UNIT X : ORGANIC CHEMISTRY

X.1. INTRODUCTION

Organic chemistry is defined as the chemistry of **CARBON** compounds. Because of the immense number of organic compounds, organic chemistry is considered to be one of the major branches of chemistry.

In spite of the fact that carbon is the focus of organic chemistry, hydrogen atoms are usually, but not always, present in organic molecules. Compounds containing only carbon and hydrogen atoms number in the hundreds of thousands and the option of adding other atoms such as oxygen, nitrogen, chlorine and so on, extends the number of known organic compounds to over 8 million.

The key to this huge number of organic compounds is the fact that carbon forms chains involving several carbon atoms linked to each other in a straight–line fashion, in a "circular" pattern, or in a branched pattern. In addition, the carbon atoms may form single, double or triple bonds to neighbouring atoms, which further extends the range of possible molecules.

Why is organic chemistry so important? A partial answer is found by looking at the organic compounds below.

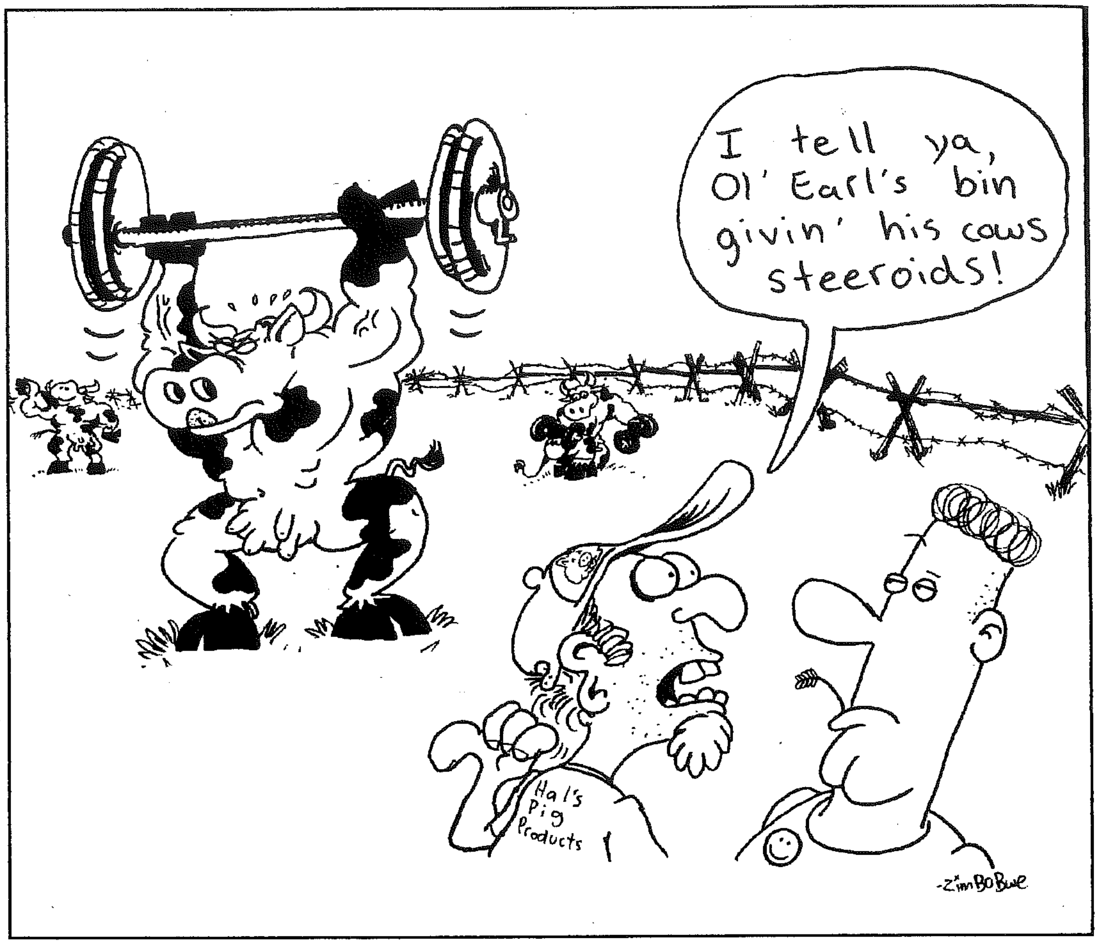
C_8H_{18} = iso–octane (the chief ingredient in gasoline)
CH_4 = methane ("natural gas")
$C_{18}H_{21}NO_3$ = codeine (pain reliever)
$C_{22}H_{25}NO_6$ = colchicine (anti–leukemia drug)
$C_8H_6O_3Cl_2$ = 2,4–D (a herbicide)
$C_{14}H_9Cl_5$ = DDT (a banned pesticide)
$C_{10}H_{19}O_6S_2P$ = malathion (an insecticide)
$C_{19}H_{28}O_2$ = testosterone (a male sex hormone)
$C_{17}H_{21}NO_4$ = cocaine
$C_{10}H_{14}N_2$ = nicotine
$C_6H_{12}O_6$ = glucose (a sugar)
C_2H_4 = ethene (a plant hormone which causes ripening of fruit)
$C_{20}H_{12}$ = 1,2–benzpyrene (a cancer–causing ingredient of cigarette smoke)
$C_{40}H_{56}$ = beta–carotene (the yellow colour in carrots; used as the colouring agent in margarine)
$[C_2H_4]_x$ = polyethylene (plastic) ["x" implies a multiply–repeated unit]
$[C_2F_4]_x$ = Teflon

