

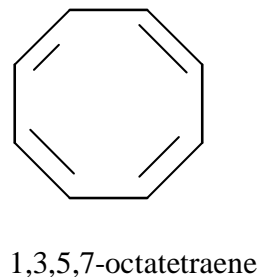
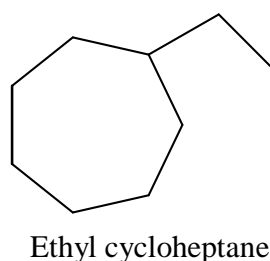
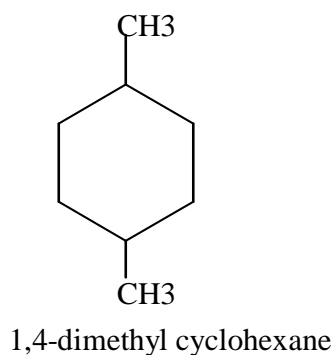
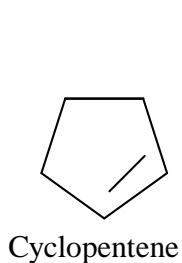
CHM 221- BASIC ORGANIC CHEMISTRY 1

ALLICYCLIC HYDROCARBONS

Allicyclic (aliphatic cyclic) hydrocarbon and their derivatives are cyclic hydrocarbons of alkane, alkene and/or alkyne. Generally, allicyclic compounds are compounds which contain at least one ring but are aliphatic hence are called allicyclic (aliphatic cyclic compounds). They are non aromatic. The saturated allicyclic compounds have the general formula C_nH_{2n} (corresponding to 1 ring), C_nH_{2n-2} (corresponding to 2 rings-bicyclo compounds) and C_nH_{2n-4} (corresponding to 3 rings), etc. The smallest numbers of carbon atoms that can be arranged in a ring is three represented by the hydrocarbon; cyclopropane. Each additional rings lowers the number of Hydrogen atoms in the general formula by 2. Aliphatic cyclic hydrocarbons having one ring are called Allicyclic hydrocarbons.

NOMECLATURE AND STRUCTURE OF CYCLIC HYDROCARBONS

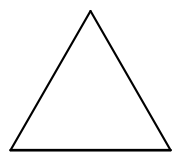
Allicyclic compounds are often shown by the topological formulations such as;



NOMECLATURE RULES

- 1) The number of carbon atoms in the ring of the cyclic compound is counted and word 'cyclo' is prefixed to the name of the alkane having the same number of carbon atoms on a straight line.

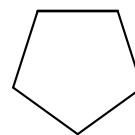
The general name of saturated cyclic hydrocarbons is cycloalkane. e.g.



cyclopropane
mp = -127°C ,
b. pt = -33°C



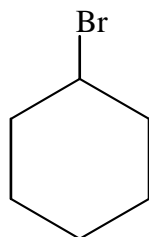
cyclobutane



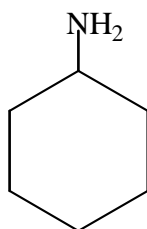
cyclopentane

(2). Substituents/functional groups are indicated by numbering and either appropriate prefixes before the word cyclo or by appropriate ending indicating the functional group. e.g

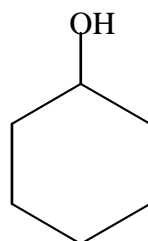
When there are more one substituents, the numbering of the carbon atom that gives the lowest sum is chosen, e.g.



