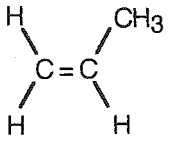
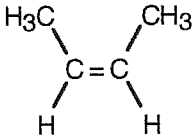
X.4. MULTIPLE BONDS ("ALKENES and ALKYNES")

Definitions: An **ALKENE** is an organic compound containing a carbon–carbon double bond.
An **ALKYNE** is an organic compound containing a carbon–carbon triple bond.
(Double and triple bonds can be either at the end of a carbon chain or in the middle.)

EXAMPLES:



or simply $CH_2=CH-CH_3$



or simply $CH_3-CH=CH-CH_3$

$H-C\equiv C-CH_3$ or simply $CH\equiv C-CH_3$

$CH_3-C\equiv C-CH_3$ or simply $CH_3C\equiv CCH_3$

The naming of compounds with double and triple bonds is quite straightforward.

RULE: If a double bond is present, change the "ane" ending of the parent hydrocarbon to "ene".
If a triple bond is present, change the "ane" ending of the parent hydrocarbon to "yne".
- Use a number to indicate the lower numbered carbon atom involved in the bond (the bond goes FROM the lower numbered carbon TO the higher numbered one). The number goes immediately in front of the name of the parent hydrocarbon, separated by a hyphen.
- Number the parent hydrocarbon to give the double/triple bond the lowest possible number. If the number is the same starting from either end, start the numbering from the end closest to the 1st branch point (where a group is attached).

Note: 1. There is an easy way to remember the bond endings.

single bonds	double bonds	triple bonds
ANE	ENE	YNE

The 1st letters (underlined) are in alphabetical order and sound like the long vowels a, e and i. (We can't use "ine" since this is used to indicate the presence of an amine group, $-NH_2$.)

2. Alkenes and alkynes are called **UNSATURATED** hydrocarbons because they have less hydrogen atoms than equivalent alkanes. Alkanes are said to be **SATURATED** hydrocarbons because they contain the maximum number of hydrogens possible.

WRITING THE CONDENSED STRUCTURE OF ALKENES AND ALKYNES

When you are given the name of an alkene or alkyne, the following process is used to arrive at the correct condensed structure.

EXAMPLES: Write the condensed formula for 2–hexene.

- Since "hex" means 6 carbon atoms are present, start by writing 6 carbons in a row.

  C C C C C C

- The "ene" ending means a C=C bond is present, and the "2" means the bond **starts** at carbon #2 and goes to carbon #3. The other carbon–carbon bonds are single.

  C – C = C – C – C – C

- Since all carbons have FOUR bonds, count the bonds between each carbon and its neighbours and subtract that number from 4. The difference is the number of hydrogens attached to each carbon. The appropriate number of hydrogens are now written into the formula.

  $CH_3–CH=CH–CH_2–CH_2–CH_3$

  3 bonds between carbons so 4th bond is to a hydrogen

Write the condensed formula for 1–pentyne .

- Similar to the reasoning above, the "yne" ending means a triple bond is present and the "1" indicates that the bond starts at carbon #1 and goes to carbon #2.

  $HC\equiv C–CH_2–CH_2–CH_3$

  4 bonds to carbons so no extra H's

  3 bonds to carbons so one bond to H

EXAMPLES: $H_2C=CH_2$ (or, $CH_2=CH_2$) = ethene (common name = ethylene)

$CH_2=CH–CH_3$ = propene

$CH_3–CH=CH–CH_3$ = 2–butene

$CH_2=C(CH_3)–CH_2–CH_3$ = 2–methyl–1–butene

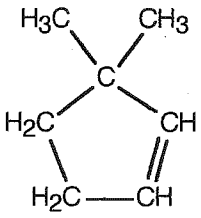
$CH_2=CH–C(CH_3)_2–CH_2–CH_3$ = 3,3–dimethyl–1–pentene

$HC\equiv CH$ = ethyne (common name = acetylene)

$HC\equiv C–CH_3$ = propyne

$CH_3–C\equiv C–CH_3$ = 2–butyne

$HC\equiv C–CH_2–CH(CH_3)–CH_3$ = 4–methyl–1–pentyne



= 3,3–dimethyl–1–cyclopentene

Note: the double (or triple) bond starts at carbon #1 and attached groups are numbered so as to have the lowest possible numbers

EXERCISES:

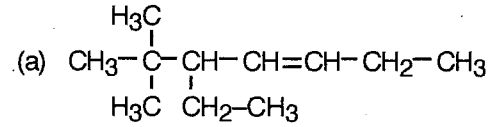
21. Look at the examples above (except for the cyclopentene) and decide on the general formula relating the ratio of carbons to hydrogens for each of the following.
    (a) an alkene (b) an alkyne
    Express your answer in a form similar to the expression C_NH_{2N+2} which was found for alkanes.

