Not for

Classes of Organic Compounds

Homologous Series

homologous series is a group of organic compounds having similar structure and similar chemical properties n which the successive compound differs by CH_2 group. Thus the molecular mass of each member differs by 4 atomic mass units. For instance, the successive member of the alkane series differs by CH_2. Methane – CH_4, Ethane - C_2H_6, Propane - C_3H_8

The homologous series is a series of compounds which have the same general formula.

The homologous series are also observed in other compounds such as the primary alcohols, aldehydes, single-ring unbranched cycloalkanes and (mono-carboxylic acids).

Compounds within a homologous series typically have a fixed set of functional groups that gives them similar chemical and physical properties. (For example, the series of primary straight-chained alcohols has hydroxyl at the end of the carbon chain.) These properties typically change gradually along the series, and the changes can often be explained by mere differences in molecular size and mass.

Successive members of a homologous series are called **homologues**.
A **homologation reaction** is a chemical process which converts one member of a homologous series to the next member.

Properties of Compounds Within the Same Homologous Series:

The **chemical and physical properties** of compounds within the same homologous series are described below.

1. Chemical Properties

Organic compounds that are part of the same homologous series generally have similar chemical properties as each other, due to the presence of the same functional group in the molecules of all compounds in the series.

Even though members of the same homologous series generally have similar chemical properties there may still be trends through the group (e.g. as reactivity and rates of reaction vary with parameters such as molecular weights).

2. Physical Properties

Physical properties of organic compounds that are part of the same homologous series follow trends through the series. The physical properties of any particular member of a homologous series depends on its size, or it's position within the homologous series.

A common example of trends within homologous series is that of the **boiling points** of the members of the series. The boiling point of the alkane increases as the chain length increases.

The trends in physical properties of compounds within a homologous series are primarily due to the progression of sizes and weights of the molecules that form the homologous series. Using the example of the boiling point

der Waals forces (intermolecular forces) with neighbouring molecules than is true to the greater number of atoms forming molecules of ethane, compared with methane

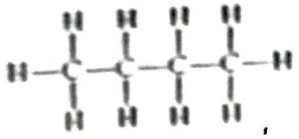
Saturated and Unsaturated hydrocarbons

ompounds that contain only carbon and hydrogen. They are the simplest class of org ber organic compounds can be viewed as hydrocarbons in which one or more hydro placed by other atoms or other groups of atoms. Each carbon atom in the molecule fo bonds with other atoms.

rbons; These are hydrocarbons that contains only single bonds. Each carbon atom in r single covalent bonds with other atoms. There are three main categories namely;

- straight chain alkanes (acyclics/aliphatics)
- branched chain alkanes (acyclics/aliphatics) and
- cyclic alkanes

linear alkanes (also known as paraffins) differ from one another by one carbon atom s, a $-CH_2-$ group homologous series. General molecular formula is same for all member s, C_nH_{2n+2}, eg. butane.



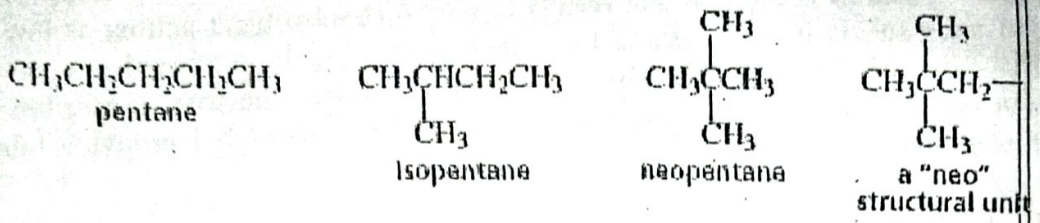
$CH_3CH_2CH_2CH_3$

ight-chain alkanes and their physical properties are shown in the table below;

