Damascus University
Faculty of Pharmacy
Pharmaceutical Organic Chemistry I

3- الألكانات وكيميائيتها الفراغية

Alkanes and Their Stereochemistry

MC-Murry-Chapter-3

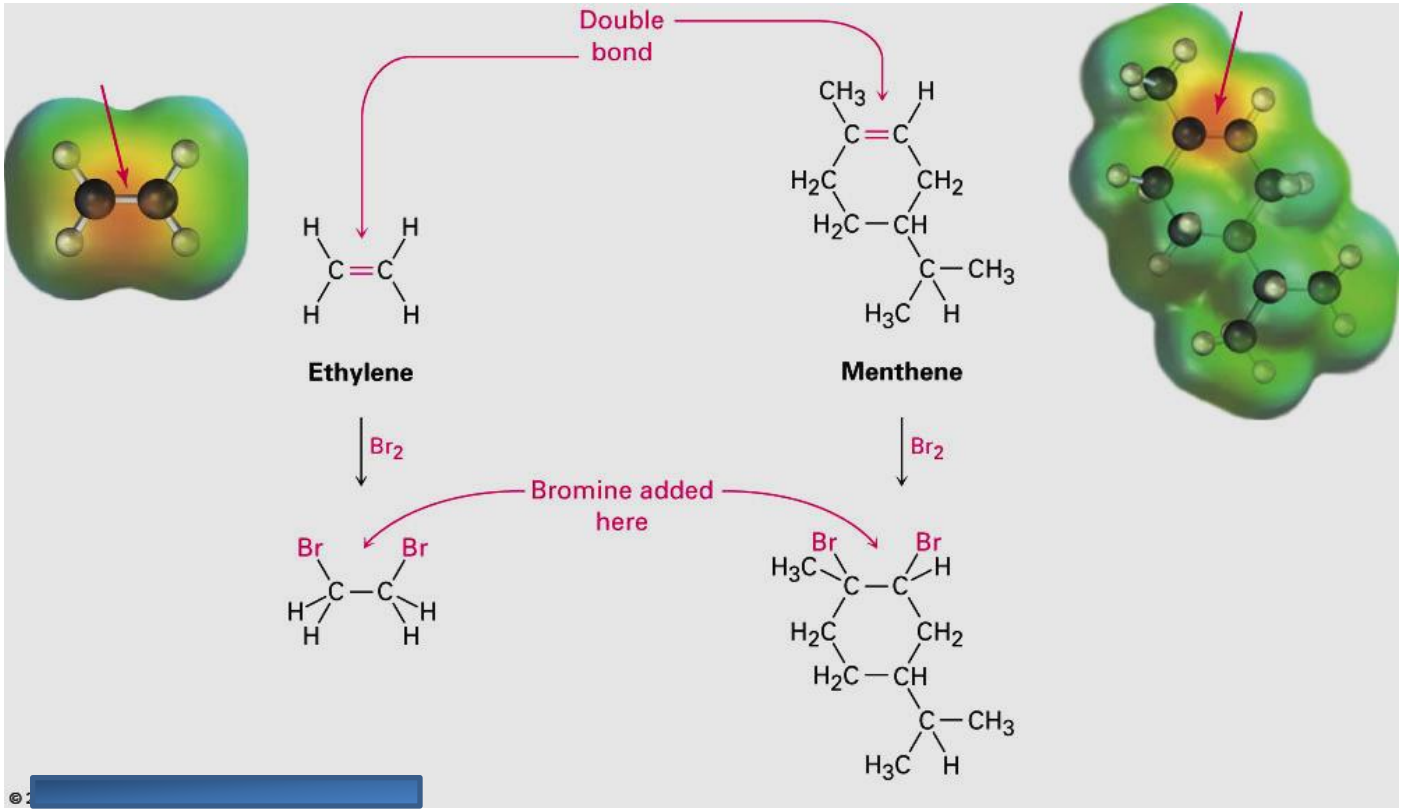
By Prof.Dr. M.Ammar Al–Khayat

2016–2017

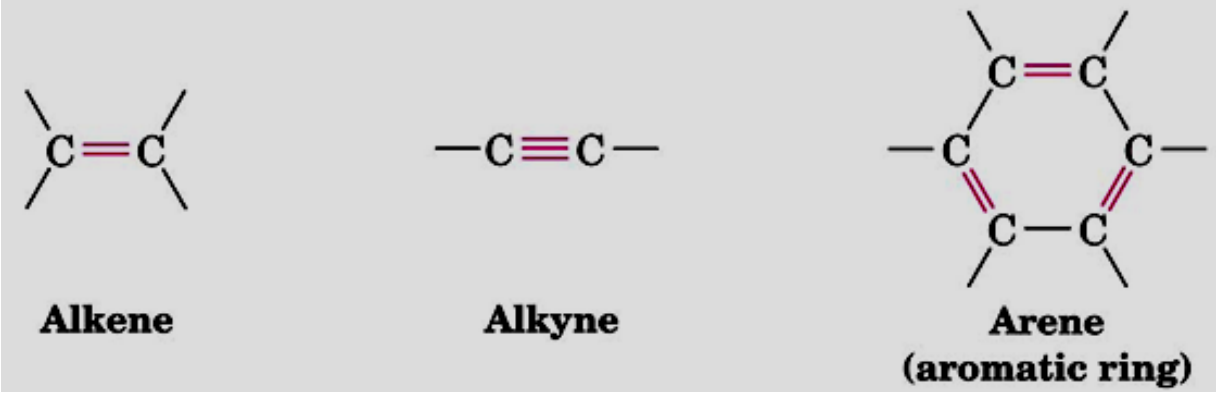
المجموعات الوظيفية

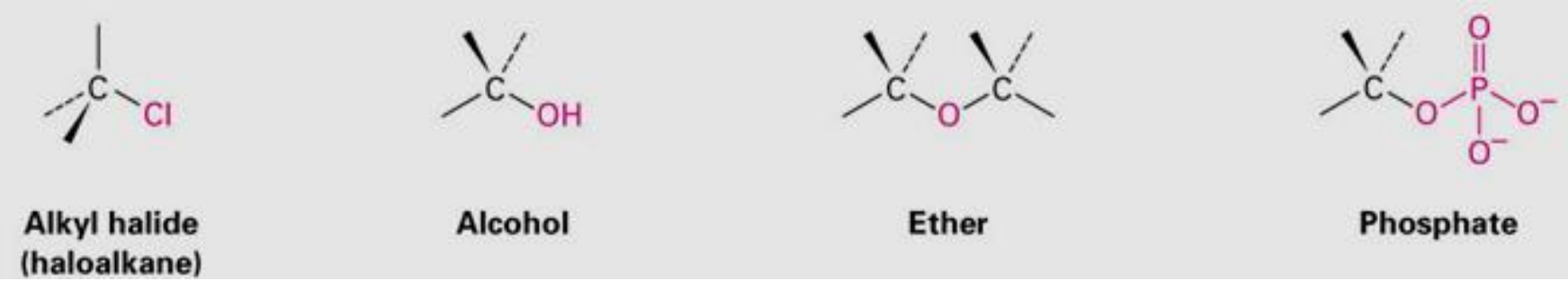
-يمكن تصنيف المركبات العضوية في عوائل وفق المجموعات الوظيفية

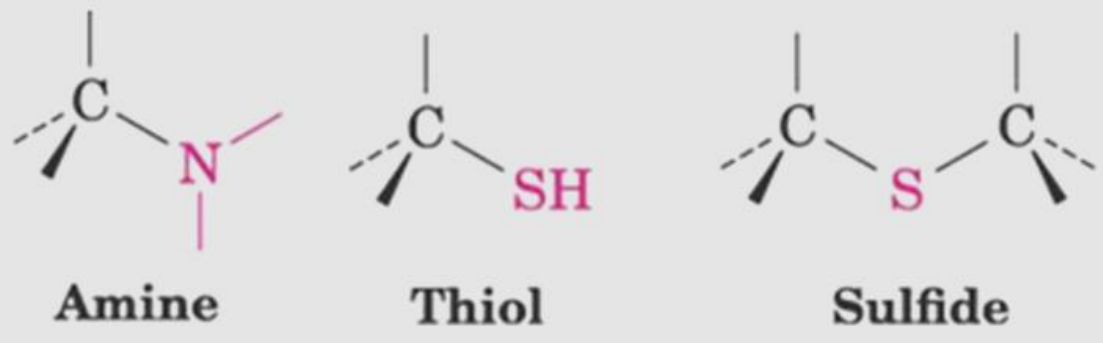
-المجموعة الوظيفية: مجموعة من الذرات ذات سلوك كيميائي مميز سواء وجدت في جزيء بسيط أو معقد البنية.



