

### **Raffles Institution** Year 5 H2 Chemistry 2022 Lecture Notes 8 – Chemical Bonding II (Hybridisation and Resonance)

#### Learning outcomes

Students should be able to:

- (a) describe sp<sup>3</sup> hybridisation, as in ethane molecule, sp<sup>2</sup> hybridisation, as in ethene and benzene molecules, and sp hybridisation, as in ethyne molecule
- (b) explain the shapes of, and bond angles in, the ethane, ethene, benzene, and ethyne molecules in relation to  $\sigma$  and  $\pi$  carbon-carbon bonds
- (c) predict the shapes of, and bond angles in, molecules analogous to those specified in (b)
- (d) interpret, and use the term "delocalisation" associated with organic reactivities.

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#### Hybridisation 1

- The theory of covalent bond formation via overlapping of atomic orbitals does not always . give good agreement with observations.
- Hybridisation is a concept used to explain the observed shapes of molecules (determined by experimental studies).
- On hybridisation, a set of atomic orbitals are mixed to generate a set of equivalent hybrid orbitals with the same shape and energy.

(Note: number of hybrid orbitals formed always equals number of atomic orbitals used for mixing.)

- Consider the electronic configuration of carbon at ground state (1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>2</sup>).
  - To form a normal covalent bond, an orbital containing one electron is required. These (i) orbitals overlap to form a covalent bond.
  - Carbon in its ground state contains only two singly occupied orbitals, thus it should (ii) form 2 covalent bonds. However, carbon tends to form 4 covalent bonds.
  - To have four singly occupied orbitals for forming 4 covalent bonds, an electron must (iii) first be promoted from the 2s orbital to the empty 2p orbital.



- > Carbon now has 4 unpaired electrons and can form 4 covalent bonds, but the atomic orbitals do not point in the correct direction for bonding.
- (iv) For example, CH<sub>4</sub> is tetrahedral with H-C-H bond angles of 109.5°, but the p orbitals  $(p_x, p_y, p_z)$  are perpendicular (at 90°) to one another.
- To explain the four C-H bonds in methane with H-C-H angles of 109.5°, the (v)hypothetical concept of hybridisation is used.

## 1.1 sp<sup>3</sup> hybridisation of carbon in methane, CH<sub>4</sub>

- Structural studies have shown that CH₄ is **tetrahedral** with all the C–H bonds being of equal bond lengths and the four H–C–H angles are all 109.5°.
  - This implies that carbon must provide four equivalent orbitals for head-on overlap with the 1s orbital from each H atom to form four identical C–H σ bonds.
  - The hybrid orbitals are oriented in a tetrahedral geometry, containing a single unpaired electron each.
  - Four equivalent hybrid orbitals for carbon are generated by mixing one 2s orbital with the three 2p orbitals, resulting in the formation of four sp<sup>3</sup> hybrid orbitals.



The large lobes of the hybrid orbitals point towards the corners of a tetrahedron.

#### Notation:

The superscripts for hybrid orbitals correspond to the number of atomic orbitals used to form them. The number "1" is not written as it is understood to be "1"

For example:  $sp^3 = s^1p^3 \Rightarrow one$  2s and three 2p orbitals used to form four  $sp^3$  hybrid orbitals.



In the ground state of C, there are only 2 unpaired electrons, thus it is able to form only 2 covalent bonds. C\* in the excited state, with 4 unpaired electrons, cannot form 4 equivalent C—H bonds to give a symmetrical tetrahedral molecule.

Four equivalent  $sp^3$  hybrid orbitals are formed from one 2s and three 2p orbitals.

Each of the four sp<sup>3</sup> hybrid orbitals of carbon overlaps with the 1s orbital of a hydrogen atom to give a tetrahedral methane molecule.



- > sp<sup>3</sup> hybridisation results in tetrahedral electron pair geometry.
- > Other examples of molecules where central atom is sp<sup>3</sup> hybridised:  $\underline{C}H_3\underline{C}H_3$ ,  $\underline{N}H_3$ ,  $H_2\underline{O}$
- 1.2 sp<sup>2</sup> hybridisation in ethene, C<sub>2</sub>H<sub>4</sub>
- Structural studies have shown that C<sub>2</sub>H<sub>4</sub> is planar with all the C-H bonds being of equal bond lengths and the H-C-H and C-C-H angles are all 120°.