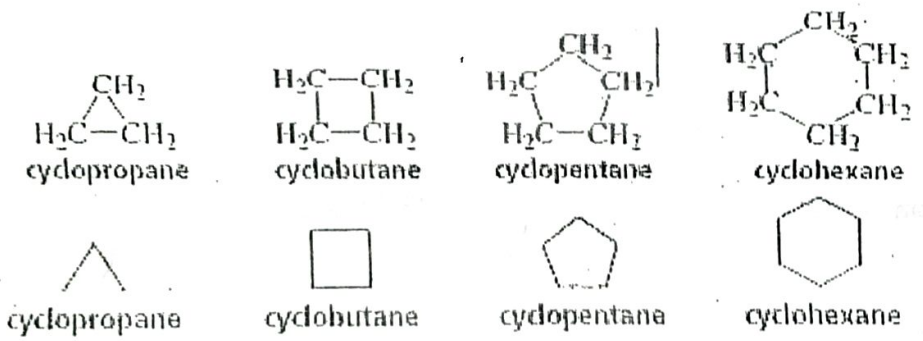
Molecular formula	Name	Condensed structure	Boiling point (°C)	Melting point (°C)	Densit (g/ml
CH_4	methane	CH_4	−167.7	−182.5	
C_2H_6	ethane	CH_3CH_3	−88.6	−183.3	
C_3H_8	propane	$CH_3CH_2CH_3$	−42.1	−187.7	
C_4H_{10}	butane	$CH_3CH_2CH_2CH_3$	−0.5	−138.3	
C_5H_{12}	pentane	$CH_3(CH_2)_3CH_3$	36.1	−129.8	0.557
C_6H_{14}	hexane	$CH_3(CH_2)_4CH_3$	68.7	−95.3	0.664
C_7H_{16}	heptane	$CH_3(CH_2)_5CH_3$	98.4	−90.6	0.68
C_8H_{18}	octane	$CH_3(CH_2)_6CH_3$	127.7	−56.8	0.70
C_9H_{20}	nonane	$CH_3(CH_2)_7CH_3$	150.8	−53.5	0.71
$C_{10}H_{22}$	decane	$CH_3(CH_2)_8CH_3$	174.0	−29.7	0.72
$C_{11}H_{24}$	undecane	$CH_3(CH_2)_9CH_3$	195.8	−25.6	0.74
$C_{12}H_{26}$	dodecane	$CH_3(CH_2)_{10}CH_3$	216.3	−9.6	0.74
$C_{13}H_{28}$	tridecane	$CH_3(CH_2)_{11}CH_3$	235.4	−5.5	0.75
	⋮	⋮	⋮		⋮
$C_{20}H_{42}$	eicosane	$CH_3(CH_2)_{18}CH_3$	343.0	36.8	0.78
$C_{21}H_{44}$	henicosane	$CH_3(CH_2)_{19}CH_3$	356.5	40.5	0.79
	⋮	⋮	⋮	⋮	⋮
$C_{30}H_{62}$	triacontane	$CH_3(CH_2)_{28}CH_3$	449.7	65.8	0.80

[illegible] The densities given are those determined at 20 °C (d^{20}).

Branched chain alkanes (acyclic); Simple branched alkanes often have a common name using a prefix to distinguish them from linear alkanes, for example *n*-pentane, isopentane, and neopentane. C_5H_{12} Pentane is the straight chain alkane. Isopentane, as its name indicates, has an iso structural unit and five carbon atoms. The third isomer is called neopentane. The structural unit with a carbon surrounded by four other carbons is called "neo." IUPAC naming conventions can be used to produce a systematic name thus; 2,2-dimethylpropane.



Cyclic alkanes; These are hydrocarbons just like alkanes, but contain one or more rings. Simple cycloalkanes have a prefix "cyclo-" to distinguish them from alkanes. Cycloalkanes are named as per their acyclic counterparts with respect to the number of carbon atoms, e.g., cyclopentane (C_5H_{10}) is a cycloalkane with 5 carbon atoms just like pentane (C_5H_{12}), but they are joined up in a five-membered ring. In a similar manner, propane and cyclopropane, butane and cyclobutane, etc. Substituted cycloalkanes are named similar to substituted alkanes — the cycloalkane ring is stated, and the substituents are according to their position on the ring.



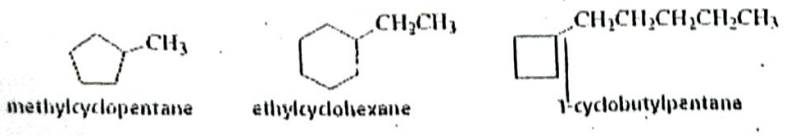
Some example of cycloalkanes

Naming the Cycloalkane

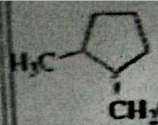
The rules for naming cycloalkanes resemble the rules for naming acyclic alkanes:

In the case of a cycloalkane with an attached alkyl substituent, the ring is the parent hydrocarbon unless the substituent has more carbon atoms than the ring. In that case, the substituent is the parent hydrocarbon and the ring is named as a substituent. Brief note on naming cyclic compounds are as shown below.