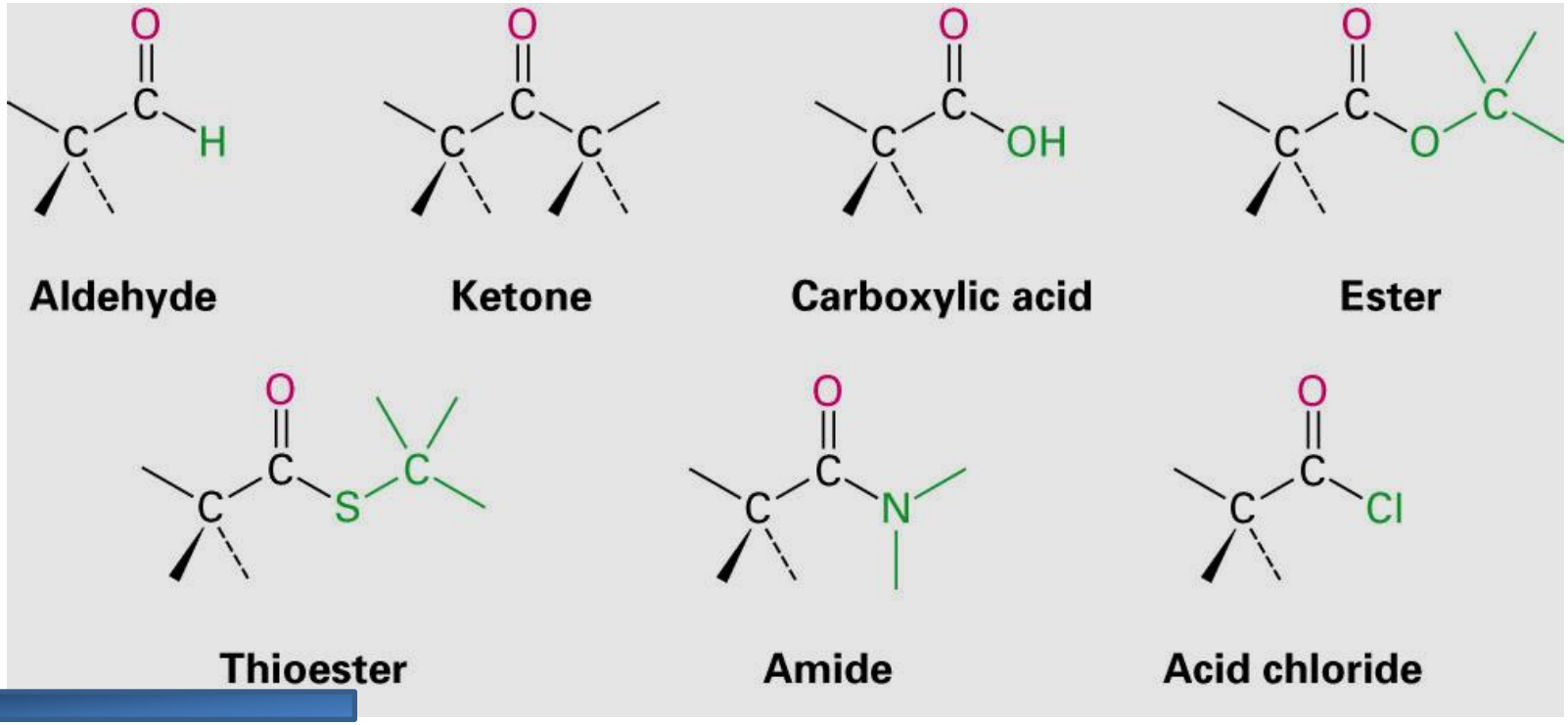
بعض المجموعات الوظيفية







بعض المجموعات الوظيفية



الألكانات

–الألكانات هي أبسط عوائل المركبات العضوية

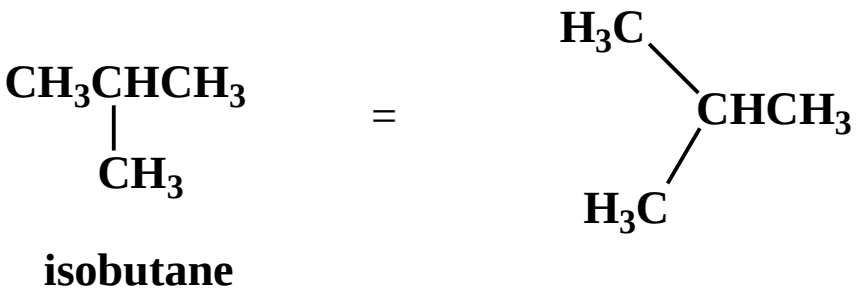
–هي مركبات هيدروكربونية مشبعة أليفاتية أي تحتوي على روابط أحادية كربون –كربون وكربون–هيدروجين

– الصيغة العامة C_nH_{2n+2}

– ألكانات مسستقيمة الساسلة **straight-chain normal alkanes**

CH_4	CH_3CH_3	$CH_3CH_2CH_3$	$CH_3CH_2CH_2CH_3$
Methane	Ethane	Propane	Butane

– ألكانات متفرعة السلسلة **branched-chain alkanes**

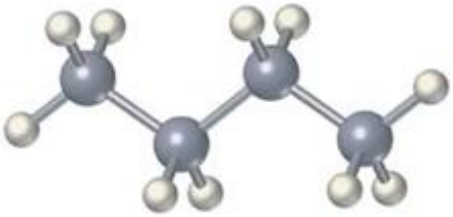


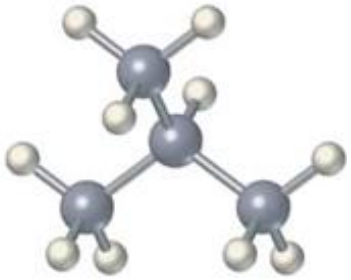
isobutane

Constitutional Isomerism التصاوغ البنائي

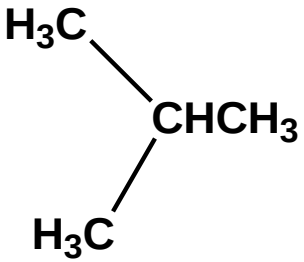
المتصاوغات: isomers مركبات لها الصيغة الجزيئية نفسها لكنها تختلف عن بعضها بصيغها البنيوية

C_4H_{10}





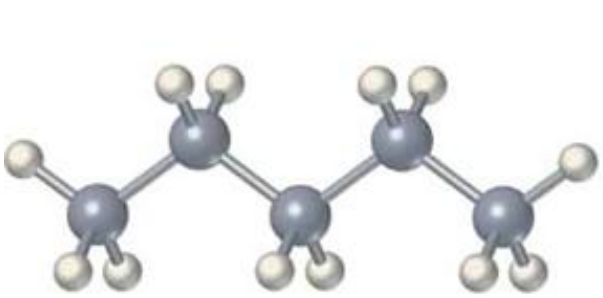
$CH_3CH_2CH_2CH_3$

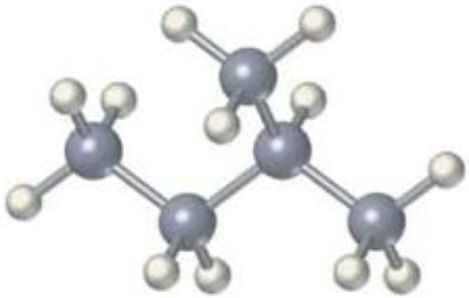


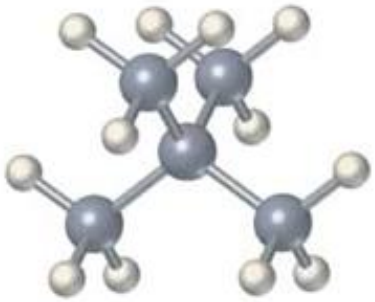
butane **isobutane**

التصاوغ البنائي

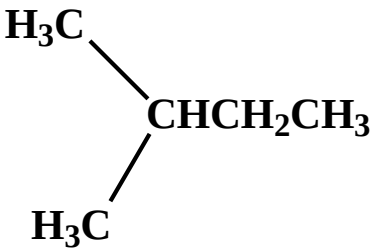
C_5H_{12}

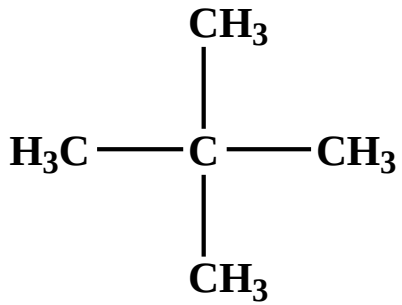






$CH_3CH_2CH_2CH_2CH_3$





pentane

isopentane

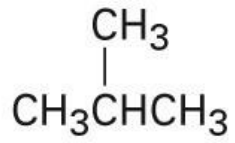
2- Methylbutane

neopentane

2,2- Dimethylpropane

التصاوغ البنائي في المركبات الوظيفية

Different carbon skeletons
C_4H_{10}



2-Methylpropane (isobutane)

and

$CH_3CH_2CH_2CH_3$

Butane

C_4H_{10}

Different functional groups
C_2H_6O

CH_3CH_2OH

Ethanol

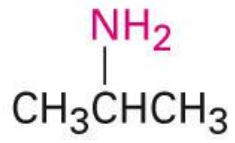
and

CH_3OCH_3

Dimethyl ether

C_2H_6O

Different position of functional groups
C_3H_9N



Isopropylamine

and

$CH_3CH_2CH_2NH_2$

Propylamine

C_3H_9N

تسمية الألكانات ذات السلسلة المستقيمة

Pent + ane ⟶ Pentane

بنت + آن ⟵ بنتان

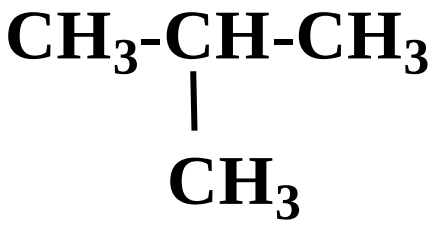
CH_4	متان
C_2H_6	إتان
C_3H_{10}	بروبان
$n\text{-}C_4H_{10}$	بوتان
$n\text{-}C_5H_{12}$	بنتان

$n\text{-}C_6H_{14}$	هكسان
$n\text{-}C_7H_{16}$	هبتان
C8	أوكتان
C9	نونان
C10	ديكان

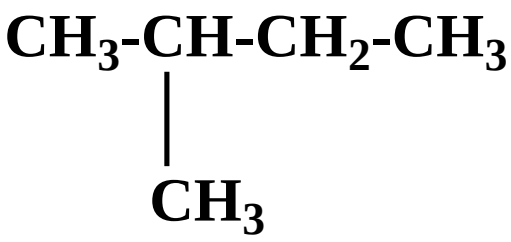
أسماء الألكانات ذات السلسلة المستقيمة (IUPAC)