Looking down the list, you may notice that all these organic compounds contain carbon, and most also contain hydrogen. Organic chemicals have an extensive range of uses and properties. Some organic chemicals occur naturally and some are produced synthetically; some are beneficial and some are hazardous.

Where do we find organic compounds? Look around you! They are found in petroleum, natural gas and all living things including trees, grasses, vegetables, insects, animals and people.

The largest industry involving organic chemistry is the manufacture of petrochemicals. Petroleum is presently the starting material for a vast range of products. Part of the complicated mixture of organic chemicals which makes up petroleum is separated ("fractionated") and refined for use in gasoline and oil, while other "fractions" of petroleum are chemically altered to serve as raw materials for a huge array of industrial processes such as the manufacture of plastics, solvents, pharmaceuticals and personal care products. The food and beverage industry alone uses a substantial amount of organic chemicals in the form of "food additives" — look at the ingredients listed on a package of your favourite "junk food" (most of those unpronouncable names are organic chemicals).

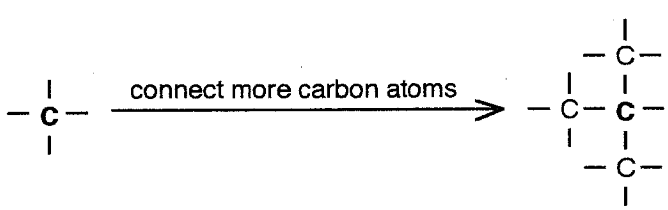
This unit starts by looking at compounds containing only carbon and hydrogen and then looks at the effects of introducing other kinds of atoms.



X.2. ALKANES

Definition: A **HYDROCARBON** is a compound containing only hydrogen and carbon.

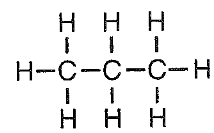
A carbon atom, such as the one shown in bold below on the left, can form bonds to four other atoms (carbon has a valence of four) — and this is the key to the wide variety ot possible carbon compounds. If one or more of the four bonds connect to other carbon atoms, each of these attached carbons can connect to three other atoms, and so on. The possible variety and complexity of the molecules increases with each carbon added.



A. UNBRANCHED ("STRAIGHT CHAIN") ALKANES

There is more than one way to represent a hydrocarbon formula, depending on how compact one wants to write the formula.

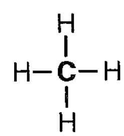
EXAMPLE: The structure of propane, C_3H_8, can be shown in three ways.

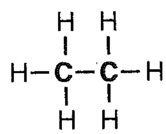
full structure: 

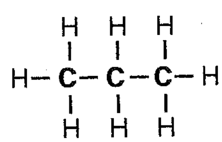
or condensed structure: $CH_3–CH_2–CH_3$ (or even $CH_3CH_2CH_3$)

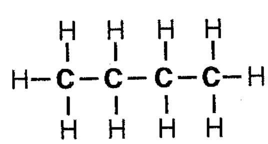
or molecular formula: C_3H_8

In the following sequence of hydrocarbons, each molecule differs by the number of carbon atoms linked to one another to form a "carbon chain". Because the chain of carbon atoms extends in a straight–line fashion, the hydrocarbons in this section are call "straight–chain" or "unbranched" hydrocarbons.