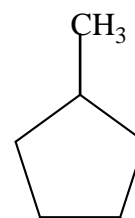
Bromocyclohexane



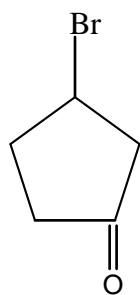
cyclohexylamine



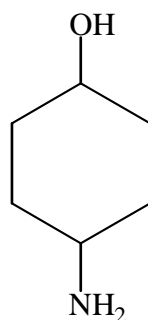
cyclohexanol



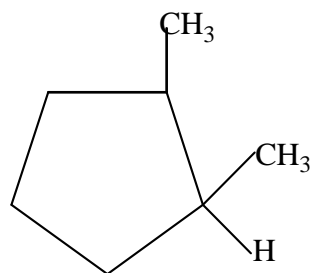
methyl cyclohexane



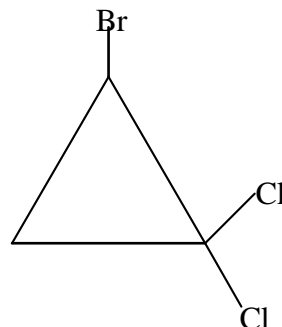
3-bromocyclopentanone



4-amino cyclohexanol

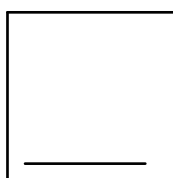


1,2-dimethyl cyclopentane

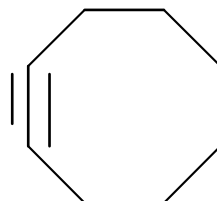


1-bromo-2,2-dichlorocyclopentane

- 3) Cycloalkene and cycloalkynes are cyclic compounds containing double bonds and triple bonds respectively. The positions of the double-bonded and triple-bonded carbons in the carbon chain are given the numbers 1 and 2 and are not prefixed to the name of cycloalkene and cycloalkyne, e.g



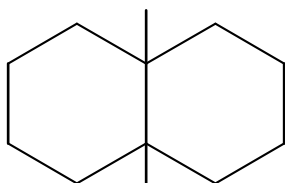
cyclobutene



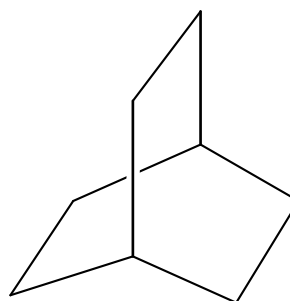
cyclohexyne

POLICYCLIC COMPOUNDS

Compounds with more than one ring of carbon atoms and whose rings share two or more same carbon atoms are known as Polycyclic compounds. Those with two rings are called bicyclic Compounds. The rings may be fused as in Decalin or bridged as in norborane.



Decalin-fused bicyclic compound

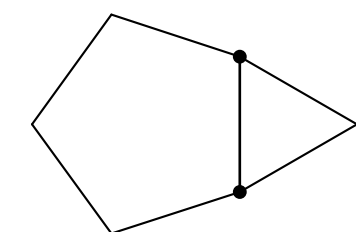


Norborane

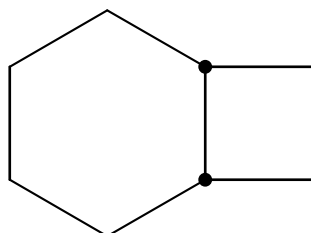
NUMECLATURE OF BICYCLIC COMPOUNDS

They are named by prefixing bicycle- to the name of the parent hydrocarbon. The name of the parent hydrocarbon is obtained by counting the total number of carbon atoms in all the rings of the compound as in norborene and decalin above. The carbon atoms attached to two rings are referred to as bridge head carbons. The number of carbon atoms between the bridge head carbons in the molecule are specified by counting from the bridge head carbon and listing each of the numbers in brackets in decreasing order prior to the parent name of the hydrocarbon. Thus norborane is named as bicyclo [2,2,1] heptanes.

Other examples are:



Bicyclo[3,1,0] hexane



Bicyclo [4,2,0] octane

The C position in a bicyclic hydrocarbons are numbered from the bridgedhead carbon around the largest ring first. Substituents are counted from the number assigned to the C positions.

Exercise;

Draw the structure of the following alicyclic compounds:

1 bicyclo [4,3,0] nonane

2 2-chloro-4-carboxy bicycle[1,1,0]butane

3 2-methyl cyclopentan-1-one-oxime

STRAIN ENERGY OF ALICYCLIC HYDROCARBONS

The measured heats of combustion of alkanes indicated that when burned, each methylene group contributes 156.5 kcal/mol to the heat of combustion. Thus, proceeding from methane to straight and branched chained alkanes, the heat of combustion increases by 156.5 kcal/mol for each progressive increase in the number of $-CH_2$ units the molecular formula of alkane. The heat of combustion of cyclic alkanes do not exhibit similar regularity. Experiment indicates that the heat of combustion of some cyclic hydrocarbons are much larger than we might expect by analogy with non-cyclic compounds. E.g the heat of combustion of cyclopropane is 9.1 kcal/mol per $-CH_2$ unit greater than that of propane. The energy released in the combustion of cyclopropane indicates that the energy content of cyclopropane is greater because of its acyclic arrangement. Similarly, cyclobutane has 6.5 kcal/mol per CH_2 unit more than expected from a non-cyclic arrangement. The difference in the measured heat of combustion of acyclic hydrocarbon and the predicted value is called the STRAIN ENERGY. The strain energy per methylene group is obtained by dividing the molecular strain energy by the number of methylene groups in the ring. Cyclopropane, cyclobutane, small ring compounds, have characteristically high strain energies. Cyclopentane, cyclohexane and cycloheptane have smaller strain energies, whereas, medium ring compounds; cyclooctane through cycloundecane (C₈-C₁₁) have strain energy around 10 kcal/mol. The large ring have little or no associated strain from the ring structure.