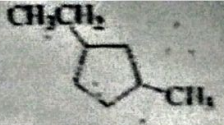
1. There is no need to number the position of a single substituent on a ring.



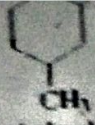
2. If the ring has two different substituents, they are cited in *alphabetical order* and the number 1 position is given to the substituent cited first.



1-methyl-2-propylcyclopentane

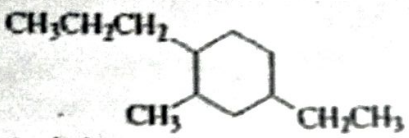


1-ethyl-3-methylcyclopentane

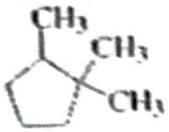


1,3-dimethylcyclohexane

3. If there are more than two substituents on the ring, they are cited in alphabetical order. The substituent given the number 1 position is the one that results in a second substituent getting as low a number as possible. If two substituents have the same low number, the ring is numbered—either clockwise or counterclockwise—in the direction that gives the third substituent the lowest possible number. For example, the correct name of the following compound is 4-ethyl-2-methyl- 1-propylcyclohexane, not 5-ethyl-1-methyl-2-propylcyclohexane:



4-ethyl-2-methyl-1-propylcyclohexane
not
1-ethyl-3-methyl-4-propylcyclohexane
because 2 < 3
not
5-ethyl-1-methyl-2-propylcyclohexane
because 4 < 5



1,1,2-trimethylcyclopentane
not
1,2,2-trimethylcyclopentane
because 1 < 2
not
1,1,5-trimethylcyclopentane
because 2 < 5

Unsaturated hydrocarbons are hydrocarbons that have double or triple covalent bonds between adjacent carbon atoms. Those with at least one double bond are called alkenes and those with at least one triple bond are called alkynes. Each double bond is represented by a number preceding the name of the base chain, representing on which hydrocarbon in the chain the double or triple bond can be found. Unsaturated hydrocarbons: Alkenes and Alkynes with more than one double or triple bond respectively are named with the appropriate numeric prefix preceding the -ene or -yne. Eg; 2,4-pentadiene or 2-butyne. Other examples of a diene, alkyne and a cyclic alkene are shown;

(4E)-hepta-1,4-diene

hept-2-yne

cyclopentene

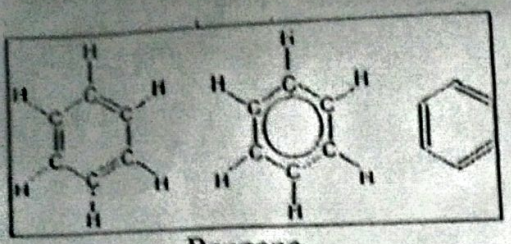
The physical properties of unsaturated hydrocarbons are very similar to those of the corresponding saturated compounds. They are slightly soluble in water. Except for aromatic compounds, unsaturated hydrocarbons are highly reactive and undergo **addition reactions** to their multiple bonds. Typical reagents added are hydrogen halides, water, sulfuric acid, elemental halogens and alcohols. Saturated hydrocarbon cannot bond with compounds any more, whereas unsaturated hydrocarbons can bond, as they contain double or triple bonds. When they bond, the double and triple bonds break and new separate single bonds are formed with hydrogens or any other external compounds.

Saturated carbons are single bonded and have a greater compliment of hydrogen. (hence, saturated) while unsaturated carbons are generally doubled bonded and thus are attached to fewer hydrogen.

General formula for alkenes with one double bond is C_nH_{2n}

Aromatic Hydrocarbons also known as **arenes** or **aromatics**, are hydrocarbon compounds that contains conjugated planar ring systems with delocalised pi electron clouds instead of discrete alternating single and double bonds. Typical examples of aromatic compounds are benzene, toluene, cumene and naphthalene. The

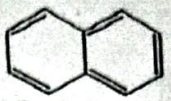
unique stability of these compounds is referred to as aromaticity. Although the term *aromatic* originally concerned odour, today its use in chemistry is restricted to compounds that have particular electronic, structural, or chemical properties.



Benzene

Toluene

cumene



Naphthalene

Some examples of aromatic hydrocarbons

Clasess of Aromatic Compounds

Aromatics compound forms various classes which includes:

Homocyclics aromatics containing one aromatic ring such as benzene, and the derivatives,

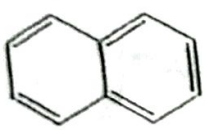
Polycyclics aromatics containing two or more fused aromatic rings than such as naphthalene, anthracene, and phenanthrene

Substituted aromatics i.e. aromatic ring with other functional groups attached such as in phenol, aniline, anisidine, acetylsalicylic acid (aspirin) and paracetamol.