methane = CH_4 = 

ethane = C_2H_6 =  = $CH_3–CH_3$

propane = C_3H_8 =  = $CH_3–CH_2–CH_3$

butane = C_4H_{10} =  = $CH_3–CH_2–CH_2–CH_3$

and similarly

pentane = C_5H_{12} = $CH_3–CH_2–CH_2–CH_2–CH_3$

hexane = C_6H_{14} = $CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$

heptane = C_7H_{16} = $CH_3–CH_2–CH_2–CH_2–CH_2–CH_2–CH_3$

octane = C_8H_{18} = $CH_3–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_3$

nonane = C_9H_{20} = $CH_3–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_3$

decane = $C_{10}H_{22}$ = $CH_3–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_3$

Definition: An **ALKANE** is a hydrocarbon in which all the carbon atoms are connected by **single** bonds.

Note: 1. The names of the above hydrocarbons end in "ane" because they are "alkanes".

2. An alkane is also called a "**SATURATED**" hydrocarbon because each carbon atom is bonded to the maximum possible number of other atoms; that is, the carbon's ability to bond to other atoms is "saturated".

EXERCISE:

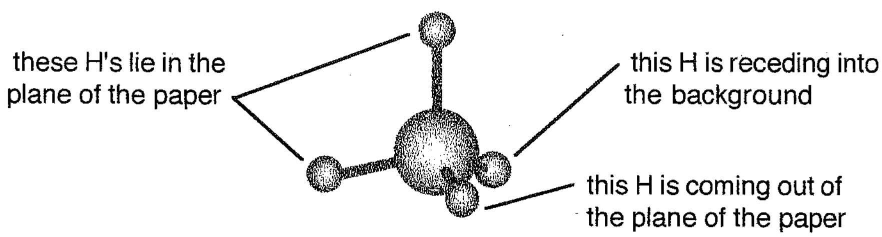
1. Look at the sequence of hydrogen atoms connected to carbon atoms in the list below.

   CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, etc.

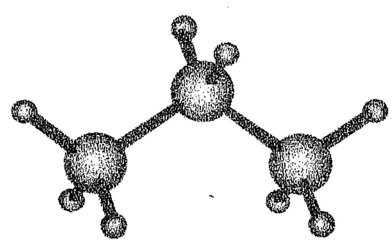
   Suggest a general formula for all straight–chain alkanes. That is, if there are "N" carbons, how many hydrogens will be present?

THE GEOMETRY OF ALKANES

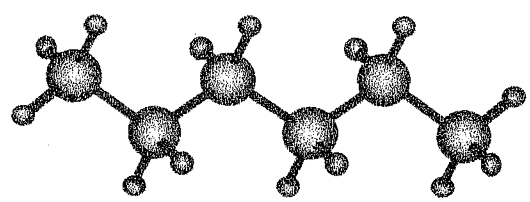
Although the bonds on a carbon atom are usually drawn as if they were run over by a steam roller, lying flat on a page at right angles to each other, the bonds are actually arranged in the shape of a 4–cornered pyramid (a "TETRAHEDRON") as shown below. All the bonds have equal lengths and all the H–C–H angles are 109°.



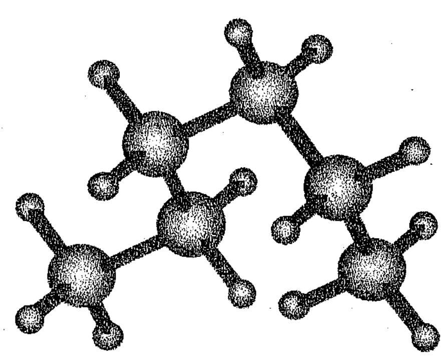
Therefore the actual shape of the propane molecule can be shown as



and a molecule of hexane might look something like the following.



Each of the single bonds between the carbon atoms is able to rotate freely, leading to a highly flexible chain which can wave about and take many shapes. The above arrangement is one shape hexane can assume; another might be the arrangement shown below.



B. ALKYL GROUPS AND BRANCHED HYDROCARBONS

A hydrocarbon chain can have "side branches" which are also hydrocarbon chains.

EXAMPLE:

$$\begin{array}{l} CH_3\text{–}CH_2\text{–}\underset{\displaystyle |}{C}H\text{–}CH_2\text{–}CH_2\text{–}CH_3 \\ \qquad\qquad\quad CH_2 \\ \qquad\qquad\quad\; | \\ \qquad\qquad\quad CH_3 \end{array}$$

These attached "groups" are called ALKYL GROUPS.