Number of carbons (n)	Name	Formula (C_nH_{2n+2})
1	Methane	CH_4
2	Ethane	C_2H_6
3	Propane	C_3H_8
4	Butane	C_4H_{10}
5	Pentane	C_5H_{12}
6	Hexane	C_6H_{14}
7	Heptane	C_7H_{16}
8	Octane	C_8H_{18}
9	Nonane	C_9H_{20}
10	Decane	$C_{10}H_{22}$
11	Undecane	$C_{11}H_{24}$
12	Dodecane	$C_{12}H_{26}$
13	Tridecane	$C_{13}H_{28}$
20	Icosane	$C_{20}H_{42}$
21	Henicosane	$C_{21}H_{44}$
30	Triacontane	$C_{30}H_{62}$

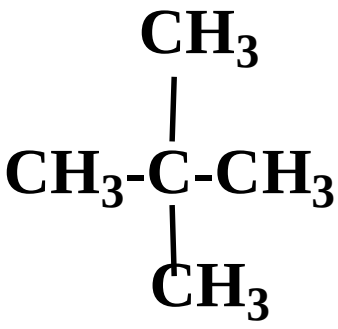
الأسماء الشائعة لبعض الألكانات المتفرعة (إيزو، نيو)



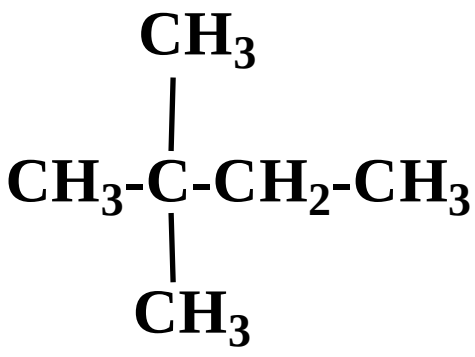
isobutane



isopentane

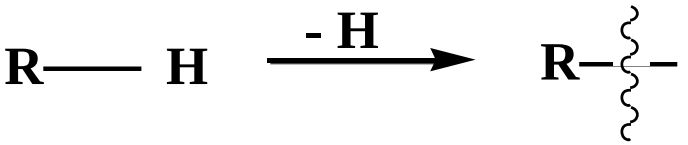


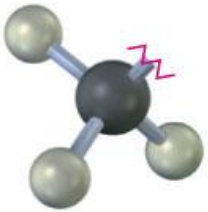
Neopentane

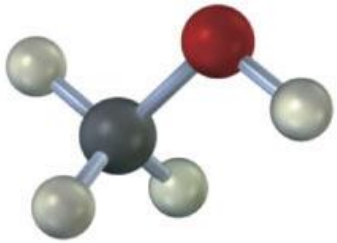


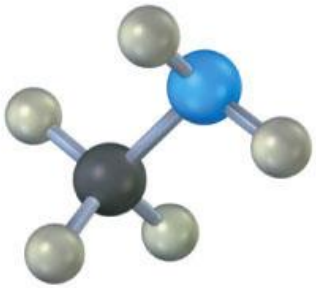
Neohexane

مجموعات الألكيل









Methane

A methyl group

Methyl alcohol
(methanol)

Methylamine

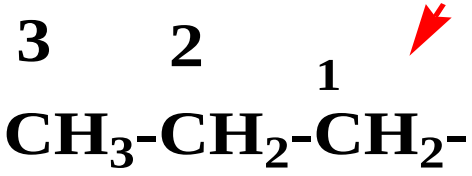
مجموعات الألكيل ذات السلسلة المستقيمة

Some Straight-Chain Alkyl Groups

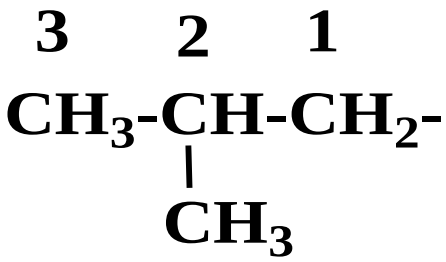
Alkane	Name	Alkyl group		Name (abbreviation)
CH_4	Methane	$-CH_3$	ميتيل	Methyl (Me)
CH_3CH_3	Ethane	$-CH_2CH_3$	إتيل	Ethyl (Et)
$CH_3CH_2CH_3$	Propane	$-CH_2CH_2CH_3$	بروبيل	Propyl (Pr)
$CH_3CH_2CH_2CH_3$	Butane	$-CH_2CH_2CH_2CH_3$	بوتيل	Butyl (Bu)
$CH_3CH_2CH_2CH_2CH_3$	Pentane	$-CH_2CH_2CH_2CH_2CH_3$	بنتيل (أميل)	Pentyl, or amyl

تسمية مجموعات الألكيل المتفرعة

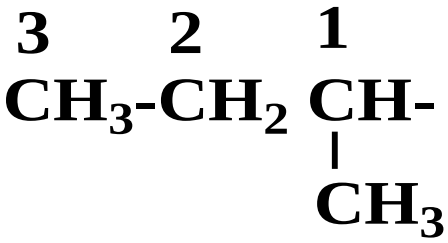
Free valence - atom



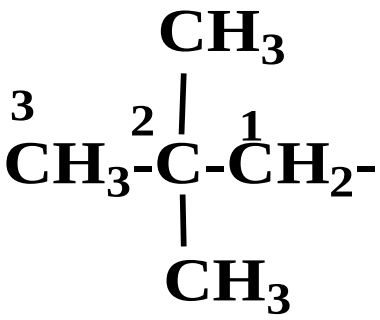
بروبيل



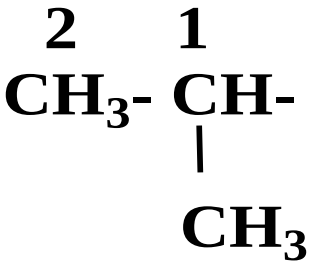
2–متيل بروبيل



١– متيل بروبيل

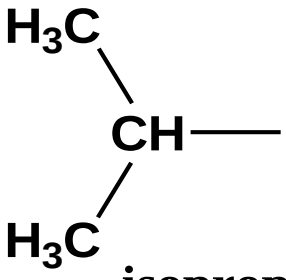


2,2-dimethylpropyl



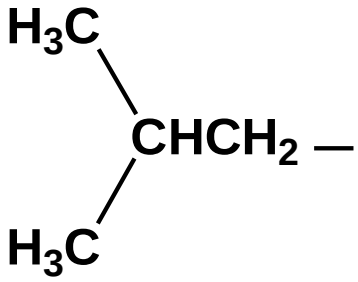
التسميات الشائعة لمجموعات الألكيل المتفرعة

(إيزو، ثانوي، ثالثي)

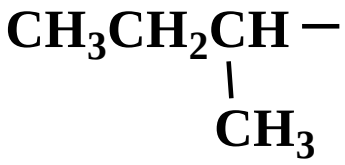


isopropyl

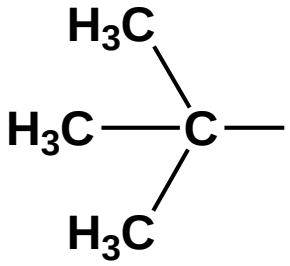
إيزو بروبيل



isobutyl



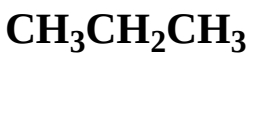
sec-butyl



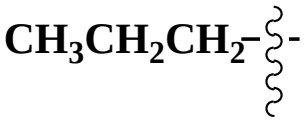
tert-butyl

إشتقاق مجموعات الألكيل من البروبان والبوتان
(إيزو، ثانوي، ثالثي)