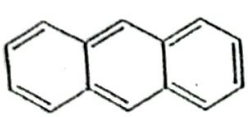
Atypical aromatics such as found in ions such as the cyclopropenyl cation/anioin.

Heterocyclics containing heteroatoms in the ring such as furan, pyridine and thiophene

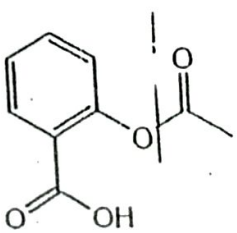
Some of the highlighted examples are shown below.



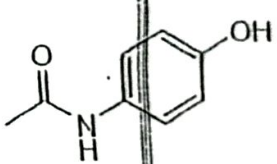
Naphthalene



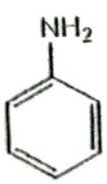
Anthracene



2-Acetoxybenzoic acid
or
Aspirin

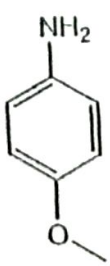


N-(4-hydroxyphenyl)acetamide
or
Paracetamol

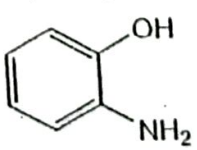


Aniline

Phenol



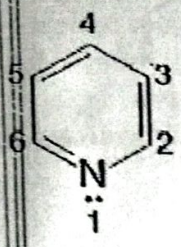
4-Methoxyaniline
or Anisidine



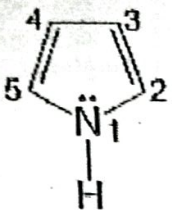
2-Aminophenol
o-aminophenol

Heterocyclic Compounds

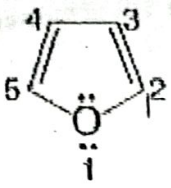
Cyclic compounds that include an element other than carbon are called heterocyclic compounds. Many of them are quite commonly encountered in nature. Heterocyclic compounds containing nitrogen, oxygen, or sulfur are by far the most common. A ring atom that is not carbon is called a **heteroatom**. Hence, the N, O and S in the cyclic compounds are heteroatoms. The name comes from the Greek word ***heteros***, which means "different". Four important examples which include pyrrole, furan and thiophene are shown in their Kekulé forms below. Most heterocyclic compounds are aromatic in nature.



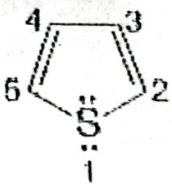
Pyridine



Pyrrole



Furan



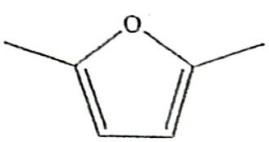
Thiophene

Various simple and complex derivatives of all the heterocyclics exist. For instance,some simplified derivatives of furan are shown below.

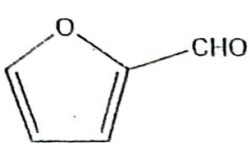
Furan

Tetrahydrofuran

2,3-dihydrofuran

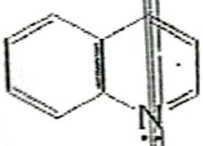


2,5-dimethylfuran

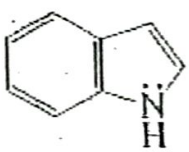


Furan-2-carbaldehyde
or
Furfural

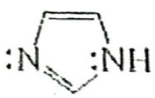
Some other examples of heterocyclic aromatic compounds are quinoline, indole, imidazole, purine, and pyrimidine.



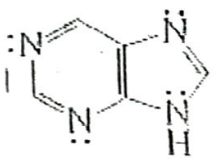
quinoline



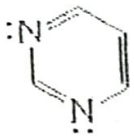
indole



imidazole

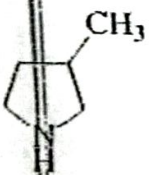


purine

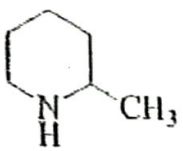


pyrimidine

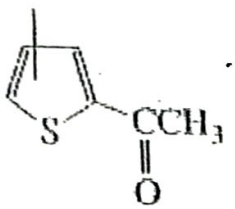
Other simple derivatives of the heterocyclic compounds are possible thus:



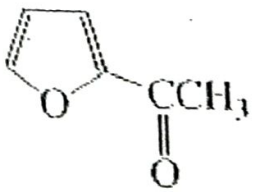
3-methylazacyclopentane
3-methylpyrrolidine



2-methylazacyclohexane
2-methylpiperidine



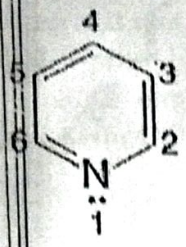
2-acetylthiophene



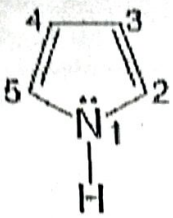
2-acetylfuran

Heterocyclic Compounds

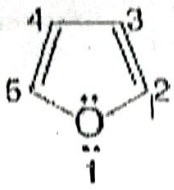
Cyclic compounds that include an element other than carbon are called heterocyclic compounds. Many of them are quite commonly encountered in nature. Heterocyclic compounds containing nitrogen, oxygen, or sulfur are by far the most common. A ring atom that is not carbon is called a **heteroatom**. Hence, the N, O and S in the cyclic compounds are heteroatoms. The name comes from the Greek word ***heteros***, which means "different". Four important examples which include pyrrole, furan and thiophene are shown in their Kekulé forms below. Most heterocyclic compounds are aromatic in nature.



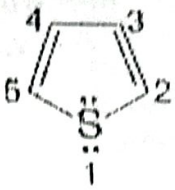
Pyridine



Pyrrole



Furan



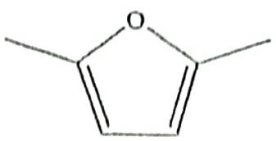
Thiophene

Various simple and complex derivatives of all the heterocyclics exist. For instance,some simplified derivatives of furan are shown below.

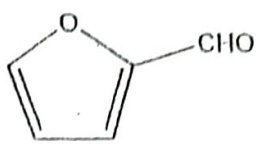
Furan

Tetrahydrofuran

2,3-dihydrofuran



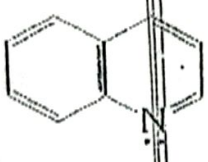
2,5-dimethylfuran



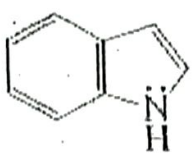
Furan-2-carbaldehyde
or
Furfural

Some othe

examples of heterocyclic aromatic compounds are quinoline, indole, imidazole, purine, and pyrimidine

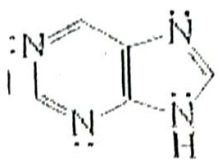


quinoline

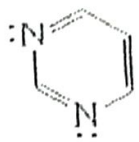


indole

imidazole

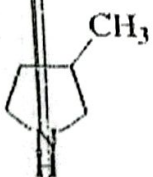


purine

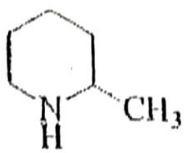


pyrimidine

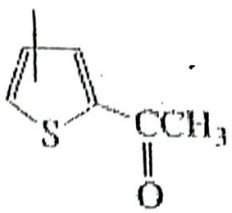
Other simple derivatives of the heterocyclic compounds are possible thus:



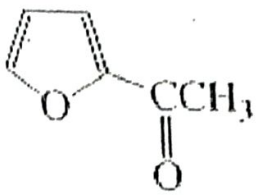
3-methylazacyclopentane
3-methylpyrrolidine



2-methylazacyclohexane
2-methylpiperidine



2-acetylthiophene



2-acetylfuran

Hückel's Rule of Aromaticity

In 1931, German Chemist and Physicist Erich Hückel proposed a theory to help determine if a planar ring molecule would have aromatic properties. Hückel's rule states that if a cyclic, planar molecule has $4n+2$ π electrons, it is considered aromatic.

Four Criteria for Aromaticity

When deciding if a compound is aromatic, go through the following checklist. If the compound does not meet all the following criteria, it is likely not aromatic.

1. The molecule is cyclic (a ring of atoms)
2. The molecule is planar (all atoms in the molecule lie in the same plane)
3. The molecule is fully conjugated (p orbitals at every atom in the ring)
4. The molecule has $4n+2$ π electrons (n=0 or any positive integer)

According to Hückel's Molecular Orbital Theory, a compound is particularly stable if all of its bonding molecular orbitals are filled with paired electrons. This is true of aromatic compounds, meaning they are quite stable. With aromatic compounds, 2 electrons fill the lowest energy molecular orbital, and 4 electrons fill each subsequent energy level (the number of subsequent energy levels is denoted by *n*), leaving all bonding orbitals filled and no anti-bonding orbitals occupied. This gives a total of $4n+2$ π electrons.