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- This implies that carbon must provide three equivalent orbitals for head-on overlap with the 1s orbital from each H atom, and with the hybrid orbital of another C atom.
- > The hybrid orbitals are oriented in a trigonal planar geometry, each containing a single unpaired electron.
- The C–H bonds in C<sub>2</sub>H<sub>4</sub> are single covalent bonds, while the carbon-carbon bond is a double bond, C=C.
  - > Each carbon forms three  $\sigma$  bonds (two with two hydrogen atoms and one with a carbon atom) and one  $\pi$  bond (with the carbon atom).
  - Each carbon atom undergoes sp<sup>2</sup> hybridisation to generate three equivalent sp<sup>2</sup> hybrid orbitals (for forming three σ bonds).
  - > An **unhybridised**  $2p_z$  orbital remains (for forming one  $\pi$  bond).



6C atom in ground state

6C\* atom in excited state before hybridisation

c\* atom in excited state after hybridisation



In the ground state of C, there are only 2 unpaired electrons, thus it is able to form only 2 covalent bonds.

When one 2s electron is promoted to vacant 2p orbital to form C\* in excited state that has four singly occupied orbitals to form four covalent bonds.

Three equivalent sp<sup>2</sup> orbitals are formed from one 2s and two 2p orbitals. There is also one unhybridised 2p orbital.

- Two of the sp<sup>2</sup> hybrid orbitals overlap with the 1s orbitals of two H atoms while the other sp<sup>2</sup> hybrid orbital overlaps with the sp<sup>2</sup> hybrid orbital of the other C atom.
- > The unhybridised  $2p_z$  orbitals of each carbon atom contains an unpaired electron. The side–on overlap of these unhybridised  $2p_z$  orbitals gives the  $\pi$ –bond.



The unhybridised p orbital is perpendicular to the plane containing the  $sp^2$  hybridised orbitals.

- sp<sup>2</sup> hybridisation results in trigonal planar <u>electron pair geometry</u>.
- > Other examples of molecules where central atom is  $sp^2$  hybridised: **<u>B</u>**F<sub>3</sub>, H**<u>C</u>HO**

#### 1.3 sp hybridisation in ethyne, C<sub>2</sub>H<sub>2</sub>

- Structural studies have shown that  $C_2H_2$  is **linear** with the **C**-H bonds being of equal bond lengths and the H-C-C and C-C-H  $H-C\equiv C-H$  angles are **180**°.
  - This implies that carbon must provide two equivalent orbitals for head-on overlap with the 1s orbital from the H atom, and with the orbital of another C atom.
  - Each hybrid orbital is oriented in a linear geometry and contains one electron.

- The C–H bonds are single covalent bonds; the carbon–carbon bond is a triple bond, C≡C.
  - Each carbon forms two σ bonds one with one H atom and one with a carbon atom.
  - Each of the carbon atoms undergoes sp hybridisation to generate two equivalent sp hybrid orbitals (to form two σ bonds).



#### 6C atom in ground state

## <sub>6</sub>C\* atom in excited state before hybridisation

# <sub>6</sub>C\* atom in excited state after hybridisation



- One of the sp hybrid orbitals overlap with the 1s orbital of one H atom while the other sp hybrid orbital overlaps with the sp hybrid orbital of the other C atom.
- > The two unhybridised 2p orbitals each contain an unpaired electron. The side-on overlap of these unhybridised 2p orbitals on the two C atoms give rise to two  $\pi$  bonds.





The unhybridised p orbitals are **perpendicular** to each other and the line containing the sp hybridised orbital.