A short digression on the "organic language"

This unit introduces some complicated words which seem like a foreign language to an outsider. In fact, the words ARE part of another language — the "organic language". As in other languages, the basic "words" are placed together to make complete names for organic molecules, similar to the way in which basic words are placed together to make complete sentences in English. The "organic" words can have their endings modified and be used like adjectives, verbs or adverbs. As you procede, always be sure you know the "syntax" or set of rules for constructing the organic "sentences" which make up the complete organic names of molecules. The rules are simple .... and there are NO IRREGULAR VERBS!

Definition: An **ALKYL GROUP** is an alkane which has lost one hydrogen atom.

EXAMPLE:

$$CH_4 \xrightarrow{\text{remove one H}} CH_3\text{–}$$

$$CH_3\text{–}CH_3 \xrightarrow{\text{remove one H}} CH_3\text{–}CH_2\text{–}$$

$$CH_3\text{–}CH_2\text{–}CH_3 \xrightarrow{\text{remove one H}} CH_3\text{–}CH_2\text{–}CH_2\text{–} \quad \text{or} \quad CH_3\text{–}\underset{|}{C}H\text{–}CH_3$$

(remove end H) (remove middle H)

The "unused" bond on the carbon atom can be connected to another hydrocarbon chain. **This unit only uses alkyl groups formed by taking a hydrogen off the END carbon of a hydrocarbon chain.**

RULE: An alkyl group is named by changing the "ane" ending of the original hydrocarbon to "yl".

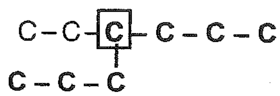
EXAMPLES:

Original hydrocarbon	Alkyl group
methane = CH_4	methyl = CH_3–
ethane = CH_3–CH_3	ethyl = CH_3–CH_2–
propane = CH_3–CH_2–CH_3	propyl = CH_3–CH_2–CH_2–
butane = CH_3–CH_2–CH_2–CH_3	butyl = CH_3–CH_2–CH_2–CH_2–

When an alkyl group is attached to another hydrocarbon, the resulting molecule is called a **SUBSTITUTED HYDROCARBON** or a **BRANCHED HYDROCARBON.**

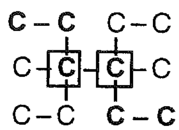
RULE: The first step in naming a substituted hydrocarbon is to find the longest continuous chain of carbon atoms. This longest chain is called the "***PARENT***" hydrocarbon.

EXAMPLES: To find the longest carbon chain, look at every "branch point" carbon (in a box in the examples below) and decide which TWO branches create the longest overall path (shown in bold). Only carbons are shown so as to make the various branches easier to see.

a) 

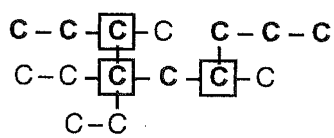
The carbon in the box has 3 branches: the longest route involves the right branch (3 carbons) and the lower branch (3 carbons).

Longest path length = 7 carbons = **heptane**

b) 

Here, no unique "longest path" exists. The longest chain involves either the upper or lower pair of carbons on the left side and either the upper or lower group of two carbons on the right. The bold path shown was selected randomly from the 4 possible choices.

Longest path length = 6 carbons = **hexane**

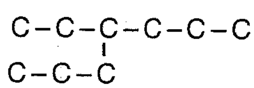
c) 

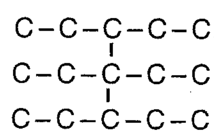
Do you agree with the bold path shown?

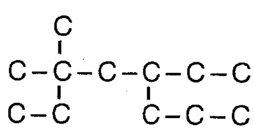
Longest path length = 9 carbons = **nonane**

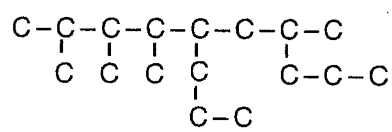
EXERCISE:

2. Determine the number of carbon atoms in the longest chain of each of the following, and name the parent hydrocarbon represented by the longest chain.

(a) 

(b) 

(c) 

(d) 

To name a substituted hydrocarbon, the basic idea is to name the longest (parent) hydrocarbon chain and then name the various alkyl groups which are attached to the parent hydrocarbon.

RULE: A substituted hydrocarbon is named by writing the following one after another
- the carbon number at which the alkyl group is attached,
- a dash,
- the name of the alkyl group, and finally
- the name of the longest or "parent" hydrocarbon chain, to which the alkyl group is attached.