Strain energies of cycloalkanes.

cycloalkanes	Strain energy per CH ₂ unit kCal/mol	Strain energy kCal/mol
cyclopropane	9.1	27.3
cyclobutane	6.5	26.0
Cyclopentane	1.2	6.0
cyclohexane	0.0	0.0
Cycloheptane	0.8	5.6
cyclooctane	1.1	8.8
Cyclononane	1.3	11.7

BONDING IN CYCLOALKANES- ANGLE STRAIN AND TORSIONAL STRAIN

Saturated compounds prefer a tetrahedral geometry about each carbon atom. Here, the bond angles are about 109, and the atoms attached to each carbon atom are at a maximum distance from each other. Small ring cycloalkanes, however, cannot assume the normal tetrahedral arrangement- characteristic of other acyclic alkanes.

The C-C bond angle of cyclopropane are those at regular triangle (60°) which is much less than (109°). Cyclobutane, likewise assumes bond angle near 90° . The orbitals of carbon in saturated organic compounds are SP^3 hybridized with axes pointing towards

the corners of tetrahedron. Bonding is a result of the overlap of these sp^3 -hybrid orbitals and atomic orbital of another atom. In acyclic alkanes, the sp^3 -orbitals of each carbon atom are directed toward one another along a line between two adjacent carbon nuclei. Overlap of atomic orbitals is maximized. The sigma bond formed from sp^3 -orbitals is most stable when the axes of the carbon orbitals are at 109° angles; deviation from 109° weakens the bond. Because cyclopropane can have bond angles no longer than 60° , the angle between two sp^3 -hybridized atomic orbitals must be compressed. Until the orbital overlap is sufficient to form a C-C bond. The C-C bonds in cyclopropane are a compromise angle for sp^3 -hybridized carbon.

The poor overlap of atomic orbitals due to deviation from 109° bond angles of sp^3 -hybridized carbon is called Angle strain. Angle strain decrease the stability of cyclic compounds accounts for most of the strain energy of small compounds. The geometry of small ring compounds fix their configurations. The formation of the three- member ring compound, cyclopropane forces the molecule into a triangular configuration in which the three carbon atoms form the corners of a triangle. Torsional strain contributes to the strain energy of cyclic compounds. The torsional strain of cyclopropane is due to the eclipsing of all the C-H bonds; a molecular bond that would decrease the torsional strain can not account for cyclopropane.

CONSEQUENCES OF ANGLE STRAIN FOR CYCLIC COMPOUNDS

Compounds with strain energies of more than 65kcal/mol have been prepared. A high strain energy does not preclude their existence. However, highly strained compounds are often highly reactive and undergo ring opening reactions that relieve strain.

Cycloalkenes with fewer than 8 carbons only exist in cis-form. Cyclohexene for example exist as cis-cyclohexene and because the trans-form is unknown, it is referred to as cyclohexene. Cyclooctene is the first cycloalkene for which cis and trans-olefin isomers are possible. Cyclooctene is the smallest ring structure in which a C-C triple bond is stable. The instability of trans- cycloalkynes in rings smaller than 8 carbon atoms is due to angle strain. The pi-bond in these unstable compounds is twisted sufficiently so that the p-atomic orbital that would make up the pi-bond tend to become perpendicular. The perpendicular p-orbitals have zero overlap and do not form a molecular orbital.