- > sp hybridisation results in linear electron pair geometry.
- Other examples of molecules where central atom is sp hybridised: <u>BeF<sub>2</sub>, CO<sub>2</sub></u>

### Summary

Type of hybridisation	sp <sup>3</sup>	sp²	sp
s and p orbitals involved	$\begin{array}{c}z\\ x\\ y\\ y\\ y\\ y\\ x \\ x \\ y\\ y$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
Diagram to show the hybrid orbitals	109.5°	120°	180°
Total no. of hybrid orbitals formed	four	three	two
Total no. of unhybridised p orbitals	0	1	2
No. of regions of electron density	4	3	2
Electron-pair geometry around atom	tetrahedral	trigonal planar	linear
Examples	ethane	ethene	ethyne

Exercise 1: For each of the circled atoms below, state the type of hybridisation it has undergone. (i) H = 0 (ii) H = 0 (iii) H = 0 (iii) H = 0 (iii) H = 0

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## 1.4 Effect of Hybridisation on Bond Length and Bond Strength

- The s orbital is spherical and electrons are closer to nucleus.
- s-character in hybrid orbitals:
  - sp<sup>3</sup> (25% s character) < sp<sup>2</sup> (33% s character) < sp (50% s character).</p>
- The higher the s-character of hybrid orbital,
  - > the less diffuse the hybrid orbital,
  - > the more tightly the shared electrons are held by the nuclei,
  - > the more effective its overlap with the orbital of the other atom,
  - > the stronger the bond and the shorter its bond length.
- Thus, moving from ethane to ethene to ethyne,
  - > C-H bond strength increases
  - C-H bond length decreases from ethane to ethene to ethyne as shown in the table below:

Compound	Ethane, C <sub>2</sub> H <sub>6</sub>	Ethene, C <sub>2</sub> H <sub>4</sub>	Ethyne, C <sub>2</sub> H <sub>2</sub>
Structural formula	н н нсн н н		н—с≡с—н
Hybrid orbitals of C	<i>sp</i> ³ (25% s-character)	<i>sp</i> ² (33% s-character)	<i>sp</i> (50% s character)
Orbitals involved in forming C–H bond	sp <sup>3</sup> hybrid orbital of C with s orbital of H	sp <sup>2</sup> hybrid orbital of C with s orbital of H	sp hybrid orbital of C with s orbital of H
C–H bond energy/ kJ mol <sup>-1</sup>	410	451	536
C–H bond length/ pm	112	110	106



#### 2 Resonance

- Some molecules / ions cannot be adequately represented by a single structure.
- Consider the anion HCONH<sup>-</sup>. Two structures are possible:



- The two structures are called resonance structures. They have the same placement of atoms but a different arrangement of electrons.
- In terms of electron arrangement, resonance structures differ in the placement of  $\pi$  bonds and non-bonding electrons. The placement of atoms and  $\sigma$  bonds stays the same.
- A molecule/ ion exhibits resonance if it has two or more resonance structures.
- In general, a molecule/ ion exhibits resonance when there is <u>continuous side-on overlap</u> of p-orbitals over at least 3 adjacent atoms, allowing for <u>delocalisation of the π</u> <u>electrons</u>.
- Resonance is discussed using the three examples of ozone, nitrate ion and benzene.

#### Example 1: Ozone, O3

- (a) Resonance structures:
- There are two possible resonance structures for O<sub>3</sub> as shown below.



The resonance structures differ in the placement of  $\pi$  bonds and non-bonding electrons. The placement of atoms and  $\sigma$  bonds stays the same.

(b) Experimental evidence of resonance in O3:

- The resonance structures suggest that the O<sub>3</sub> molecule would be unsymmetrical, with the O=O bond shorter than the O→O bond.
- However, when the oxygen-oxygen bond lengths in O<sub>3</sub> are measured, both are found to be the same, and mid-way between O–O and O=O bond lengths in other molecules.

Bond	Bond length /nm	
O–O single bond	0.148	
O–O bond in ozone	0.128	
O=O double bond	0.121	

- (c) Explanation:
- Both resonance structures are NOT the correct representations of the O<sub>3</sub> molecule.
- In reality, the actual structure of the molecule is a *hybrid* of the resonance structures, known as the **resonance hybrid**.
  - > In the resonance hybrid,  $\pi$  electrons are delocalised over the 3 adjacent oxygen atoms, via the continuous side-on overlapping of *p* orbitals, which are perpendicular to the plane of the molecule (containing  $\sigma$  bonds).





resonance structures (or canonical forms)

resonance hybrid

The continuous side-on overlap of p orbitals over three O atoms allows for delocalisation of the  $\pi$  electrons over the three O atoms.

