electronegative than Carbon therefore *there is a -I effect on the  $\sigma$  bond* between the N atom and the C atom, but the unhybridised '2p' electron in the N atom is locked into the delocalised  $\pi$  ring on the Benzene molecule and that increases the electron density on the  $\pi$  ring – and this causes a +M effect. In a sense therefore, there are now 7 delocalised electrons in the Benzene  $\pi$  ring<sup>6</sup> and this **+M effect always outweighs the -I effect**.
- **An M effect always outweighs an I effect.**



- If you are doing an Entrance exam, then you may be asked about the +M effect of a substituent on a double bonded molecule such as Ethene, but it is much more likely that you will be asked about the +M effect of a substituent<sup>7</sup> on a benzene or a benzene derived (i.e. a "phenyl" or perhaps an "aryl") molecule<sup>8</sup>. When we come to the Chapters on Benzene and its derivatives, we will talk in some detail about substitution, and also about activation and deactivation (but for the moment could you just lodge at the back of your brain somewhere that the Mesomeric effect is unbelievably important in Aromatic Chemistry).

## b) The Negative (-M) Mesomeric Effect

- **In the -M effect, the electron density of the  $\pi$  ring DECREASES.**  
In  $C_6H_5NO_2$  below, the O atom (acting through the N atom) pulls electron density off the  $\pi$  ring.
- To illustrate the -M effect, I am going to use a Nitrobenzene ( $C_6H_5NO_2$ ) molecule. It is somewhat difficult to discuss the three-dimensional attributes of any molecule, but there is a free application

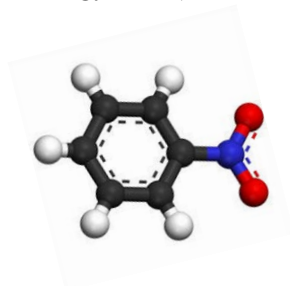
<sup>6</sup> ... but please remember that **there is no double bond between the N atom and the C atom**.

<sup>7</sup> "Substituent" from the verb to "substitute" i.e. something that substitutes for something else (but I myself prefer the term "replacement").

<sup>8</sup> The old name for benzene-derived molecules was "aromatic" (because the first benzene derived molecules that were discovered all smelt nice), but the adjective that is used today as the adjective for Benzene is either "phenyl" or "aryl" .

on the internet called “Jmol” that allows those who are interested in Chemistry (and *I presume that the people who are not, will not use it*) to view molecules in 3-D and to manipulate them. If you can view it in your search engine/browser, then you might want to use it to view C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>.

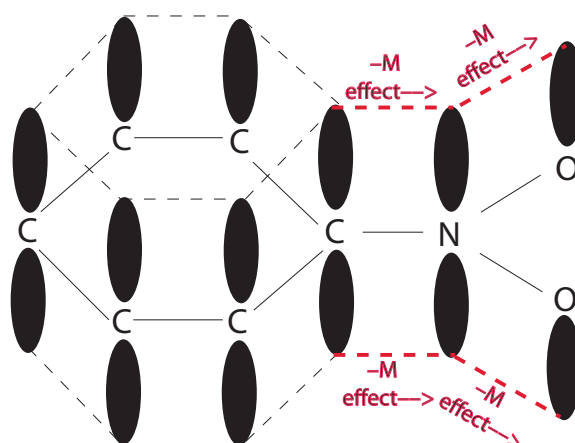
- The diagram below, is a ball-and-stick Lewis model of Nitrobenzene rather than the resonance structure of the molecule. I cannot find anything on the web that attempts a 3-D representation, so I have tried to create one using Adobe Illustrator and I show it to you overleaf. (For all I know, you are miles more adept at using computer technology than I am – and at my age I am astounded that I am able to use any modern technology at all.)