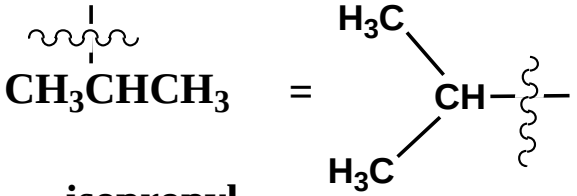
C_3



propane

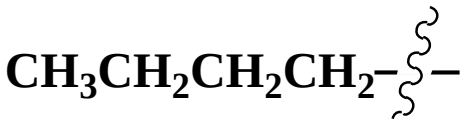


propyl



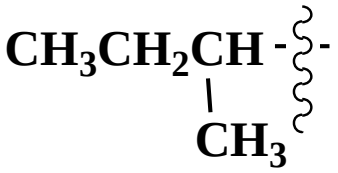
isopropyl

إيزو بروبيل



butyl

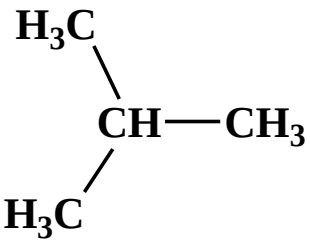
بوتيل



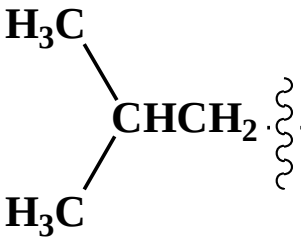
sec-butyl

ثانوي بوتيل

C_4

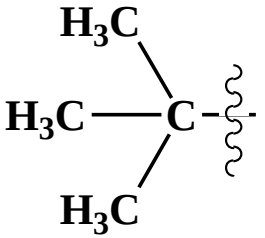


isobutane



isobutyl

إيزو بوتيل

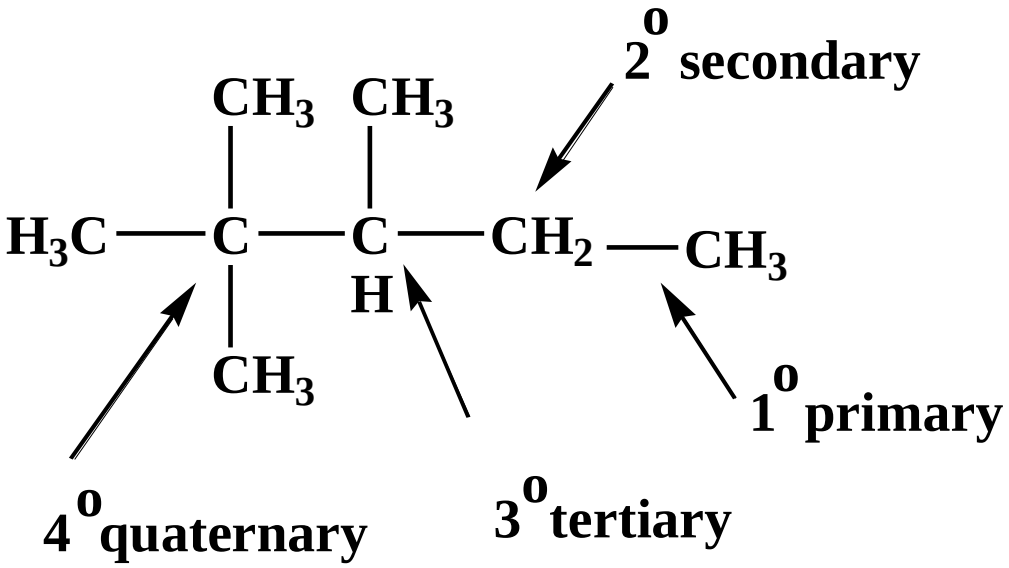


tert-butyl

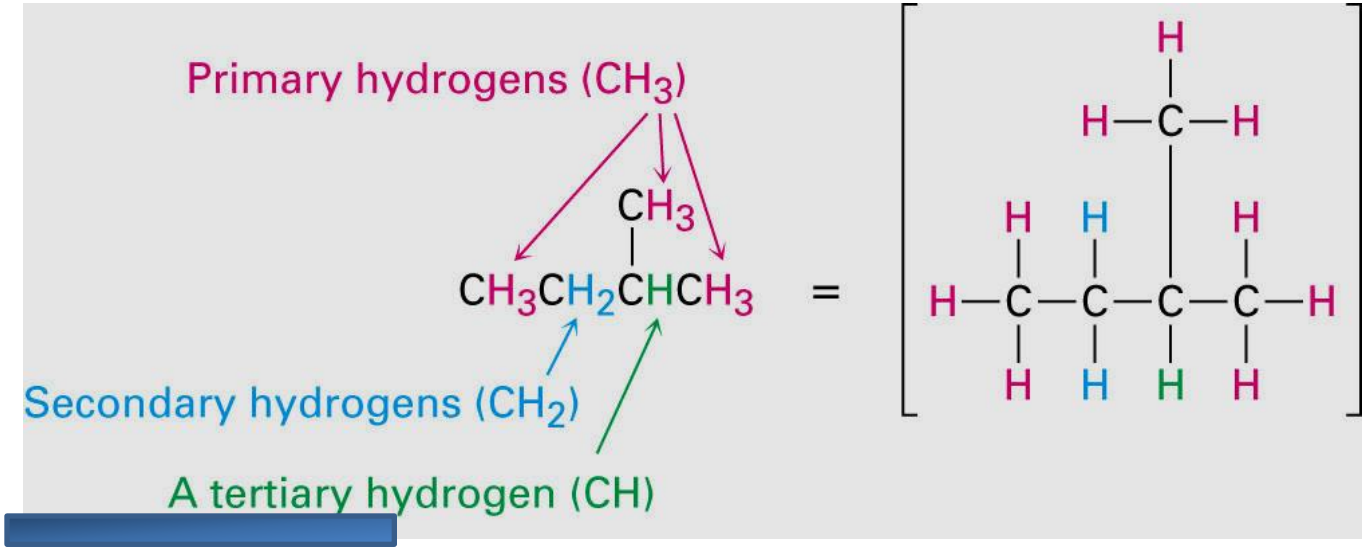
ثالثي بوتيل

أنماط ذرات الكربون وذرات الهيدروجين

كربون أولي | كربون ثانوي | كربون ثالثي | كربون رابعي



أنماط ذرات الهيدروجين

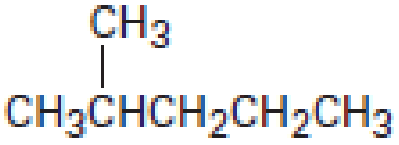


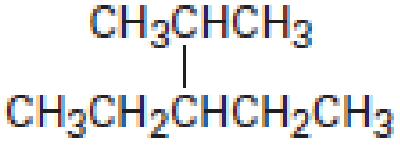
Problem 3.7

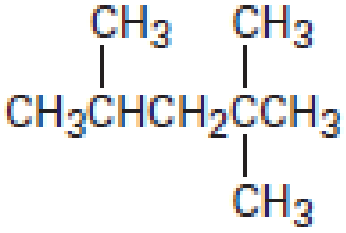
Draw the eight 5-carbon alkyl groups (pentyl isomers).

Problem 3.8

Identify the carbon atoms in the following molecules as primary, secondary, tertiary, or quaternary:

(a) 

(b) 

(c) 

Problem 3.9

Identify the hydrogen atoms on the compounds shown in Problem 3.8 as primary, secondary, or tertiary.

Problem 3.10

Draw structures of alkanes that meet the following descriptions:

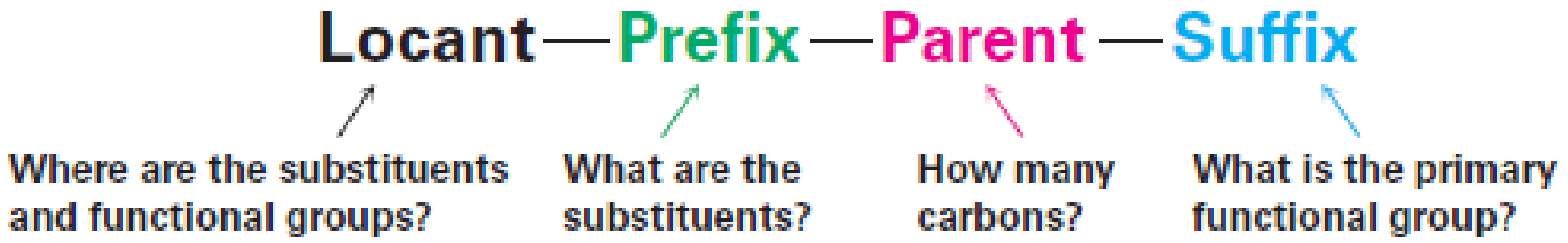
(a) An alkane with two tertiary carbons

(b) An alkane that contains an isopropyl group

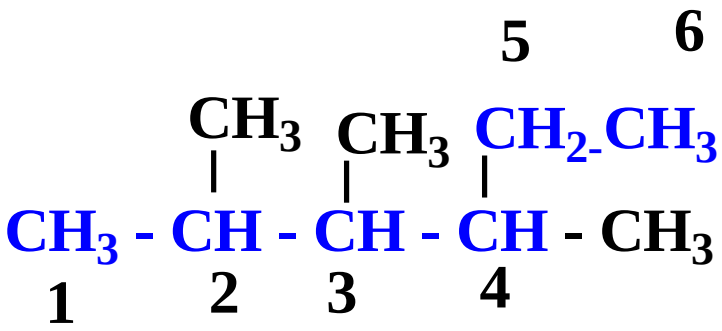
(c) An alkane that has one quaternary and one secondary carbon

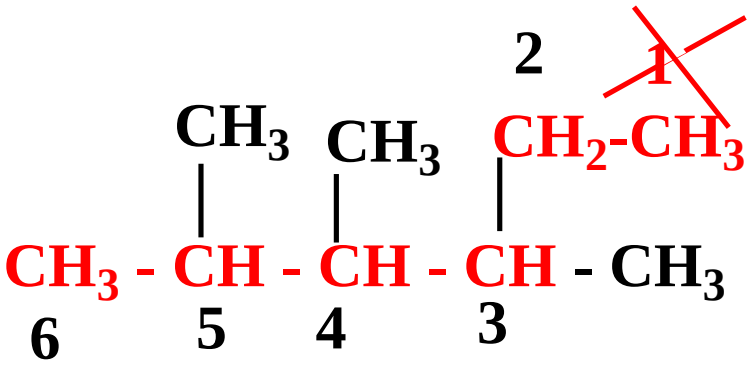
التسمية المنهجية للألكانات وفق قواعد الاتحاد الدولي

The chemical name typically has four parts in the IUPAC system of nomenclature: prefix, parent, locant, and suffix. The prefix identifies the various substituent groups in the molecule, the parent selects a main part of the molecule and tells how many carbon atoms are in that part, the locants give the positions of the functional groups and substituents, and the suffix identifies the primary functional group