 The resonance hybrid is more stable than any one of the resonance structures because it delocalises electron density over a larger volume.

#### NOTE:

- "Resonance" does not mean the species 'flip-flops' back and forth between the 2 canonical forms. "↔" does not mean the resonance forms are in equilibrium.
- π electrons are <u>localised</u> if they are shared between 2 atoms of the π bond only, for example in ethene, CH<sub>2</sub>=CH<sub>2</sub>.
   π electrons are <u>delocalised</u> if they are shared among more than 2 atoms through continual overlap, for example in O<sub>3</sub> and other molecules/ ions which exhibit resonance.

Example 2: Nitrate ion, NO3-

- (a) Resonance structures:
- There are three possible resonance structures for NO<sub>3</sub><sup>-</sup> as shown below.



- (b) Experimental evidence of resonance in NO3-:
- Experimental evidence again reveals that all the nitrogen-oxygen bonds are identical and intermediate between an N–O single bond and an N=O double bond:

Bond	Bond length /nm
N–O single bond	0.136
N–O bond in NO₃ <sup>–</sup>	0.121
N=O double bond	0.115

- (c) Explanation:
- The resonance structures are **NOT** the correct representations of the molecule.
  - > In reality, the **actual structure** of the molecule is a **hybrid** of them.
  - > In the resonance hybrid,  $\pi$  electrons are delocalised over adjacent N and O atoms, via the continuous side-on overlapping of *p* orbitals which are perpendicular to the plane of the molecule (containing  $\sigma$  bonds).





Resonance hybrid,

- contains delocalised electrons,
- the negative charge is not localised on one O atom but delocalised over the three O atoms.

Other examples of ions which show resonance:

(i) Carbonate, CO32-



(ii) Ethanoate, CH<sub>3</sub>COO<sup>-</sup>



π electrons are delocalised over –OCO group.
 -ve charge is delocalised over two O atoms.

#### Example 3: Benzene, C<sub>6</sub>H<sub>6</sub>

The carbon atoms are arranged in the form of a regular hexagon, with all bond angles in the molecule corresponding to 120°.

Each of the six carbon atoms in benzene is sp<sup>2</sup> hybridised with an unhybridised p-orbital perpendicular to the plane.

(a) Resonance structures:

Benzene has the following resonance structures.



- (b) Experimental evidence of resonance in benzene:
  - Both structures **a** and **b** show that of the six carbon-carbon bonds, three are single bonds while three are double bonds.
  - The bond length of a C–C single bond is longer than a C=C double bond. However, experimentally, it is found that all C–C bond lengths in benzene are equal and this bond length is <u>intermediate</u> between a C–C single bond and C=C double bond.

Bond	Bond length /nm
C-C single bond	0.154
C-C bond in benzene	0.139
C=C double bond	0.133



- (c) Explanation:
  - Neither of the 2 resonance structures / canonical forms is an accurate representation but each contributes to the actual structure.
  - The real molecule is described by an <u>average</u> of the 2 resonance forms:



- Structure c, the resonance hybrid of structures a and b, is more stable than any one of the resonance structures, a or b.
- The resonance hybrid is more stable because of <u>delocalisation</u> of the  $\pi$  electrons. The six carbon atoms in the benzene molecule are  $sp^2$  hybridised. Each carbon atom has an **unhybridised p orbital** containing one electron.



- The six unhybridised p orbitals in benzene overlap side-on continuously. This allows the six electrons in the p orbitals to interact, forming a plane of delocalised  $\pi$  electron cloud above and below the plane of the benzene ring.
- The delocalisation of  $\pi$  electrons in benzene results in stabilisation. The resonance stabilisation of benzene is evident from its enthalpy change of hydrogenation. Refer to lecture notes on Arenes for details.