22. Draw the condensed structure for the following.
    (a) 1–hexene (c) 3–decene (e) 2–octene
    (b) 4–nonyne (d) 2–heptyne (f) 1–octyne

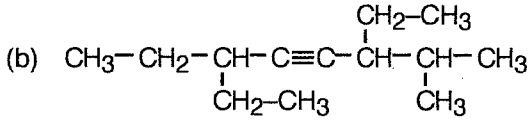
23. Name the following.
    (a) $CH_3–CH_2–CH=CH–CH_2–CH_3$
    (b) $CH_3–CH_2–CH_2–CH_2–CH_2–C\equiv CH$
    (c) $CH_3–CH_2–CH_2–C\equiv C–CH_2–CH_2–CH_2–CH_2–CH_3$
    (d) $CH_3–CH_2–CH=CH–CH_2–CH_2–CH_3$

24. Draw the condensed structure for each of the following.
    (a) 4–ethyl–3–methyl–2–hexene
    (b) 3–methyl–4–octyne
    (c) 1–ethyl–1–cyclononene
    (d) 3–ethyl–4–methyl–1–hexyne
    (e) dimethyl–2–butene
    (f) 3,6–dimethyl–1–cyclohexene
    (g) cyclopropyne
    (h) 1,3–dimethyl–1–cyclopentene

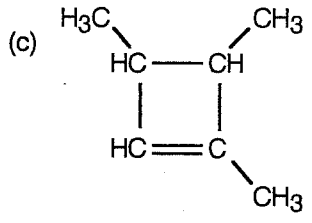
25. Name the following compounds.



(a)



(b)



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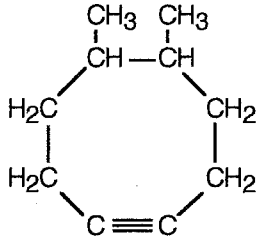

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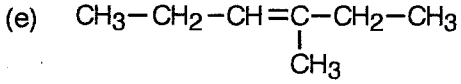

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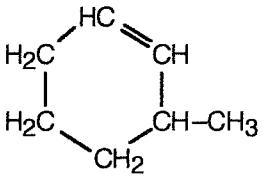
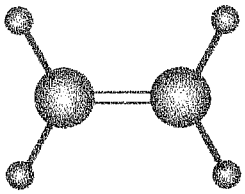


(f)

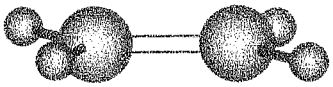
THE GEOMETRY OF ALKENES AND ALKYNES

In alkanes, each carbon atom is bonded to four other atoms in a tetrahedral shape. The resulting structure is very flexible as a result of atoms being able to rotate freely around the axis of each single bond.

Alkenes have a geometry in which the three atoms connected to each carbon lie flat, arranged 120^{o} from each other in a plane.



which looks like this from the side:



Alkynes have a geometry in which the two atoms attached to the central carbon lie in a straight line, such that the attached atoms are 180^{o} from each other.

Whereas alkanes have flexible structures, alkenes have very rigid structures. The double bonds effectively "lock" the structure to prevent the attached atoms from "twisting" around the double bond.

The triple bond in alkynes is also very rigid, and a series of triple bonds will form straight "needle–like" structures. For example, molecules similar to the following have been detected in interstellar space, where the molecules act as radio antennae.

$$H-C\equiv C-C\equiv C-C\equiv C-C\equiv C-C\equiv C-C\equiv C-C\equiv C-H$$

On the other hand, in a molecule such as

$$CH_3-C\equiv C-CH_3$$

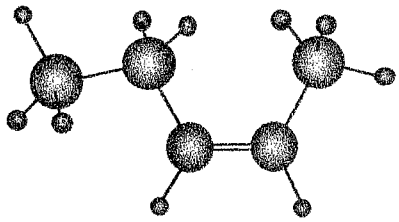
the carbons involved in the triple bond are locked to each other, but the single bonds extending from the triply–bonded carbons to the methyl carbons allow free rotation of the methyl groups.

The rigid structure of the alkene carbons has an immediate and important consequence: a new kind of isomerism.