STEREOCHEMISTRY AND CYCLIC HYDROCARBONS

Formation of cyclic hydrocarbon has the effect of constraining the carbon atoms into a fixed configuration relative to the straight chain. In cyclopropane, the H atoms lie either below or above the plane. Unlike the linear hydrocarbons, cyclic hydrocarbons have all groups attached to the cyclic structure arranged in a fixed position relative to each other. As a result, geometric isomerism is possible with the cyclic hydrocarbons in exactly the same way that they were possible with alkenes. e.g, 1,2-dimethylcyclopropane. The ring carbon atoms of cyclopropane must lie in a single plane. The two configurations above are stereoisomers. They have different melting point and boiling points, different NMR and Infrared spectra and different chemical properties. There is no way in which two geometric isomers can be converted except by the breaking of a C-C bond.

Stereoisomerism also occurs when substituents are attached at more remote positions. E.g the geometric isomers of 1,3-dimethylcyclobutane and 1,4-dimethylcyclohexane.

A convenient way to describe geometric isomerism in cycloalkene is to write ring in a planer form that represents the general geometry of the molecule.

BAEYER'S STRAIN THEORY (1885);

In order to account for the graded stability of cycloalkanes and their derivatives, Baeyer in 1885 proposed a strain theory which was based on the arrangement in space of the four valencies of the carbon atoms. His assumptions are:

- i) the molecule of cycloalkene is planar
- ii) the normal angle between any two such valencies is $109^{\circ}28'$ and that any deviation from this value causes a strain in the molecule of cycloalkane. The greater the deviation the greater the strain and the less stable and the lesser the reactivity.

Cyclopentane from Baeyer's theory is the most stable.

DEVIATIONS FROM BAEYER'S STRAIN THEORY

The theory is based on mechanical concept of valency and on the assumptions that all the rings are planar. Physical methods have shown that except for cyclohexane the rings are not planar. Plankton mechanical calculations do not permit very large distortion of bond angles. e.g heat of combustion of open chain alkane/ CH_2 is around 663KJ corresponding to C6 and C8 and we can assume there is no strain. The value obtained for C6 is similar to straight chain C6 alkane hence strainless ring occur in C6, C7, C8. cyclic molecules containing C6, C7, C8, C9 and more carbon atoms might be as stable as cyclopentane and this led to the assumption that the strainless

ring occurs in two or more stereoisomeric form and therefore cyclohexane is not a regular hexagon. Cyclohexane exists in two conformations; chair and boat.

According to SACHSE' in cyclohexane, the ring is packet and the normal valency is retained and this produces strainless rings. Cyclohexane exist in two forms both of which are strainless. The two forms are called the chair and boat conformation.

However , the two forms differ in energy content and therefore in stability. Stability depends on steric repulsion or non-bonded interaction of the hydrogen atoms.

Non-bonded interaction is lesser in the chair form than the boat form, hence the chair form is more stable than the boat. The two forms are however interconvertible and the energy required is 37.7-46.0kj/mol. The energy barrier is not large enough for this interconversion but large enough to permit each conformation to retain its identity.

OCCURRENCE

Cyclopentane and cyclohexane compounds are usually obtained from petroleum or occur naturally. Because of their strain energies, cyclopropane and cyclobutane s are not abundant in nature and are generally prepared by synthesis.

3,4,5-member alicyclic alkane occurs in terpenes (natural product) as cyclic terpenes.

PREPARATION/SYNTHESIS

- 1) Lower cycloalkanes are prepared by α,ω -dihalogen derivatives of the alkanes with sodium or zinc. Elimination of Halogen from the 1,3 position form the propane ring in a method called Baeyer ring closure.
- 2) The methylene insertion reaction involving the addition of a CH_2 unit across the C-C double bond of an alkene. (Simmon Smith reaction; diiodomethane is used as the source of CH_2)

PREPARATION OF CYCLOPROPANE

- 1) methylene insertion (Simmon-Smithr reaction)
- 2) Baeyer ring closure
- 3) by distillation of Ca or Ba salt of dicarboxylic acid. E.g barium adipate ester
(Barium (ii) 1,6-hexane durate acid)
- 4) from Benzene derivatives (for cyclohexane)

PREPARATION OF CYCLOBUTANE

Cyclobutane compounds are normally more difficult to prepare than cyclopropane. The Baeyer ring closure reaction do not form good yield of cyclobutane.

PREPARATION OF CYCLOALKANES via:

1) DIELS-ALDER REACTION: A conjugated diene and alkene form cyclohexene.

Relative alkenes called dienophiles have electron attracting group on their unsaturated carbons .

The reaction above can be considered as 1,4-addition of an olefine (ethene) to a conjugated diene(1,3-butadiene) and such is called [4+2] cycloaddition reaction.