#### Exercise 3:

Which of the following ions/ molecules show resonance?



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### 3 Structures of some giant molecular structures and their properties (revisited)

#### (a) Diamond



C-C bond length = 0.154 nm

- Each carbon atom is sp<sup>3</sup> hybridised and is covalently bonded to four other carbon atoms arranged tetrahedrally around it.
- This tetrahedral arrangement is repeated throughout the whole molecule giving rise to interlocking hexagonal units so that the resultant structure is extremely strong and rigid.
- Diamond is an electrical insulator as it does not have delocalised electrons and are made up of neutral atoms.
- Due to the strong covalent bonds between the carbon atoms in diamond,
  - diamond has a very high melting point of 3550 °C.
  - diamond does not dissolve in water or other solvents

#### Exercise 4:

Silicon has the same structure as that of diamond. Explain why silicon has a lower melting point (1410 °C) than diamond.

#### Answer:

Since the valence orbitals of Si are larger and <u>www. fiftum</u> than that of C, there is a <u>lux</u> <u>(ffucture)</u> between the orbitals of Si, resulting in the Si–Si bond being weaker than the C–C bond. Less energy is required to overcome the weaker Si–Si bonds in silicon than the stronger C–C bonds in diamond, hence silicon has a lower melting point than diamond.

#### (b) Graphite

- Graphite has a layer structure and is made up of planes of interconnected hexagonal rings of carbon atoms.
- Each carbon atom is sp<sup>2</sup> hybridised and forms three σ-bonds with three other carbon atoms.
  - The electron-pair geometry is trigonal planar with bond angles of 120<sup>o</sup> around each carbon atom.



- Each carbon has an unhybridised p-orbital which contains a single electron.
  - > The p-orbital of one carbon atom overlaps continuously with the p-orbitals of its immediate neighbours, resulting in an **extended**  $\pi$ -electron cloud above and below the plane containing the carbon atoms.



- > The  $\pi$ -electrons are **delocalised** over the whole layer so that graphite is an **electrical conductor**.
- > However, since the  $\pi$ -electrons are only delocalised within each layer, graphite can only conduct electricity in a direction parallel to the layers.
- The attraction between carbon atoms within each layer is due to strong covalent bonding, but the attraction between different layers is due to weak instantaneous dipole-induced dipole forces.
  - Due to strong covalent bonds within each layer, a lot of energy is required to overcome these strong forces of attraction, resulting in graphite having a very high melting point of 3730 °C.
  - Its high melting point results in the use of graphite as crucibles for molten metals and reentry nose cones of rockets.
  - The weak instantaneous dipole-induced dipole forces between each layer allows the layers to glide over each other.
  - > Hence graphite is soft and is used in pencils and as lubricants.

#### Exercise 5:

Graphite has a melting point of 3730 °C while diamond has a melting point of 3550 °C. Explain why graphite have a higher melting point than diamond in terms of structure and bonding.

#### Answer:

Both diamond and graphite have a giant covalent structure and melting involves the breaking of covalent bonds between the carbon atoms.

In diamond, the carbon atoms are  $\underline{s\rho}^{\mu}$  hybridised while in graphite, the carbon atoms are  $\underline{s\rho}^{\nu}$  hybridised.

Each carbon atom in graphite has an unhybridised p orbital containing one electron each. The p orbital of one carbon atom overlaps collaterally with the p orbitals of its immediate neighbor. Thus, there is additional electron density between the carbon atoms holding the nuclei more closely, hence strengthening the C–C bond.

Also, the hybrid orbitals of the carbon atoms in graphite has high S church i than diamond, thus are less diffuse and the overlap of the sp<sup>2</sup> hybrid orbitals in graphite is more effective than the overlap of the sp<sup>3</sup> hybrid orbitals in diamond.