Note: The carbon atoms in the parent hydrocarbon are numbered consecutively from the end of the hydrocarbon which gives the LOWEST POSSIBLE SET OF NUMBERS to the attached groups.

EXAMPLES:

1 2 3 4 5
$CH_3-CH-CH_2-CH_2-CH_3$ = 2–methylpentane
(branch CH_3 on C-2)

8 7 6 5 4 3 2 1
$CH_3-CH_2-CH_2-CH_2-CH_2-CH-CH_2-CH_3$ = 3–methyloctane
(branch CH_3 on C-3)

1 2 3 4 5 6 7 8
$CH_3-CH_2-CH_2-CH-CH_2-CH_2-CH_2-CH_3$ = 4–ethyloctane
(branch CH_2-CH_3 on C-4)

3 4 5 6 7
$CH_3-CH-CH_2-CH_2-CH_2-CH_3$ = 3–methylheptane
(branch CH_2-CH_3 on C-3, numbered 2 1)

EXERCISE:

3. Name the following hydrocarbons. Care: e and f are tricky!

(a) $CH_3-CH_2-CH-CH_2-CH_2-CH_3$ (branch CH_3 on the third carbon)

(b) $CH_3-CH_2-CH_2-CH-CH_2-CH_2-CH_3$ (branch CH_3-CH_2 on the fourth carbon)

(c) $CH_3-CH_2-CH-CH_2-CH_2-CH_2-CH_2-CH_3$ (branch CH_2-CH_3 on the third carbon)

(d) $CH_3-CH-CH_2-CH_2-CH_2-CH_3$ (branch CH_3 on the second carbon)

(e) $CH_3-CH_2-CH_2-CH_2-CH_2-CH-CH_3$ (branch $CH_2-CH_2-CH_3$ on the sixth carbon)

(f) $CH_3-CH-CH_2-CH_2-CH_2-CH_3$ (branch CH_2-CH_3 on the second carbon)

Since carbons have FOUR bonds, count the bonds between a given carbon atom and its neighbours and subtract that number from 4. The difference equals the number of hydrogen atoms which must be attached to each carbon. That is, the number of bonds to hydrogens PLUS the number of bonds to other carbons equals four. The required number of hydrogens is then written into the formula.

EXAMPLES: When a carbon is attached to ONE other carbon —

4 bonds – 1 bond used = 3 H's added and **C** $-CH_3$ becomes $\mathbf{CH_3}-CH_3$

When a carbon is attached to TWO other carbons —

4 bonds – 2 bonds used = 2 H's added and $CH_3-\mathbf{C}-CH_3$ becomes $CH_3-\mathbf{CH_2}-CH_3$

When a carbon is attached to THREE other carbons —

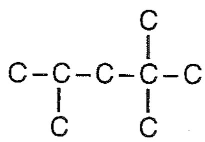
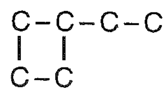
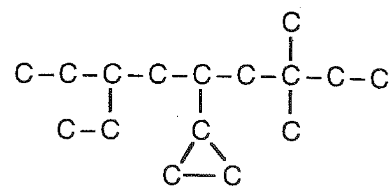
4 bonds – 3 bonds used = 1 H added and $CH_3-\mathbf{C}-CH_3$ (with CH_3 below the C) becomes $CH_3-\mathbf{CH}-CH_3$ (with CH_3 below the CH)

When a carbon is attached to FOUR other carbons —

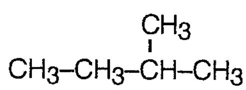
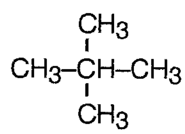
4 bonds – 4 bonds used = ***NO*** H's added and $CH_3-\mathbf{C}-CH_3$ (with CH_3 above and CH_3 below the C) needs ***no*** extra H's on the central C

EXERCISES:

4. Re–write the following structures to show the hydrogens attached.

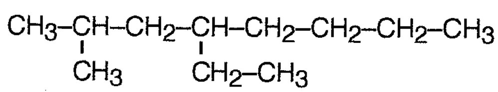
(a)  (b)  (c) 

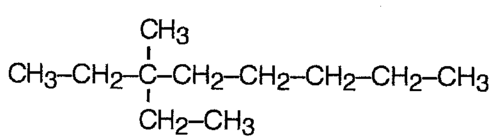
5. Draw the following hydrocarbons. Include all hydrogens.
   (a) 3–methylhexane
   (b) 4–ethyloctane
   (c) 2–methylpentane
   (d) 4–propylnonane
   (e) 3–ethylheptane
   (f) 5–propyldecane