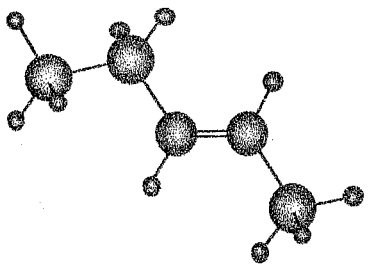
This kind of isomerism, called **CIS–TRANS ISOMERISM,** is possible whenever a molecule has:

- a double bond present, AND
- groups (other than a hydrogen atom) which are attached to each of the carbons involved in the double bond. (The attached groups do not have to be identical; all that is required is that they not be hydrogen atoms.)

EXAMPLE: 2–pentene has two different isomers possible.



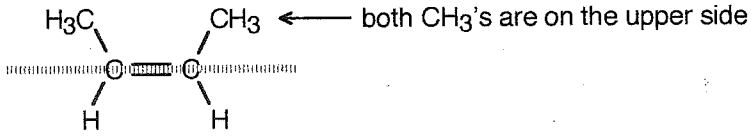
cis–2–pentene



trans–2–pentene

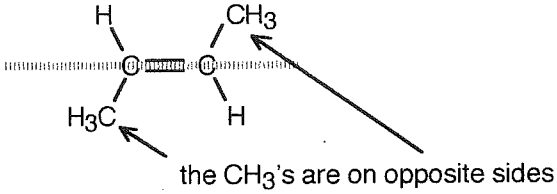
In the above example, the methyl and ethyl groups on opposite ends of the double bond are either "cis" or "trans" to each other.

Note: In a "**CIS**" isomer, the two groups are on the **SAME SIDE** of the double bond.



← both CH_3's are on the upper side

In a "**TRANS**" isomer, the two groups are "**TRANSVERSE**" to each other (that is, on opposite sides of the double bond).



the CH_3's are on opposite sides

EXERCISES:

26. Draw the actual shape of the following molecules using condensed structures.
    (a) trans–2–hexene (c) cis–3–octene (e) 2–butyne
    (b) 3–hexyne (d) trans–4–decene (f) 4–methyl–cis–2–pentene

27. Which of the following molecules can exhibit cis–trans isomerism?
    (a) 1–butene (c) 4–heptyne (e) 3–ethyl–3–hexene
    (b) 3–hexene (d) 2–octene (f) 2,5–dimethyloctane

28. Name the following as "cis" or "trans" isomers.

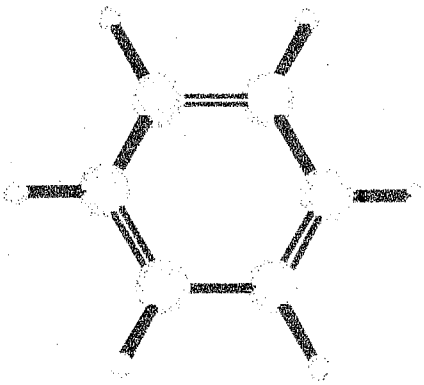
(a) $CH_3–CH_2$ $CH_2–CH_3$ (b) H $CH_2–CH_3$ $CH_3–CH_2–CH_2–CH_2$

(c) H $CH_2–CH_2–CH_2–CH_3$ CH_3 H

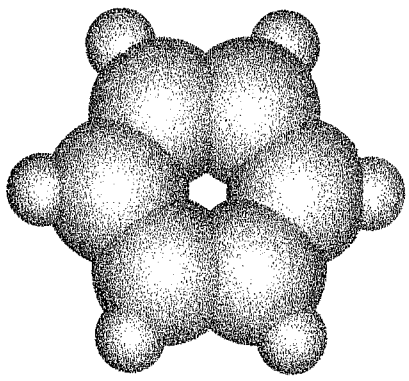
(d) H H $CH_3–CH_2–CH_2$ $CH_2–CH_2–CH_3$

X.5. AROMATIC COMPOUNDS

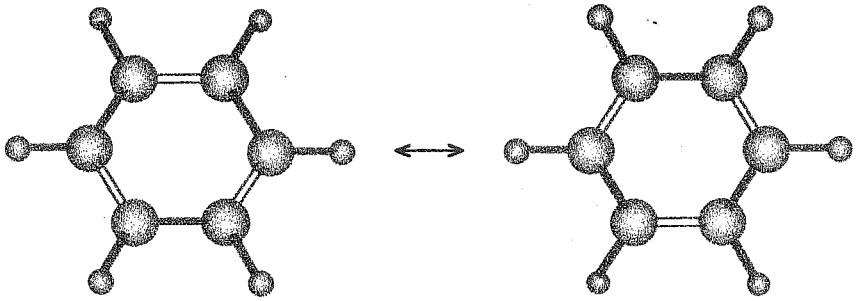
Benzene, C_6H_6, is an important molecule having the following structure.