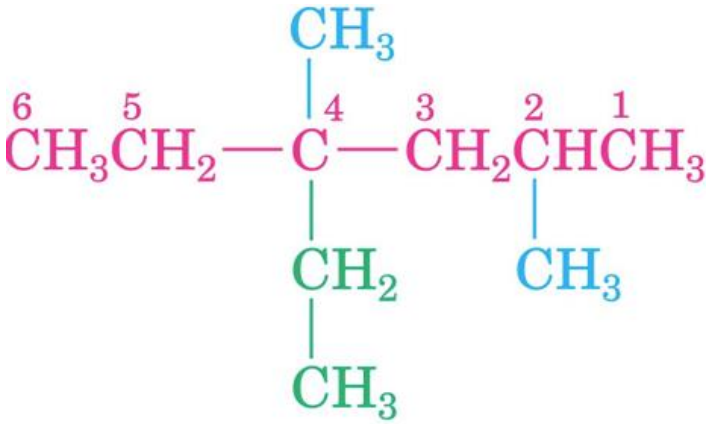


التسمية المنهجية للألكانات وفق قواعد الاتحاد الدولي

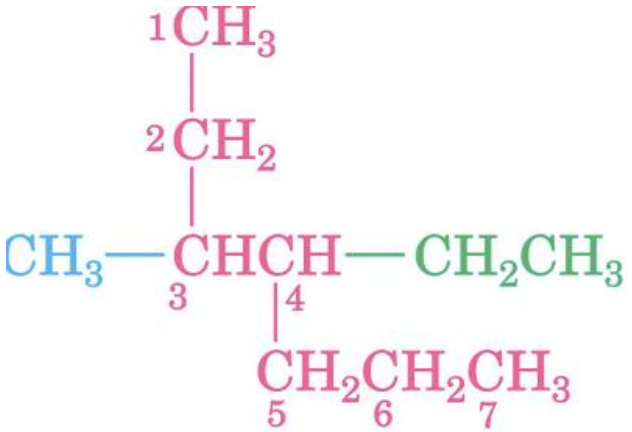




4،3،2 – ثلاثي متيل الهكسان



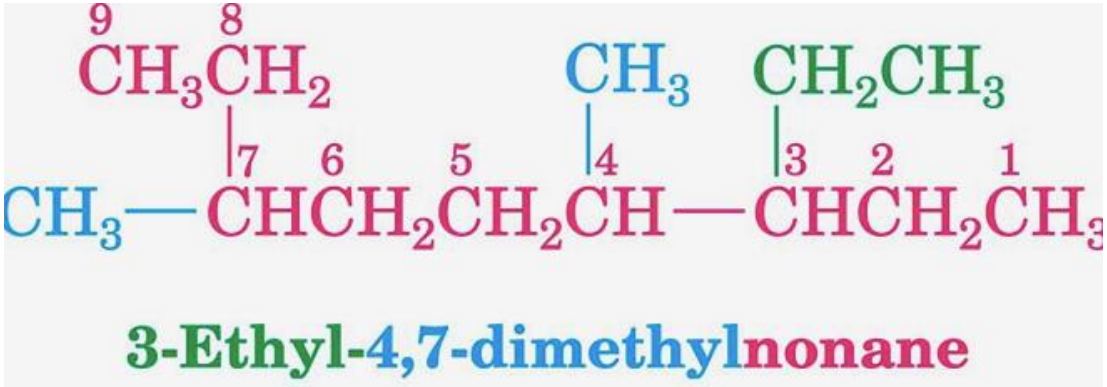
4-Ethyl-2,4-dimethylhexane



4-Ethyl-3-methylheptane

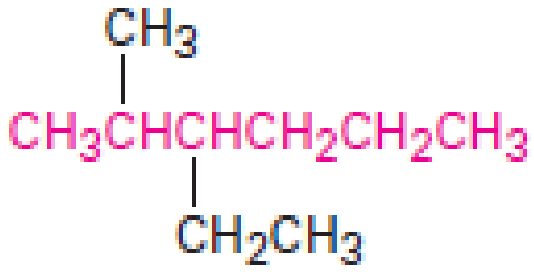
التسمية المنهجية للألكانات وفق قواعد الاتحاد الدولي

-في حال وجود خيارين متماثلين لترقيم السلسلة ،يبدأ الترقيم من الطرف الأقرب للمتبادل الأسبق هجائيا)



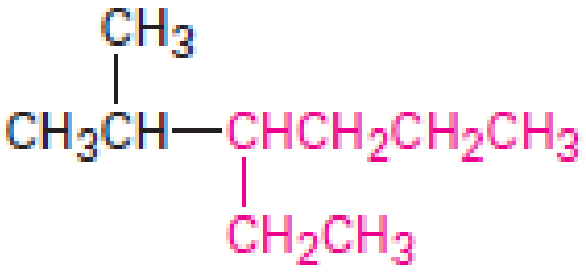
التسمية المنهجية للألكانات وفق قواعد الاتحاد الدولي

-في حال وجود سلسلتين مختلفتين ولهما الطول نفسه يتم اختيار السلسلة الأكثر تفرعا



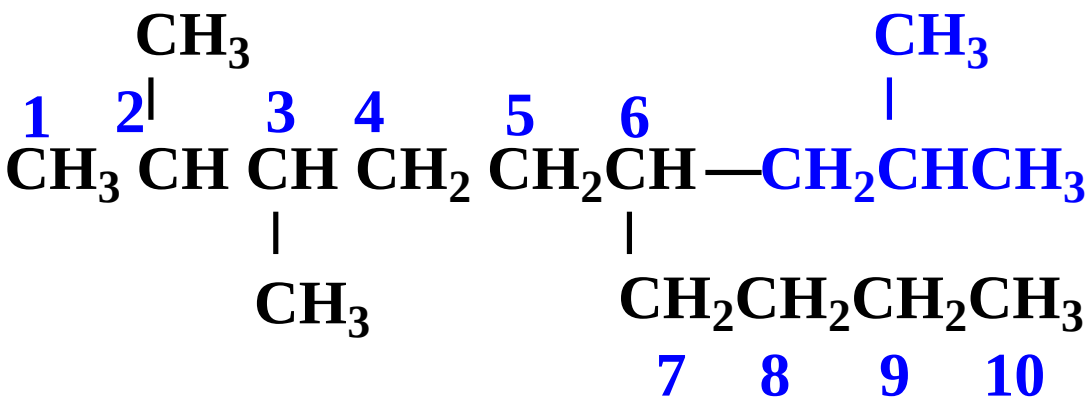
Named as a hexane with *two* substituents

NOT



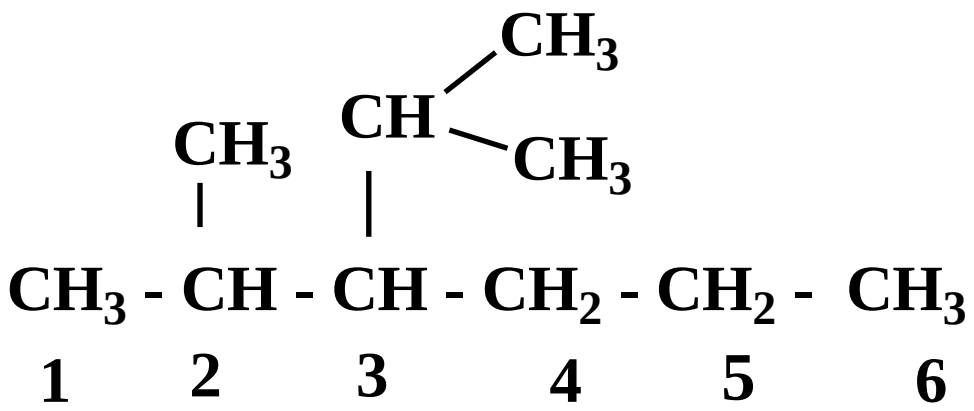
as a hexane with *one* substituent

التسمية المنهجية للألكانات وفق قواعد الاتحاد الدولي (متبادل مركب)



2,3-dimethyl-6-(2-methylpropyl)decane

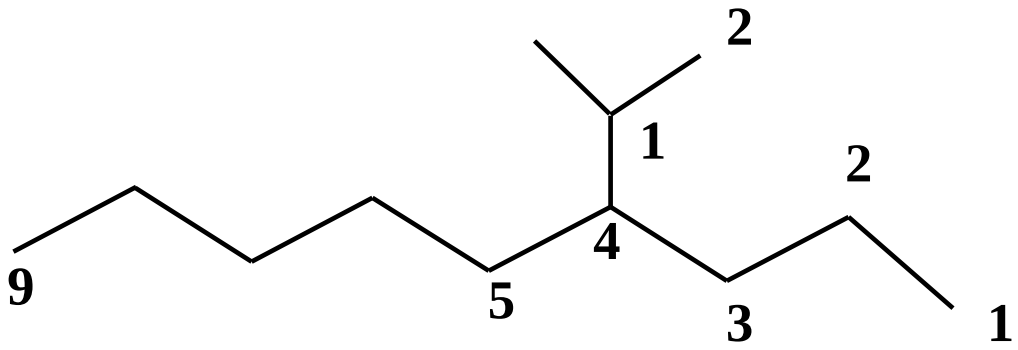
التسمية المنهجية للألكانات وفق قواعد الاتحاد الدولي



2-methyl-3-(1-methylethyl)hexane

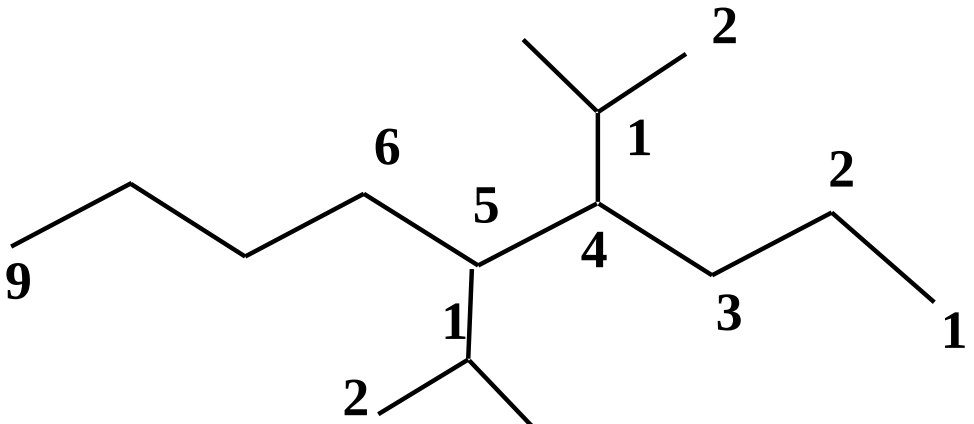
3-isopropyl - 2-methylhexane

التسمية المنهجية للألكانات وفق قواعد الاتحاد الدولي



4 -isopropylnonane

4- (1-methylethyl) nonane



٤ ، ٥- بيس (١- متيل اتيل) النونان

4,5- di-isopropylnonane

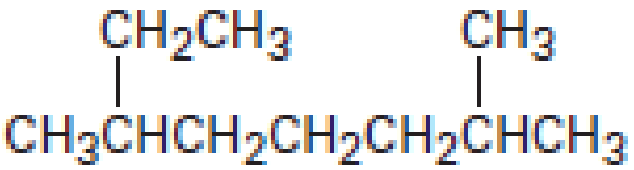
4,5-Bis- (1-methylethyl)nonane

3 = Tris

4 = Tetrakis

Naming Alkanes Worked Example 3.2

What is the IUPAC name of the following alkane?