Application of the 4n+2 Rule

To apply the $4n+2$ rule, first count the number of π electrons in the molecule. Then, set this number equal to $4n+2$ and solve for n. If is 0 or any positive integer (1, 2, 3,...), the rule has been met. For example, benzene has six π electrons:

$$4n + 2 = 6$$
$$4n = 4$$
$$n = 1$$

For benzene, we find that n=1, which is a positive integer, so the rule is met.

Application of Hückel's Rule

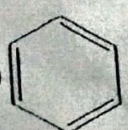
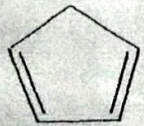
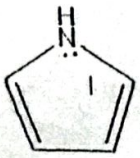
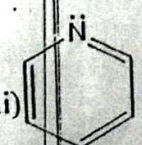
Hückel's Rule: If the number of pi electrons in the cyclic system is:

(4N + 2), the system is **aromatic**;

(4N), the system is **antiaromatic** (i.e., the compounds meets three criteria for aromaticity, but delocalization of the pi electrons over the ring increases the electronic energy)

If (4N + 2) or (4N) rule is not observed, then the compound is termed **nonaromatic** or **aliphatic**.

Using the criteria for aromaticity, determine if the following molecules are aromatic, non-aromatic or anti-aromatics

(i) 
(ii) 
(iii) 
(iv) 
(v) 
(vi) 
(vii) 

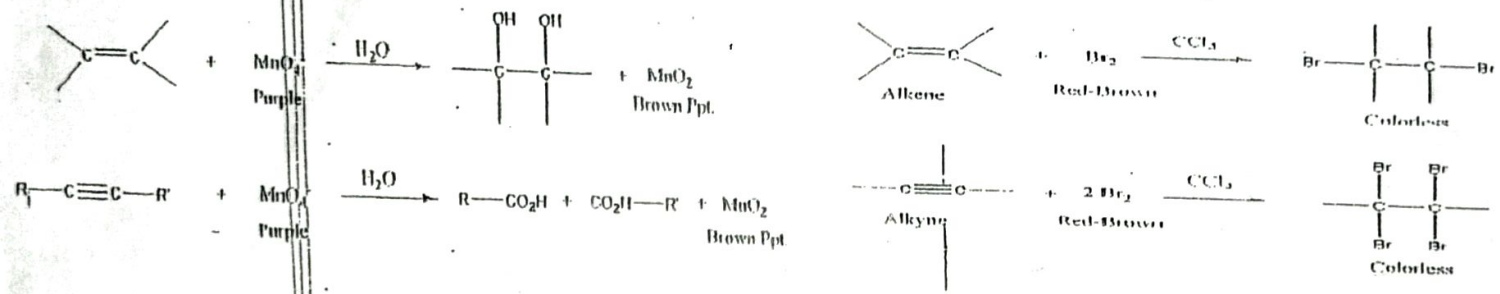
i. Benzene is aromatic because it has 6 π electrons and n = 1 and all other criteria are met
ii. Cyclopentadiene is simply non-aromatic because it is not conjugated
iii. ???
iv. Cyclobutadiene is anti-aromatic because there are 4 π electrons, n=1/2
v. ???
vi. ???
vii. ???

Test for Unsaturation

To test whether the hydrocarbon is unsaturated, add bromine water or potassium permanganate (**the Baeyer Test**). In both cases, if the bromine water becomes decolourised (goes colorless) then it is unsaturated. If no visible reaction, then the compound is saturated.

Bromine test: Bromine will add to the carbon-carbon double bond of alkenes to produce dibromoalkanes and with alkynes to produce tetrabromoalkanes. When this reaction occurs, molecular bromine is consumed, and its characteristic dark red-brown color disappears if bromine is not added in excess. The *rapid* disappearance of the bromine color is a positive test for unsaturation.

Potassium Permanganate (the Baeyer Test): The second qualitative test for unsaturation, the Baeyer test, depends on the ability of potassium permanganate to oxidize the carbon-carbon double bond to give alkanediols or the carbon-carbon triple bond to give carboxylic acids.