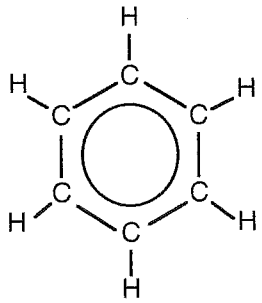
or, using a "space–fillling" form



The ring–like structure of benzene can be written in either of two **RESONANCE STRUCTURES,** differing only in the placement of the double bonds. Each resonance structure consists of alternating single and double bonds between carbon atoms.



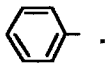
Strictly speaking, drawing benzene in either of its two resonance structures is not correct. The actual arrangement of electrons in the carbon ring is a mixture of both resonance structures. In order to better show the situation which occurs, benzene is frequently represented as follows.



Benzene's resonance structures give it unusual stability; that is, it is highly resistant to chemical attack. Atoms attached to the benzene ring can be replaced, but only the strongest chemical attack (such as combustion) will affect the ring itself.

The benzene ring, also known as an "aromatic ring", is present in a large number of molecules and many molecules contain two or more aromatic rings joined together.

Definition: An **AROMATIC MOLECULE** is a molecule containing one or more benzene rings.

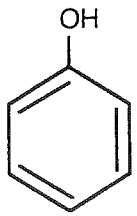
The aromatic ring (benzene ring) is frequently shown as:  .

The origin of the term "aromatic" comes from the fact that many molecules containing benzene rings are quite fragrant and pleasant smelling (although many others are quite disagreeable). In the past, aromatic molecules were obtained primarily from the distillation of coal, but modern industry obtains them from a process called the **catalytic reforming** of petroleum.

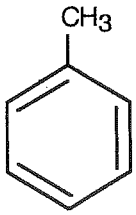
The naming of simple aromatic compounds formed by adding groups to a benzene ring is almost identical to the naming procedure used for other cyclic hydrocarbons. Two exercises on the next page allow you to apply what you know to naming aromatic compounds.

The example molecules which follow do not have to be memorized; they are shown for your information.

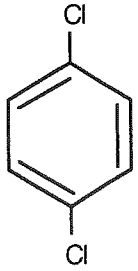
EXAMPLES:



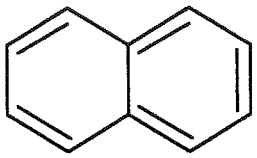
hydroxybenzene
or "phenol"



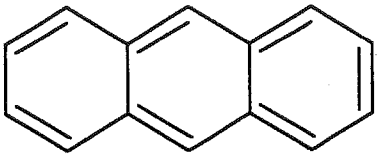
methylbenzene
or "toluene"



1,4–dichlorobenzene
or "paradichlorobenzene"



naphthalene



anthracene

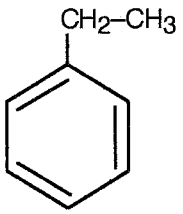
EXERCISES:

29. (a) One resonance structure was drawn for naphthalene (above). Draw two other resonance structures.
    (b) One resonance structure was drawn for anthracene (above). Draw three other resonance structures.

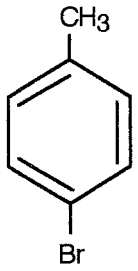
30. Draw the structures of the following compounds.
    (a) 1,3,5–trimethylbenzene
    (b) 1–bromo–4–chlorobenzene
    (c) fluorobenzene
    (d) 1,4–dibromo–2–methylbenzene
    (e) 1,3–diethylbenzene
    (f) hexylbenzene

31. Name the following compounds.

(a)



(b)



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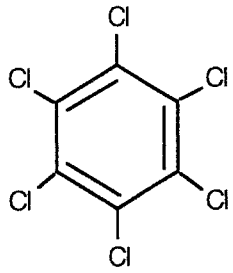

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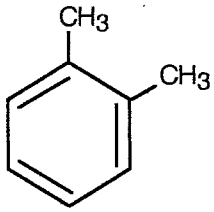

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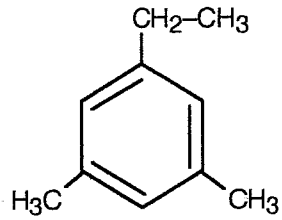

(f)