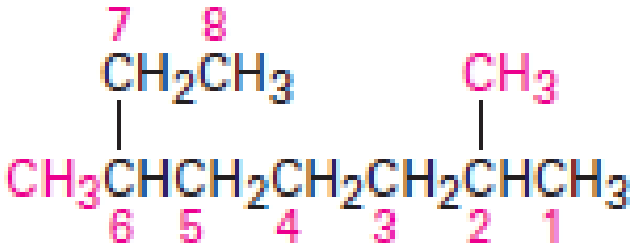


Strategy

Find the longest continuous carbon chain in the molecule, and use that as the parent name. This molecule has a chain of eight carbons—octane—with two methyl substituents.

Numbering from the end nearer the first methyl substituent indicates that the methyls are at C2 and C6

Solution



2,6-Dimethyloctane

Converting a Chemical Name into a Structure Worked Example 3.3

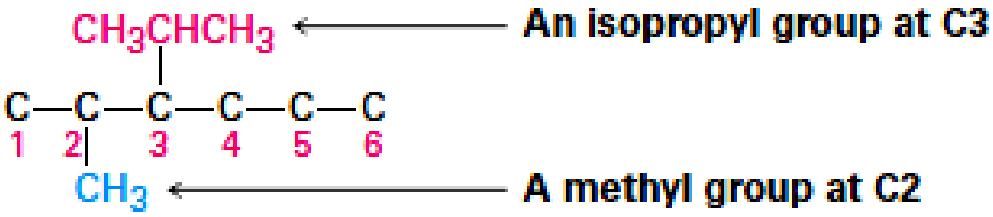
Draw the structure of 3-isopropyl-2-methylhexane.

Strategy

This is the reverse of Worked Example 3.2 and uses a reverse strategy. Look at the parent name (hexane), and draw its carbon structure.

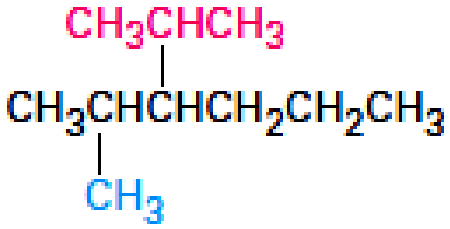
Hexane

Next, find the substituents (3-isopropyl and 2-methyl), and place them on the proper carbons.



Finally, add hydrogens to complete the structure.

Solution



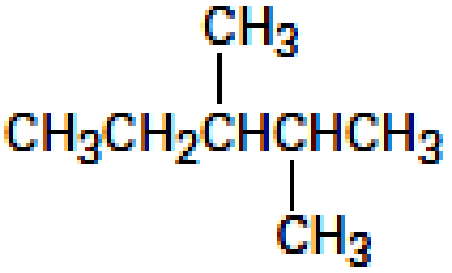
3-Isopropyl-2-methylhexane

Problem 3.11

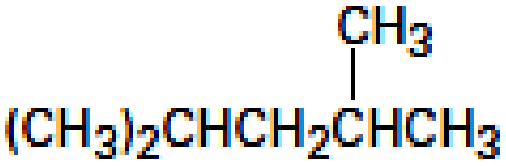
Give IUPAC names for the following compounds:

(a) The three isomers of C_5H_{12}

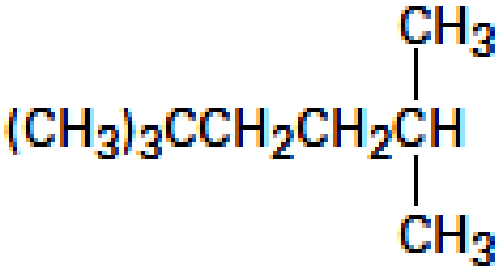
(b)



(c)



(d)



Problem 3.12

Draw structures corresponding to the following IUPAC names:

(a) 3,4-Dimethylnonane

(b) 3-Ethyl-4,4- dimethylheptane

(c) 2,2-Dimethyl-4-propyloctane

(d) 2,2,4-Trimethylpentane

Problem 3.13

Name the eight 5-carbon alkyl groups you drew in Problem 3.7.

Problem 3.14

الخواص الكيميائية للألكانات Chemical Properties

- Chemically inert ,called paraffins.
- Alkanes do, however, react with oxygen, halogens, and a few other substances under appropriate conditions
- Used as a fuel (engine, furnace): reaction with oxygen during combustion produces CO_2, water and heat

- تدعى الألكانات في بعض الأحيان بالبارافينات وهي كلمة مشتقة من اللاتينية وتعني قليلة الفعالية.
- الألكانات هي مركبات خاملة كيميائيا تجاه معظم الكواشف الكيميائية
- تتفاعل الألكانات مع الأوكسجين والهالوجينات وبعض المركبات الأخرى في شروط ملائمة
- يتم التفاعل مع الأوكسجين خلال عملية الاحتراق في المحركات أو في الأفران عند استخدامها كوقود حييث يتشكل الماء وغاز ثنائي أوكسيد الكربون مع تحرر كمية كبيرة من الحرارة

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O + 890\ kJ/mol\ (213\ kcal/mol)$$

الخواص الكيميائية للألكانات Chemical Properties

•The reaction of an alkane with Cl_2 occurs when a mixture of the two is irradiated with ultraviolet light (denoted *hν where ν is the Greek letter nu). Depending* on the relative amounts of the two reactants and on the time allowed, a sequential substitution of the alkane hydrogen atoms by chlorine occurs, leading to a mixture of chlorinated products. Methane, for instance, reacts with Cl_2 to yield a mixture of CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4.

• تتفاعل الألكان مع الكلور عند تعريضها للأشعة فوق البنفسجية بحصول تفاعل استبدال متسلسل مؤديا إلى تشكل مزيج من المنتجات المكلورة ويتوقف ذلك على الكميات النسبية لكلا المتفاعلين وزمن التعرض

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

$$CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 + HCl$$

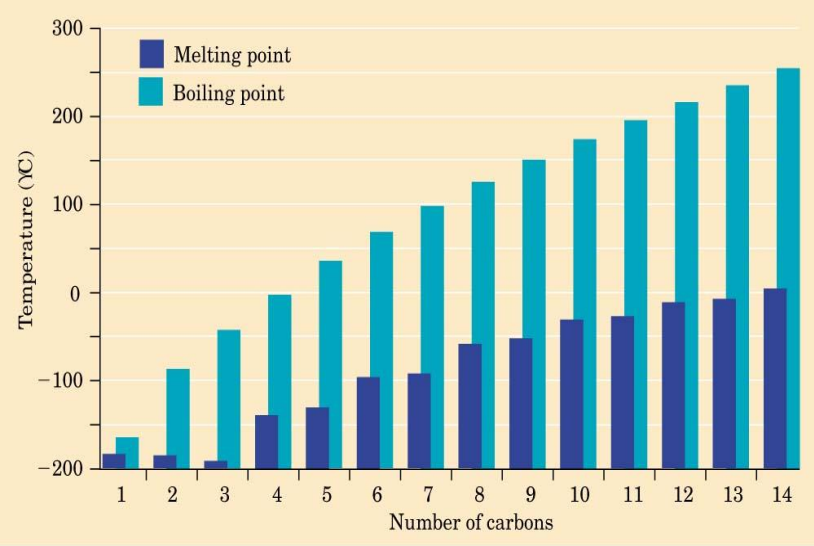
$$CHCl_3 \xrightarrow{Cl_2} CCl_4 + HCl$$