Degree of Unsaturation

Degree of unsaturation: Alkanes contain the maximum number of carbon–hydrogen bonds possible, that is, they are saturated with hydrogen—they are called **saturated hydrocarbons**. In contrast, alkenes are called **unsaturated hydrocarbons**, because they have fewer than the maximum number of hydrogens. The total number of π bonds and/or rings in an alkene is called its **degree of unsaturation**.

Calculation of the Degree of Unsaturation or Double Bond Equivalent

A calculation of the **degree of unsaturation** (DU) or **Double Bond Equivalent** (DBE) or **Index of hydrogen deficiency** (IHD) is a good way to start a spectroscopy problem. It tells you how many rings and double bonds or Triple bonds are in the molecule; thus, you know if you should look for a carbonyl or a carbon-carbon double bond, or a ring or an aromatic ring.

The degree of unsaturation can be calculated readily from the molecular formula of all compounds containing carbon, hydrogen, oxygen, nitrogen, sulfur, or the halogens, by applying the following rules:

- **Rule 1:** Replace all halogens in the molecular formula by hydrogens.
- **Rule 2:** Omit oxygens and sulfurs. (because replacing a C=C with a C=O does not affect the total number of hydrogens in the compound)
- **Rule 3:** For each nitrogen, omit the nitrogen and one hydrogen.

Applications of these rules reduce the molecular formula in question to the molecular formula of the hydrocarbon which has the same degree of unsaturation. The degree of unsaturation of a hydrocarbon is easily deduced if one remembers that a saturated hydrocarbon has the formula C_nH_{2n+2}. Thus for the formula C_nH_m,

$$\Omega = \frac{(2n+2)-m}{2} = n - \frac{m}{2} + 1$$

Applying these rules to the molecular formula C_8H_8NOBr.

- **Rule 1**, replace halogens with hydrogens: C_8H_9NO
- **Rule 2**, omit oxygens: C_8H_9N
- **Rule 3**, omit the nitrogen and one hydrogen: C_8H_8

Therefore, Degree of Unsaturation =

$$\Omega = 8 - \frac{8}{2} + 1 = 5$$

This means that the molecule has five rings and/or pi bonds (or any combination of the two). A degree of unsaturation greater than or equal to 4 doesn't demand but should suggest the possibility of an aromatic (benzene) ring.

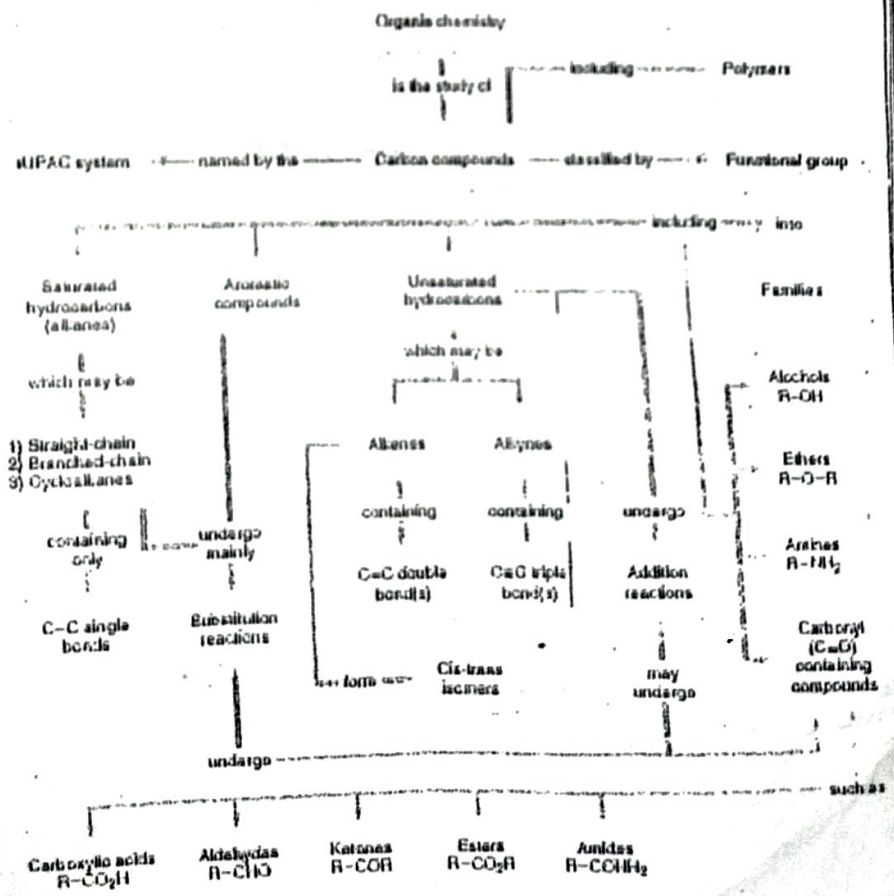
Note;

A ring counts as one degree of unsaturation.