### (c) Quartz (silicon dioxide, SiO<sub>2</sub>)

Quartz is silicon dioxide and has the following structure:



- Each silicon atom is covalently bonded to four oxygen atoms tetrahedrally and each oxygen is bonded to two silicon atoms.
- The arrangement of silicon atoms in quartz is similar to that of carbon in diamond, but in quartz there is an oxygen atom between each pair of silicon atoms.
- Since there are no delocalised electrons and silicon(IV) oxide is made up of atoms, silicon(IV) oxide is an electrical insulator in all states.
- Due to the strong covalent bonds between all silicon and oxygen atoms and the rigid
   3-dimensional structure, quartz is very hard and is insoluble in all solvents.

Exercise 6: N2005/P1/6	
Silicon carbide (carborundum) is a shiny, hard chemically inert material with a very high melting point. It can be used to sharpen knives and make crucibles.	
Which type of structure explains these properties?	
<ul> <li>A a giant structure with covalent bonds between silicon and carbon atoms</li> <li>B a giant structure containing metallic bonding</li> <li>C a giant layer structure with covalent bonds between atoms and instantaneous dipole-induced dipole interactions between the layers</li> <li>D a simple molecular structure with covalent bonds between the atoms of silicon and carbon</li> </ul>	
Answer:	



### RAFFLES INSTITUTION YEAR 5 H2 CHEMISTRY 2022 Tutorial 8: Chemical Bonding II

#### 1. N2012/1/19 (Modified)

Covalent bonds are formed by orbital overlap. The shape of unsaturated hydrocarbon molecules can be explained in terms of hybridisation of orbitals.

Which bond is **not** present in the molecule below?



- A a  $\pi$  bond formed by 2p–2p overlap.
- **B** a  $\sigma$  bond formed by 1s–2sp overlap.
- **C** a  $\sigma$  bond formed by 2sp-2sp<sup>2</sup> overlap.
- **D** a σ bond formed by 2sp<sup>2</sup>-2sp<sup>3</sup> overlap.

## 2. N2011/1/19 (Modified)

Which statement about the molecule but-2-yn-1-ol is not correct?



- A The centre carbon atoms (2 and 3) are sp hybridised.
- B The O atom is sp<sup>3</sup> hybridised.
- C The terminal carbon atoms (1 and 4) are sp<sup>2</sup> hybridised.
- D The terminal carbon atoms (1 and 4) have tetrahedral geometry.
- 3. (a) Draw the shape of an ethene molecule,  $C_2H_4$ , showing the value of the bond angle.
  - (b) The two carbon atoms of ethene can be described as being joined by a  $\sigma$  bond and a  $\pi$  bond. Briefly explain the terms in *italics*, using diagrams, where appropriate.
  - (c) What type of hybridisation is present in the ethene molecule?
  - (c) What type of hybridisation is present in the entern molecule.
     (d) Sketch the shapes of the hybrid orbitals around one carbon atom in the ethene molecule, showing the value of the bond angle.
- BeF<sub>2</sub> reacts with F<sup>-</sup> ions to form [BeF<sub>4</sub>]<sup>2-</sup>. The hybridisation of Be changes when BeF<sub>2</sub> forms [BeF<sub>4</sub>]<sup>2-</sup>.
  - (a) Draw the structures of BeF<sub>2</sub> and [BeF<sub>4</sub>]<sup>2-</sup>, showing clearly their shapes and the types of bonds between Be and F.
  - (b) State the hybridisation of Be and sketch the hybrid orbitals around Be for both  $BeF_2$ and  $[BeF_4]^{2^-}$ .
- 5. (a) Draw the dot-and-cross diagram of the nitrite ion,  $NO_2^-$ .
  - (b) State the shape and bond angle about nitrogen in the nitrite ion.
  - (c) State the hybridisation of the nitrogen atom in the nitrite ion.
  - (d) It was found experimentally that the 2 nitrogen oxygen bond lengths in the nitrite ion are identical. Explain clearly why this is so with relevant diagrams.
- 6. Boron nitride, BN, crystallises in a form similar to that of graphite, in which atoms of boron and nitrogen alternate.
  - (a) Draw a structure for a layer of BN and describe its bonding.
  - (b) By considering your answer in (a), explain why the electrical conductivity of BN is lower than that of graphite.