Diels Alder reaction is a [4+2] cycloaddition reaction- in this case, the new molecule is formed from a conjugated 4pi-electron system on the one hand and a 2pi electron system on the other hand. Other examples are as follows, involving derivatives of the cycloaddition product;

3) ELECTROCYCLIC REACTION

This is an intramolecular cyclisation of polyenes

CHEMICAL PROPERTIES OF CYCLIC HYDROCARBONS

Most reactions of cyclic hydrocarbons are similar to those of acyclic alkanes and alkenes. E.g cycloalkanes undergo heat or light-induced halogenation in a manner similar to the halogenation reaction of the acyclic alkanes.

Cycloalkenes also exhibit the same reactions as their acyclic counterparts.

Other derivatives behave like acyclic hydrocarbon in their reactivity.

However, cyclopropane is unique among the cyclic hydrocarbons in its reactions with halogens. cyclopropane undergoes ring opening much more easily than we might expect for a molecule that has only C-C single bond. This occurs in cyclopropane easily because of its high strain, the release of strain energy provides the driving force for the ring opening process.

a) halogenation reaction of cyclopropane

b) hydrogenation reaction

Above reactions show how cyclopropane behaves like an alkene.. ring opening reaction of cyclobutane requires higher temperature and more severe reaction conditions than those for cyclopropane. Cycloalkanes with ring sizes greater than four are completely resistant to ring opening reaction.

AROMATIC HYDROCARBON

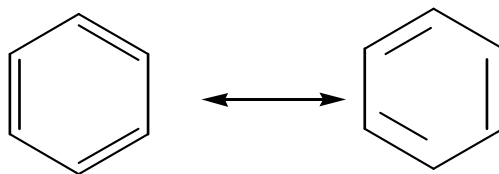
BENZENE AND AROMATICITY

Aromatic compounds are compounds containing benzene ring or closely related ring.

By aromaticity, it implies that the Pi-electrons are delocalized over the entire ring system and they are stabilized by the Pi-electron delocalization called

RESONANCE. For instance, Benzene is represented by the Kekule structure.

RESONANCE STRUCTURE OF BENZENE



In fact, benzene is a hybrid of two equal energy (Kekule) structures, differing only in the location of the double bond. In the structures of Benzene above, the six bond angles are equal (120°), hybridization is sp^2 and planar from x-ray analysis. The bonding in benzene is a multicenter bonding or delocalized bonding. The pi-electrons in the benzene is delocalized and not restricted to any carbon atom- a kind of multicenter bonding or delocalized bonding. The two canonical forms exist. The implication of the parameter highlighted above is an indication that the double bonds in benzene is unlike that found in alkene. In fact experiment has shown that benzene does not undergo addition reaction, expected in a C-C double bond in alkene.

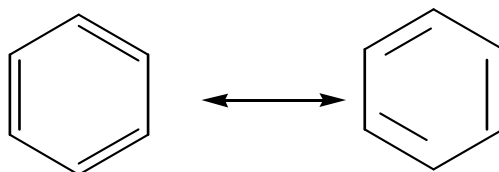
Benzene- a colourless compound, boiling point of 80°C was first isolated by Michael Faraday in 1825 from the oily residue collected in the illuminating gas lines of London. The molecular formula is C_6H_6 . For comparison, a saturated alkane of six carbon atoms has the molecular formula C_6H_{14} and saturated cycloalkane of six carbon atoms has molecular formula of C_6H_{12} .

Considering benzene's high degree of unsaturation, one might expect it to be highly reactive and to exhibit reactions characteristic of alkenes and alkynes. However, this is not so, benzene does not undergo addition, oxidation and reduction reactions, characteristic of alkenes and alkynes. E.g. it does not decolorize bromine water, not oxidized by $KMnO_4$ or Chromic acid (CrO_3) under conditions that readily oxidize alkenes and alkynes. In fact, benzene undergoes substitution reaction just like alkanes.

STRUCTURES OF BENZENE

Kekulé's model;

In 1865, Kekulé proposed that the six carbon of benzene are arranged in a six-membered ring with one hydrogen attached to each carbon. To maintain the then established tetravalency of carbon, Kekulé further proposed that the ring contains three double bonds that shift back and forth so rapidly that the two forms (1a and 1b below) cannot be separated.



The model above is called Kekule's structure.