Physical Properties الخواص الفيزيائية للألكانات

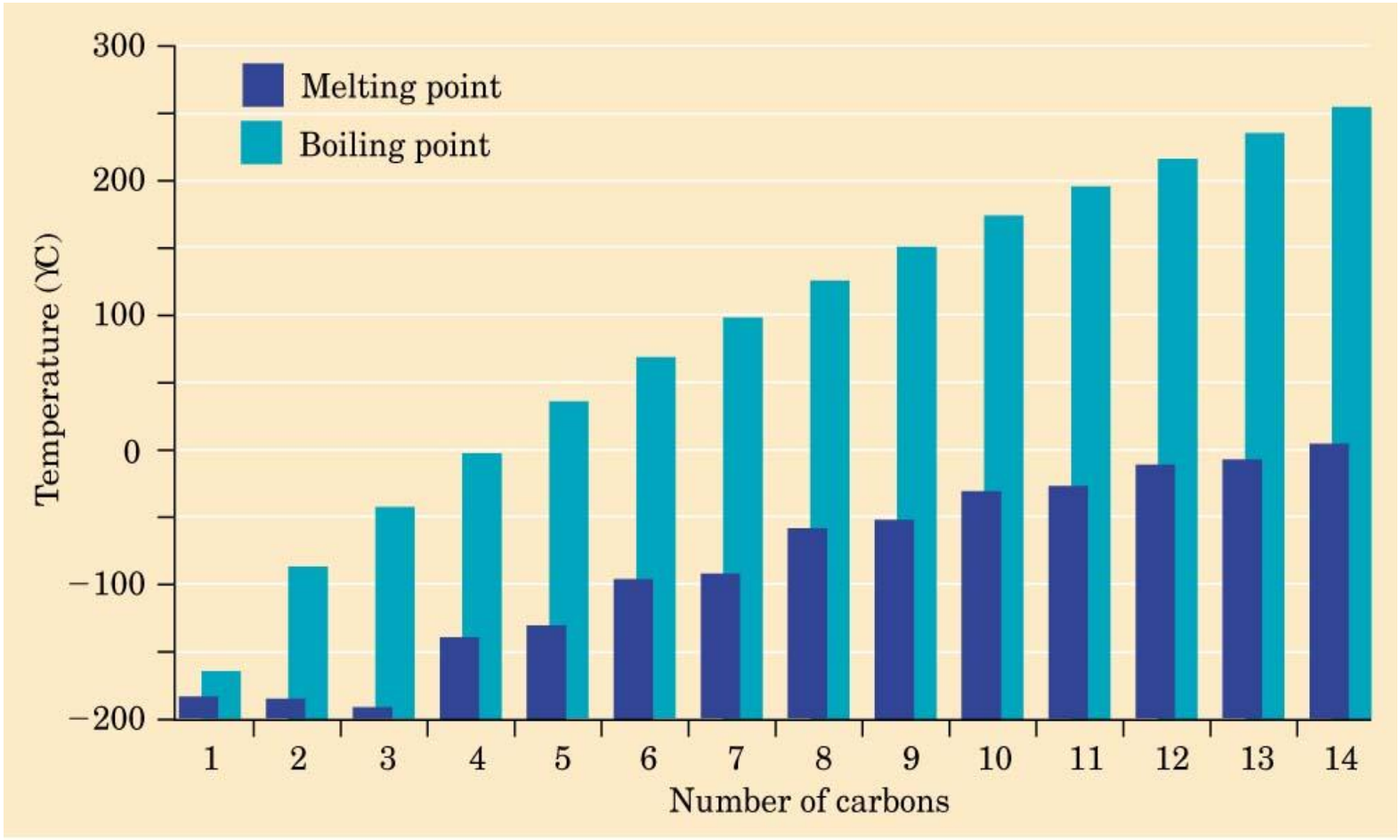
Alkanes show regular increases in both boiling point and melting point as molecular weight increases (Figure 3.4), an effect due to the presence of weak dispersion forces between molecules (Section 2.12). Only when sufficient energy is applied to overcome these forces does the solid melt or liquid boil. As you might expect, dispersion forces increase as molecule size increases, accounting for the higher melting and boiling points of larger alkanes.

Another effect seen in alkanes is that increased branching lowers an alkane's boiling point. Thus, pentane has no branches and boils at 36.1 °C, isopentane (2-methylbutane) has one branch and boils at 27.85 °C, and neopentane (2,2-dimethylpropane) has two branches and boils at 9.5 °C

- تزداد درجات غليان الألكانات ودرجات انصهارها بشكل منتظم مع ازدياد الكتلة الجزيئية وهذا ناتج عن قوى التبعثر بين الجزيئات التي تزداد مع ازدياد حجم الجزيء . ومن جهة أخرى تنخفض هذه الدرجات مع ازدياد تفرع السلسلة



Physical Properties الخواص الفيزيائية للألكانات



الكيمياء الفراغية– الهيئات الفراغية
Stereochemistry–conformations

الكيمياء الفراغية :تمثيل ثلاثي الأبعاد للجزيئات

تنتج الهيئات الفراغية من الدوران الحر حول الرابطة البسيطة سيغما وتسمى متصاوغات هيئاتية أو مشاكيل جمع مشكال conformer

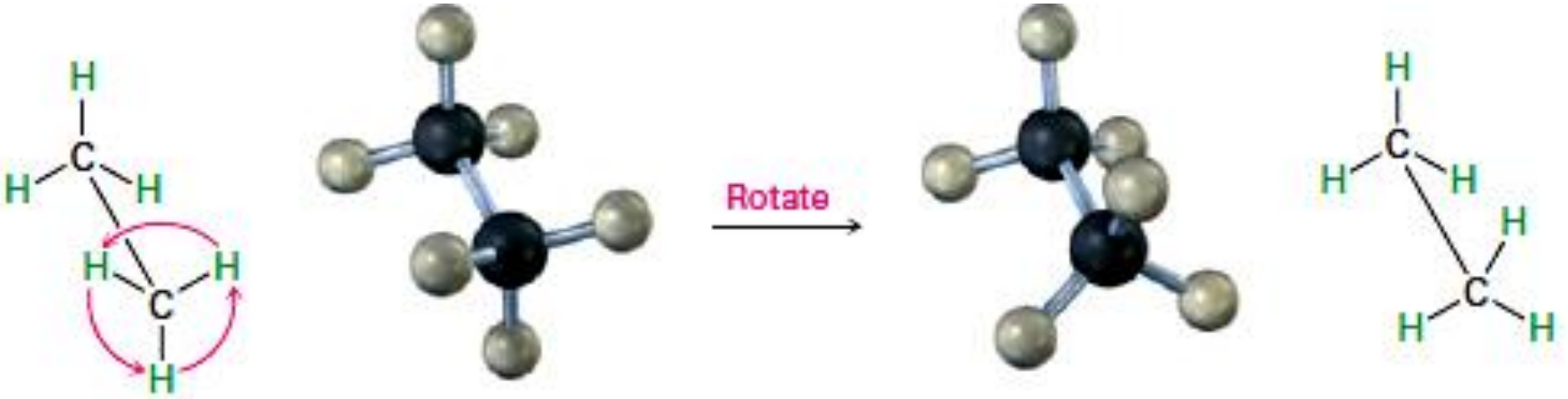
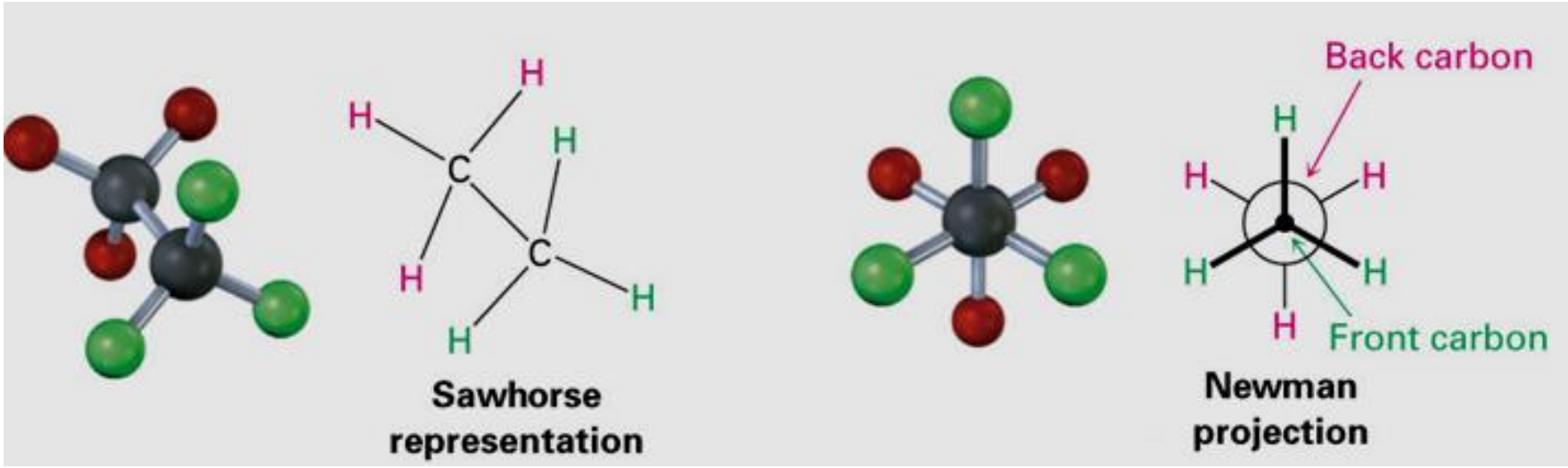


Figure 3.5 Rotation occurs around the carbon–carbon single bond in ethane because of *s bond cylindrical* symmetry

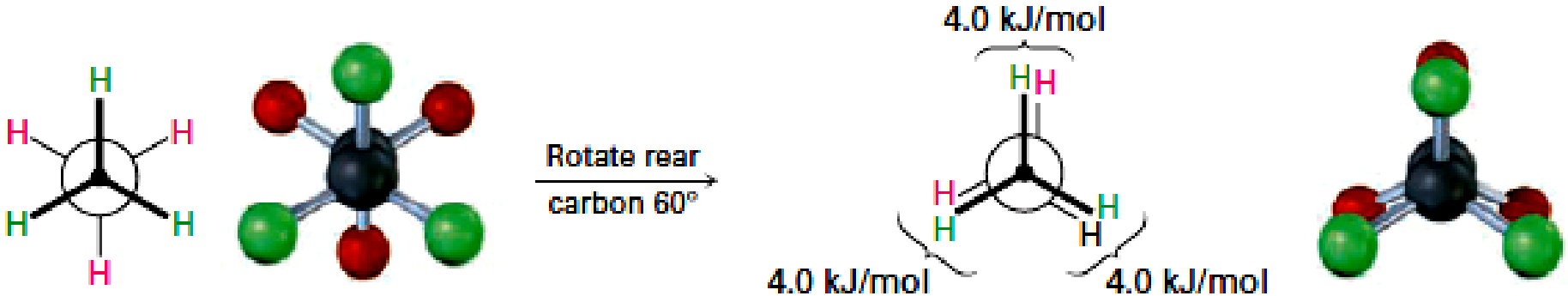
تمثيل الهيئات الفراغية للإيتان



تمثيل حصان النشر

تمثيل إسقاط نيومان

الهيئة المكسوفة والمتباعدة للإتان (الإجهاد الالتوائي أو إجهاد الفتل)