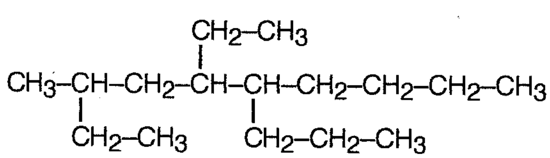
6. What is wrong with each of the following? (You may have to sketch the molecule to see the error in some cases.)
   (a) 6–methylheptane
   (b) 1–ethylbutane
   (c) 
   (d) 

RULE: If more than one DIFFERENT alkyl group is attached to a hydrocarbon, then
- list the alkyl groups alphabetically,
- precede each alkyl group by its number, and
- put a dash between each alkyl group and its number.

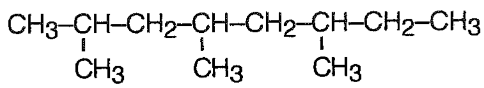
EXAMPLES:

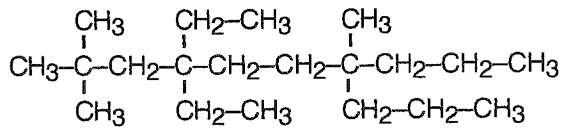
 = 4–ethyl–2–methyloctane

 = 3–ethyl–3–methyloctane (note that there can be 2 groups attached to the same carbon)

 = 5–ethyl–3–methyl–6–propyldecane (TRICKY! Can you see why?)

RULE: If an alkyl group is repeated, then
- list each carbon number where the repeated group is attached, separated by commas, and
- prefix the repeated group name by **di, tri, tetra,** etc. to show how many identical groups are attached.

EXAMPLES:  = 2,4,6–trimethyloctane

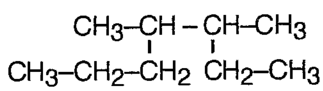


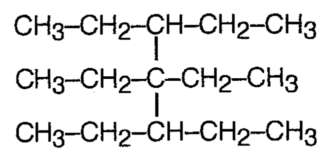
= 4,4–diethyl–2,2,7–trimethyl–7–propyldecane

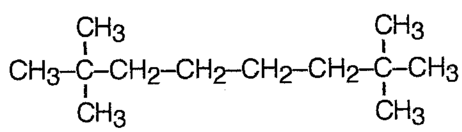
EXERCISES:

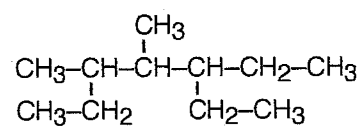
7. Count up the number of carbons and hydrogens in the two example molecules above. The general formula for a simple straight–chain hydrocarbon (methane, ethane, etc.) is C_NH_{2N+2}. What is the general formula for a branched hydrocarbon?

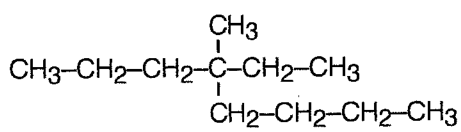
8. Name the following molecules.

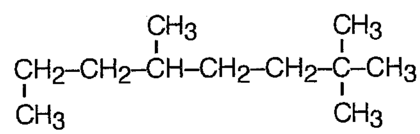
(a) 

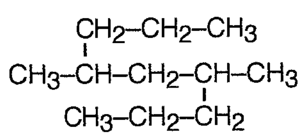
(b) 

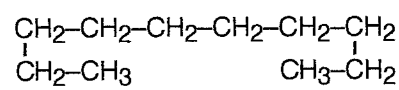
(c) 

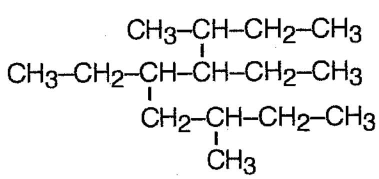
(d) 

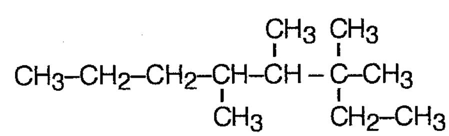
(e) 

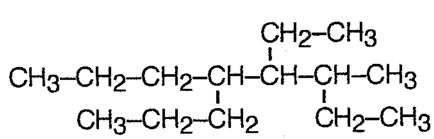
(f) 