The Kekule's structure was found to be consistent with many experimental observations.

HOME PRACTICE: If benzene contain three double bonds, why does it not show reaction typical of alkene?

BONDING IN BENZENE

Each carbon atom is sp^2 hybridizes and is sigma bonded and is sigma bonded to two other carbon atoms and one hydrogen atom. These sigma bonds comprised the skeleton of the molecule. Each C atom has one electron in a p-orbital at right angle to the plane of the ring. These p-orbitals overlap equally with each of the two adjacent p-orbital to form a pi-electron system parallel to and above and below the plane of the ring. The six p-electrons in the pi-system are associated with six carbon atoms. They are therefore more delocalized and this accounts for the great stability and large resonance energy of aromatic rings. ie,

The unusual properties of benzene collectively known as aromatic characters are;-

- thermal stability
- substitution rather than addition reaction with polar reagents such as HNO_3 , H_2SO_4 and Br_2 . The unsaturated bonds in the ring is preserved in this reaction
- resistance to oxidation by aq $KMnO_4$ or HNO_3
- unique NMR spectra.

CALCULATING THE RESONANCE ENERGY

The observed heat of combustion of benzene is -3301.6KJ/mol . Theoretical values are calculated for C_6H_6 by adding the contributions from each bond obtained experimentally for other compounds. E.g $\text{C}=\text{C}$ is -492.5KJ/mol , $\text{C}-\text{C}$ is -206.3KJ/mol and -225.9KJ/mol for $\text{C}-\text{H}$. these data can be used to calculate the heat of combustion for benzene. The difference between this value and the experimental value gives the resonance energy. For example, in benzene, there are; 6 $\text{C}-\text{H}$ bonds, 3 $\text{C}-\text{C}$ bonds, 3 $\text{C}=\text{C}$ bonds.

$$6 \text{ C-C bonds} = (6 \times -225.9) \text{ KJ/mol} = -1355.4\text{KJ/mol}$$

$$3 \text{ C-C bonds} = (3 \times -206.3) \text{ KJ/mol} = -618.9 \text{ KJ/mol}$$

$$3 \text{ C=C bonds} = (3 \times -492.5)\text{KJ/mol} = -1477.5\text{KJ/mol}$$

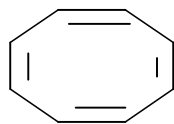
$$\text{Calculated value} = \text{total } \Delta H_c = -3451.8\text{KJ/mol}$$

$$\text{Experimental value} = \underline{-3301.6\text{KJ/mol}}$$

$$\text{Difference} = \underline{150.2\text{KJ/mol}}$$

This difference is the resonance energy of benzene. Hence , the resonance energy $=150.2\text{KJ/mol}$.

HOME PRACTICE;-

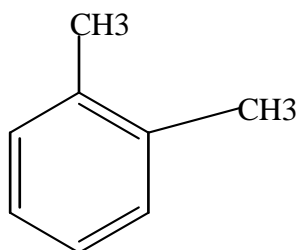
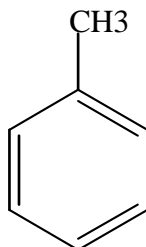


Given the cyclooctatetraene, calculate the enthalpy of combustion of the various bonds and hence the resonance energy ; assuming the experimentally enthalpy of combustion of cyclooctatetraene is -4581.5KJ/mol .

[C-H = -225.9KJ/mol , C-C = -206.3KJ/mol and C=C is -492.5KJ/mol]

NUMENCLATURE

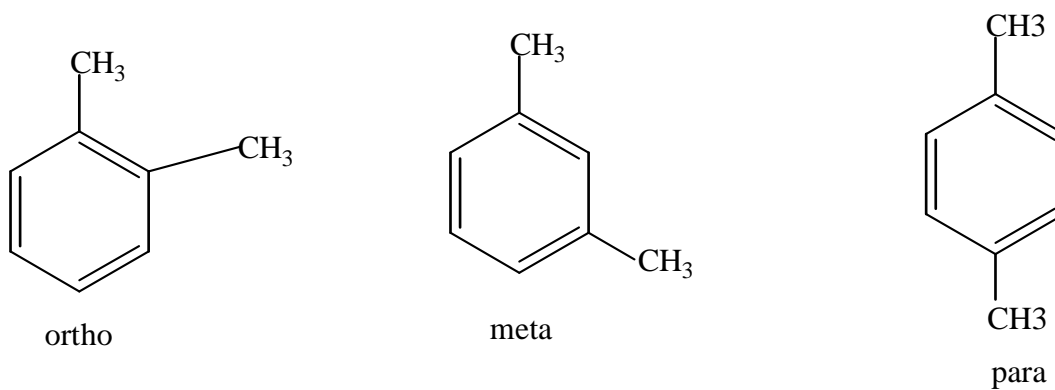
a) monosubstituted benzene;-



b) Disubstituted Benzene;