One double bond counts as one degree of unsaturation

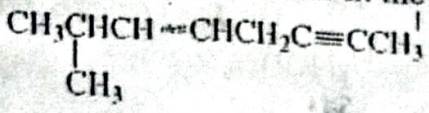
One triple bond counts as two degrees of unsaturation

Summary Chart:

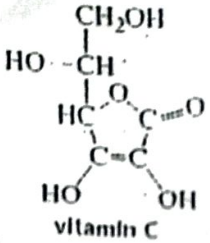


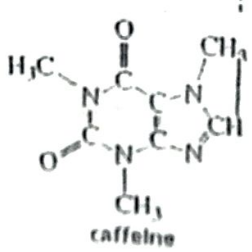
Tutorials

1. Which of the bonds of a carbon–carbon double bond has more effective orbital–orbital overlap, the σ bond or the π bond?
2. Why would you expect a C-C σ bond formed by sp^2–sp^2 overlap to be stronger than a σ bond formed by sp^3–sp^3 overlap?
3. What is the hybridization of each of the carbon atoms in the following compound?

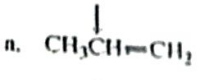


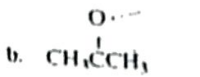
4. What is the hybridization of each of the carbon, oxygen, and nitrogen atoms in the following compounds?

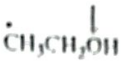

vitamin C

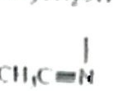

caffeine

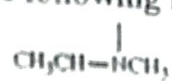
5. What is the hybridization of the indicated atom in each of the following molecules?

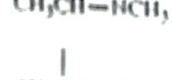

a.


b.

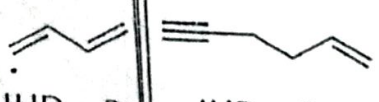

c.


d.


e.

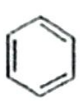

f.

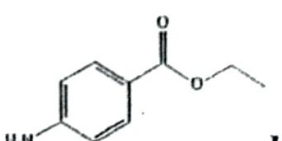
6. Which of the following molecules have tetrahedral bond angles?
   H_2O, H_3O^+, $^+CH_3$, BF_3, NH_3, $^+NH_4$ and $^-CH_3$
7. Determine the molecular formula for a hydrocarbon with (a) 5-carbon with one π bond and one ring (b) 10-carbon with one bond and two rings.
8. Determine the degree of unsaturation for the hydrocarbons with the following molecular formulas:
   (a) $C_{10}H_{16}$ (b) $C_{20}H_{34}$ (c) C_8H_{16} (d) $C_{12}H_{20}$ (e) $C_{40}H_{56}$
9. Determine the degree of unsaturation, and then draw possible structures, for compounds with the following molecular formulas: a. C_3H_6 b. C_3H_4 c. C_4H_6
10. Calculate the DBE or IHD of the compounds shown below;
    Hint; Their respective IHD are as shown.

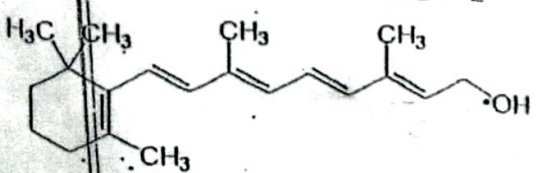

IHD = 2

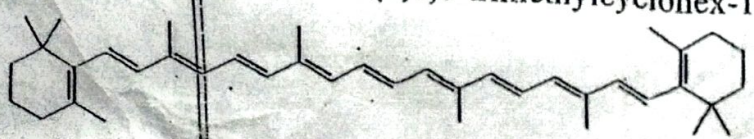
IHD = 3


IHD = 2


IHD = 4


IHD= 5


Vitamin A. 3,7-dimethyl-9-(2,6,6-trimethylcyclohex-1-enyl)nona-2,4,6,8-tetraen-1-ol **IHD = ?**



Beta- Carotene. 3,7,12,16-tetramethyl-1,18-bis(2,6,6-trimethylcyclohex-1-enyl)octadeca-1,3,5,7,9,11,13,15,17-nonaene