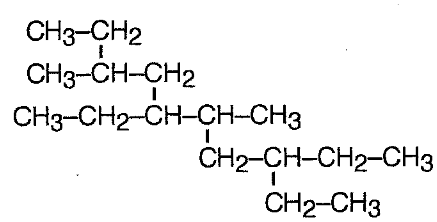
(g) 

(h) 

(i) 

(j) 

(k) 

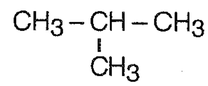
(l) 

9. Sketch the following molecules.
   (a) 3–ethyl–2,3–dimethylhexane
   (b) 2,2–dimethyl–5,6–dipropylnonane
   (c) 4–ethyl–3–methyl–5–propyloctane
   (d) 2,2,3,3–tetramethylpentane
   (e) 3,4–diethylhexane
   (f) 5–butyl–6,6–diethyl–3,3,7–trimethyldecane
   (g) dimethylpropane (why were no numbers used?)
   (h) 4–ethyl–2–methyloctane
   (i) hexamethylpentane
   (j) 3,6–diethyl–4–methyl–5–propyloctane

STRUCTURAL ISOMERS

Definition: **STRUCTURAL ISOMERS** are compounds which have the same molecular formula but a different arrangement of atoms.

EXAMPLE: C_4H_{10} can refer to either $CH_3-CH_2-CH_2-CH_3$ or



Each structural isomer has a set of chemical and physical properties which differ from those of other isomers with the same chemical formula.

EXERCISES:

10. Write the condensed structure and name for the three structural isomers having the molecular formula C_5H_{12}.
11. Write the condensed structure and name for the two structural isomers that involve a single methyl group attached to hexane.
12. Write the condensed structure and name of the four structural isomers that involve two methyl groups attached to pentane.
13. How many isomers of C_8H_{18} contain no side chains other than a single methyl group?

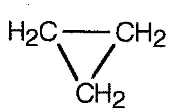
THE PROPERTIES OF ALKANES

- Alkanes are very unreactive because C–C and C–H bonds are strong and not easily broken.
- Methane, ethane, propane and butane are gases at room temperature (butane is easily liquified under pressure). Pentane and longer chains are liquids.
- Very long chains ($C_{16}H_{34}$ and longer) are solids and are commonly called WAXES or PARAFFINS.

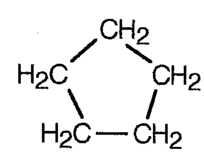
C. CYCLOALKANES

Hydrocarbon chains which connect in a head–to–tail "circle" are called CYCLIC HYDROCARBONS or CYCLOALKANES. The first members of the cycloalkane series are shown below.

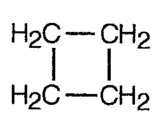
cyclopropane = C_3H_6 =



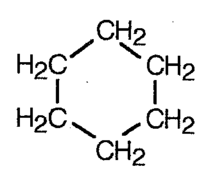
cyclopentane = C_5H_{10} =



cyclobutane = C_4H_8 =



cyclohexane = C_6H_{12} =



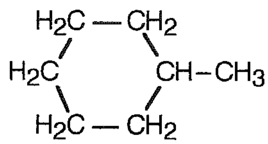
EXERCISE:

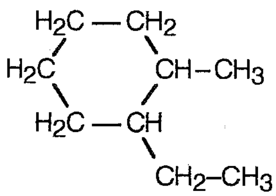
14. What is the general formula for a cycloalkane?

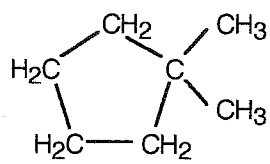
SUBSTITUTED CYCLOALKANES

RULE: Substituted cycloalkanes follow the same rules as straight–chain alkanes, except that

- a ***single*** substituent does not use a number to indicate the position of attachment (all carbons in the cycloalkyl group are identical).
- if there is more than one substituent, the first substituent is assumed to be at the "1" position and the remaining substituents are numbered either clockwise or anticlockwise so as to have the lowest set of overall values.