When two substituents are on benzene ring; three structural isomers are possible,

based on the position of the substituent on the benzene ring e.g.



HOME PRACTICE1. Give the structural formula for ;

- 2,4,6- tribromoaniline
- m-toluene sulphonic acid
- p-bromobenzaldehyde

PROOF OF AROMATICITY

For an organic compound to be aromatic , it must be;

- cyclic
- planar
- possess delocalized pi-electrons and
- obey Huckel's rule of $4n+2 = \Pi$ -electrons.

AROMATICITY AND HUCKEL'S RULE

Huckel's rule (1931) for aromaticity states that if the number of pi-electrons is equal to $4n+2$, where n equals zero or a whole number integer, the compound is aromatic. This rule applies to C-containing monocyclics in which each carbon is capable of being sp^2 hybridized to provide a p-orbital for extended pi-bonding. The rule has been extended to unsaturated heterocyclic compounds and fused ring compounds.

AMINES AND DERIVATIVES

Amines are the principal organic base which are structurally equivalent to ammonia OR put simply a derivative of ammonia in which one or more of its H atom is replaced by alkyl group(s). Amines are classified as primary (1^0), secondary (2^0) or tertiary (3^0) depending on the number of H atom replaced by alkyl on NH_3

At times, the H atom may be replaced by a benzyl or aryl or phenyl group (Aromatic amine)

To some extent, 1^0 , 2^0 and 3^0 amines share some common physical and chemical properties, though the difference in the environment of the N atom in each class brings about some major difference.

Note that the general formula of amines is $\text{C}_n\text{H}_{2n+1}\text{NH}_2$ or RNH_2 . The functional group is $-\text{NH}_2$ (amine group).

NOMENCLATURE OF AMINE

Nomenclature of amines is based on that of aliphatic side chain i.e according to the alkyl group attached to the nitrogen, the general suffix –amine is used .

GENERAL CHARACTERISTICS OF AMINE

PHYSICAL PROPERTIES

Generally, amines have fishy odour and are basic specifically, they are Lewis base, an electron- pair donor. Amines smell like ammonia, though less pungently.

There is less evidence of hydrogen bonding in the amines than in alcohol even though they exhibit trend in physical properties like boiling points and solubility. Low molecular weight amines are soluble in water and this has been attributed to the formation of H-bonds between the amine and water molecule. i.e

Amines are basic. More basic than ammonia i.e

The K_b of NH_3 is 1.8×10^{-5} while the K_b of CH_3NH_2 is 5.0×10^{-4}

Due to the basicity of amine, it is soluble in aqueous mineral acids, this distinguishes amine from ammonia and other classes of organic compounds. Amine are as well nucleophilic. The basicity and nucleophilicity of amine is due to the presence of unshared pair of electrons on the nitrogen atom.

The amine, salts formed from the reaction between amine and mineral acid is odourless, water-soluble crystalline solids with the usual characteristics of ionic compounds. Amine salts like ammonium salts, are readily decomposed by alkalis to regenerate the amines i.e

The properties above make it easy to separate amines from mixtures with other organic compounds.

(2) Reaction with Nitrous Acid (HNO_2)

(a) Ice-cold aqueous solution of NaNO_2 mixed with ice-cold aqueous or ethanolic solution of 1° amine at 0°C and the mixture treated with cold HCl gives effervescence and N_2 gas is quantitatively evolved.

The yield of N_2 (g) in the reaction above is quantitative hence its effervescence serves a chemical test to distinguish 1° amines from 2° and 3° which do not evolve N_2 under the same condition.

(b) The 2° react under the same condition above to form yellow in soluble oily product, nitrosamines. No N_2 gas is evolved. The nitrosamines are decomposed by boiling dilute mineral acids to give the amine salts from which the original amine can be regenerated by neutralization with a strong base..