- Right, let me try to explain the -M effect.
- If a species that possesses an unhybridised ‘p’ orbital joins onto a pair of  $\pi$  bonded atoms and **DECREASES** the electron density in the existing overlap of the unhybridised ‘p’ orbitals, then the Mesomeric effect is said to be a negative Mesomeric effect.
- We must now ask the question “How does this *decrease* in electron density occur?”, and the answer to this question is “through differences in electronegativity”.
- The unhybridised ‘p’ orbital on the N atom of C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> is in close proximity to that of the C atom to which it is bonded, but here the unhybridised ‘p’ orbitals on the two O atoms are also in close proximity to the unhybridised ‘p’ orbitals on the N atom<sup>9</sup>, and it is this proximity that allows the electrons in the N atom and the two O atoms to wander into and get trapped in the delocalised  $\pi$  ring of the benzene part of the molecule – *this being the M effect*.
- However, Oxygen is the second most electronegative element in the Periodic Table and the two O atoms via the N atom thus draw the electron cloud/electron density from the delocalised  $\pi$  ring onto themselves, and **it is this reduction of the electron density in the delocalised  $\pi$  ring (caused by –NO<sub>2</sub>) that is called the “–M effect”**.
- If the atom of the substituent species (i.e. the N atom) is itself bonded to one or more atoms that are more electronegative than it itself is (as is the case here because Oxygen is more electronegative than Nitrogen), then those more electronegative O atoms **will pull electron density off the N atom, and it in turn will pull electron density off the  $\pi$  ring of benzene and that decreases the electron density on the  $\pi$  ring**.

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<sup>9</sup> ..... and they are all in the same vertical plane (at right angles to the horizontal plane of the benzene part of the molecule).



NB In the diagram above I have not shown the full extent of the  $-M$  withdrawal of electron density because I was not able to draw in all the different bits of the unhybridised 'p' orbitals on the O atoms. However, there may be a University that publishes (on the web) good three-dimensional diagrams of molecules. American Universities are much better at sharing such information freely than British Universities are.

- Once you have got the hang of how it operates, then the workings of the  $-M$  effect are just as simple as the workings of the  $+M$  effect. All that you need to remember is that **if the bonding atom of the substituent species is itself bonded to one or more electronegative atoms than it itself is, then a  $-M$  effect will occur.**

### $+M$ or $-M$ Mesomeric effect?

- The easiest way of seeing what is happening is to draw the species concerned, and then to look and see which species is pushing and which is pulling! For example, one can straight away see that
  - i) an H atom cannot participate in a Mesomeric effect because an H atom **has no 'p' orbitals** (hybridised or unhybridised)! Equally, saturated Carbon atoms have no *unhybridised* 'p' orbitals (because their atomic '2s' and '2p' orbitals have been hybridised into four 'sp<sup>3</sup>' molecular orbitals) therefore
  - ii) Alkyl groups also **CANNOT** participate in Mesomeric effects.
- However, in the exams **I do not want you to try to work out from first principles whether or not a substituent species that joins onto a system of  $\pi$  bonded atoms** (in a poly-alkene molecule or in an aryl molecule) does or does not have an unhybridised 'p' orbital – **and it would be monstrously unfair of the examiners to expect you to do so.** All that they can do is to give you a bog-standard joining species that is well-known for having either a negative or a positive Mesomeric effect and then test your understanding of the consequences of its effect.

### NEGATIVE MESOMERIC EFFECT

Electron density on the  $\pi$  ring **DECREASES**

- NO<sub>2</sub> (Nitro compounds)
- COOH (Benzoic Acid group)
- C=O (Carbonyl groups)
- C≡N (Nitriles)
- SO<sub>3</sub>H (Sulphonic groups)

### POSITIVE MESOMERIC EFFECT

Electron density on the  $\pi$  ring **INCREASES**

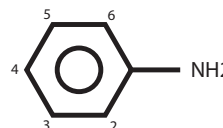
- NH<sub>2</sub> (Amine derivatives)
- NRR where R has no unhybridised 'p' orbitals
- OH (Alcohols)
- OR' where R has no unhybridised 'p' orbitals

### Activation/Deactivation

- All that I will say here is that

**Activation** causes electrophilic substitution at 2,4,6 whereas **deactivation** causes electrophilic substitution at 3,5.

- In a Benzene ring it does not matter where you start your counting, but once you have put something onto your ring, then you must start your counting from that point and it does not matter whether you go clockwise or anti-clockwise. In space (since there is no reference point and thus no left/no right/no up/no down) there is no way of going clockwise or counter-clockwise.



- Before I leave the topic of Mesomerism, I ought to warn you that “Mesomerism” is a term that we use in England because of the work done by Sir Christopher Ingold. Linus Pauling did similar work (I think at CalTech), and in America chemists refer to the Mesomerism that I have talked about as “electron donating” or “electron withdrawing” (and in India, they use the term “Mesomerism” slightly differently from the way in which we use it in the UK). However, please be aware that no electrons can be donated in a molecular structure because that would then form an IONIC structure. **The American terminology is thus technically INCORRECT!**