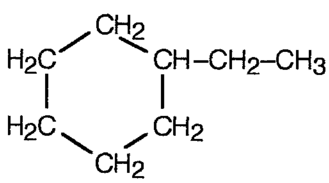
EXAMPLE:  = methylcyclohexane

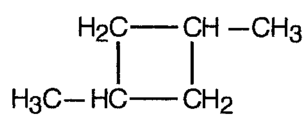
 = 1–ethyl–2–methylcyclohexane

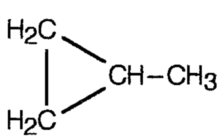
 = 1, 1–dimethylcyclopentane

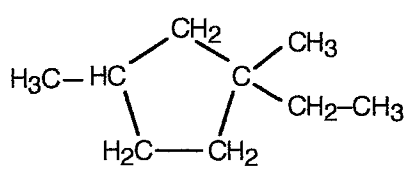
EXERCISES:

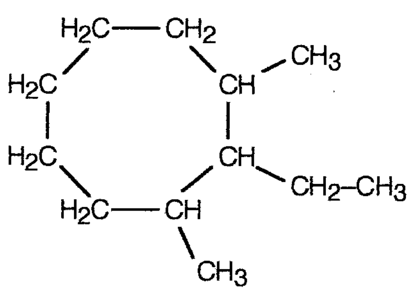
15. Name the following compounds.

(a) 

(b) 

(c) 

(d) 

(e) 

16. Sketch the following compounds.

(a) 1,2–dimethylcyclobutane
(b) 1,1,2–trimethylcyclopropane
(c) 1,3–dipropylcyclopentane
(d) propylcyclopropane
(e) 1,3–diethyl–2,2–dimethylcyclooctane
(f) 1,2,4–triethylcycloheptane

X.3 ALKYL HALIDES

The naming of alkyl halides (halogens – F, Cl, Br or I – attached to alkanes) is straightforward.

RULE: Name **alkyl halides** in the same manner used for alkyl groups.

- Attached F, Cl, Br and I atoms are called "fluoro", "chloro", "bromo" and "iodo" groups. (The general term for an attached halogen atom is a "halo" group.) Use a number to indicate the position of attachment on the hydrocarbon chain.
- If more than one of the same kind of halogen is present, use the prefixes di, tri, etc.
- If a compound contains both alkyl and halo groups, list the attached groups in alphabetical order. Start numbering from the end which gives the lowest set of numbers.

EXAMPLES: $CH_3–Cl$ = chloromethane

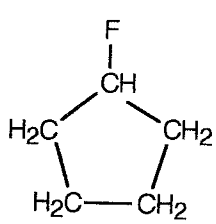
$CH_3–CH–CH_3$ (F on the CH) (or $CH_3–CHF–CH_3$) = 2–fluoropropane

Note: Unlike the situation involving the addition of alkyl groups to a straight–chain hydrocarbon, halo groups can be placed at the 1–position.

$CCl_3–CF_3$ = 1,1,1–trichloro–2,2,2–trifluoroethane

$CH_2–CH_2–CH–CH_2–CH_2–CH–CH_2–CH_2–CH_3$ (I on C1, Br on C3, I on C6) = 3–bromo–1,6–diiodononane

$CH_3–C–CH–CH_2–CH_2–CH_3$ (Br, Br on C2; CH_3 on C3) = 2,2–dibromo–3–methylhexane



= fluorocyclopentane

PROPERTIES OF ALKYL HALIDES

- Alkyl halides tend to be insoluble in water (similar to alkanes).
- Compounds with many fluorine atoms tend to be unreactive ("inert"). "Teflon" is a highly fluorinated hydrocarbon which is inert to almost all chemical attack.
- Chloro and bromo compounds are susceptible to chemical attack, but require relatively drastic conditions. Iodo compounds are more reactive.

EXERCISES:

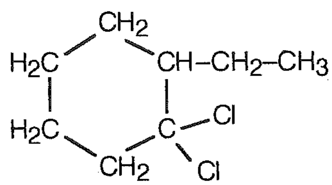
17. Name the following molecules.

    (a) CH_3–CH_2–Cl

    (b) Br–CH_2–CH_2–CH_2–Br

    (c) CH_3–CH(CH_3)–CH_2–CH_2–CH_2–I

    (d) CH_2F–$CHCl_2$

    (e) 

18. Draw the following molecules.
    (a) trichloromethane (common name = chloroform)
    (b) 1,2–dichloroethane
    (c) 1,3,5–tribromocyclohexane
    (d) 4–bromo–2–chloro–3–ethyloctane
    (e) 1,1,1–trifluoro–2–methylpentane

19. Draw and name the 8 structural isomers of $C_5H_{11}Cl$.

20. Draw and name the 9 structural isomers of $C_5H_{10}Cl_2$ that have no methyl groups.