Ethane—staggered conformation

متباعدة (أكثر ثباتا)

Ethane—eclipsed conformation

مكسوفة (أقل ثباتا)

total torsional strain: 12KJ/mol

مخطط الطاقة

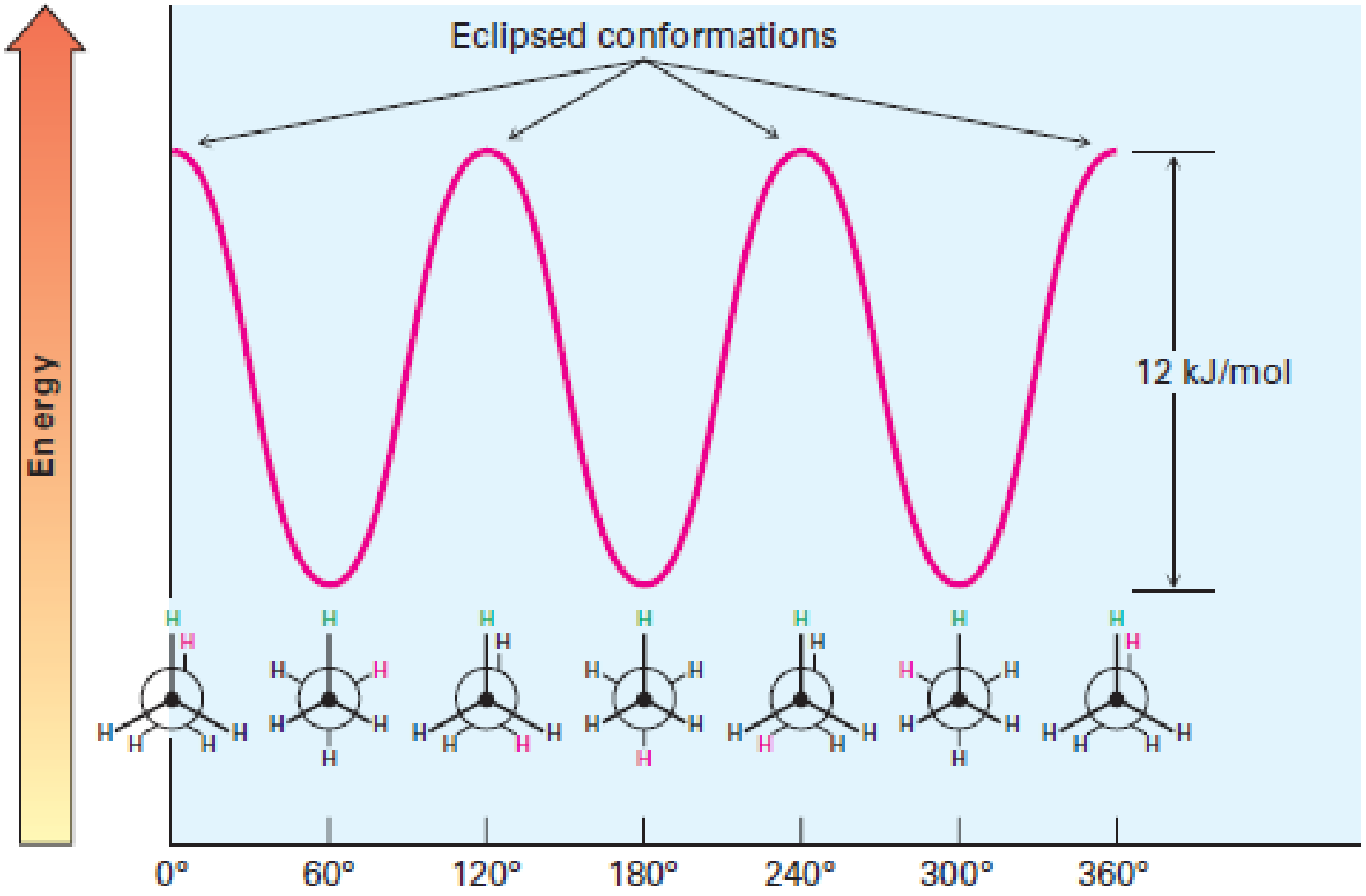
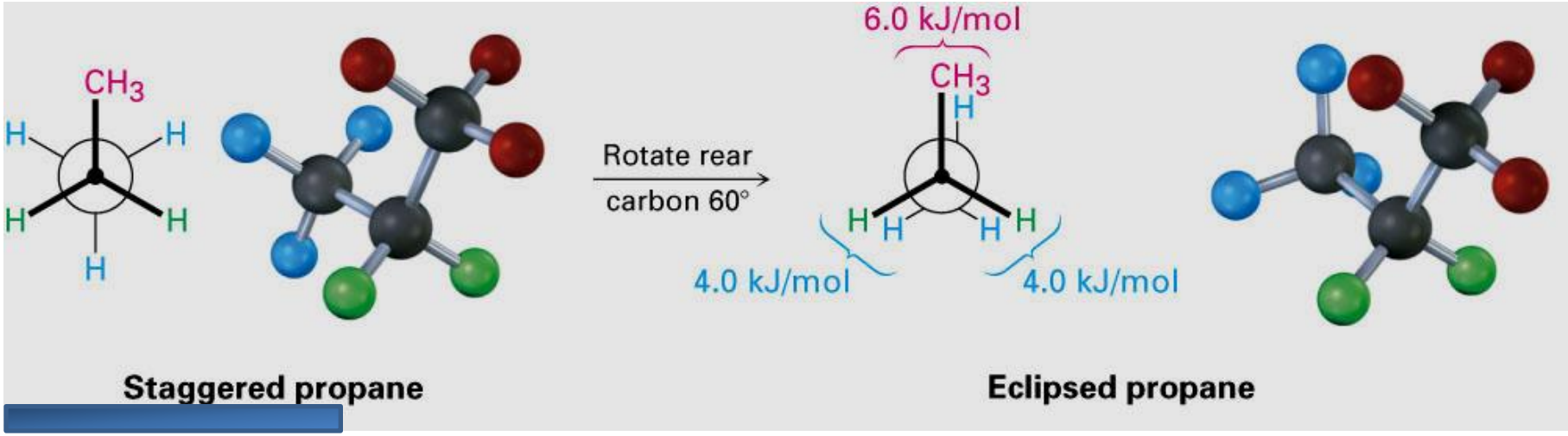


Figure 3.7 A graph of potential energy versus bond rotation in ethane. The staggered conformations are 12 kJ/mol lower in energy than the eclipsed conformations.

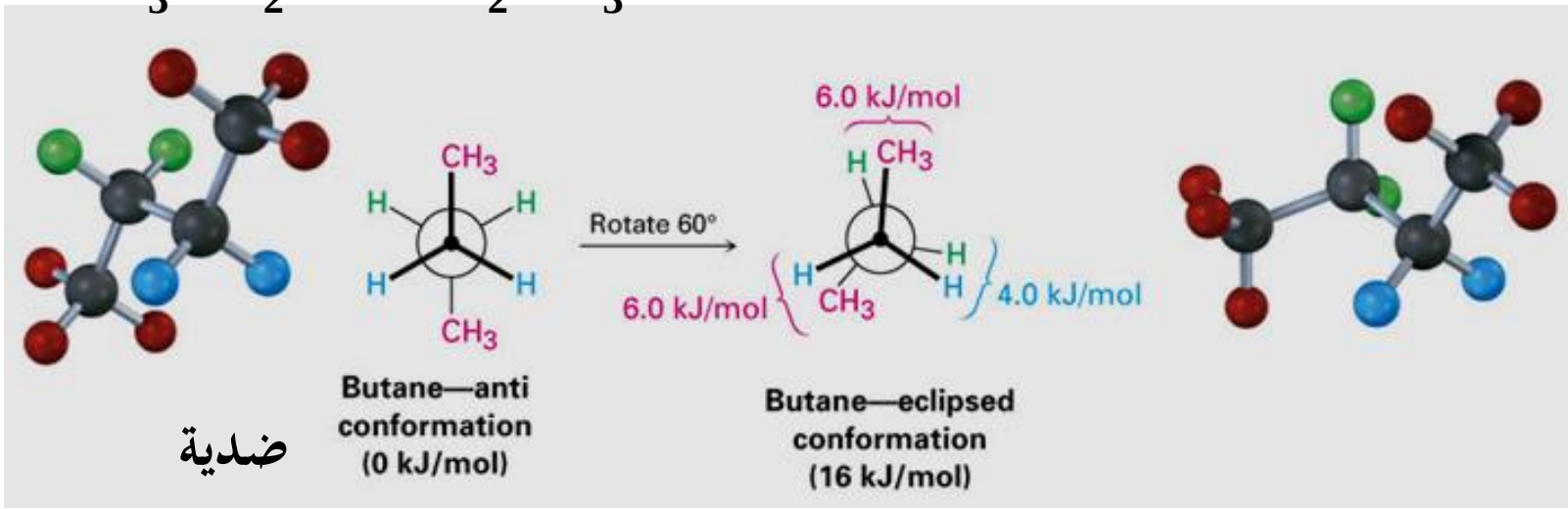
الهيئة المكسوفة والمتباعدة في البروبان
Torsional strain (الإجهاد الالتوائي)

$CH_3—CH_2CH_3$

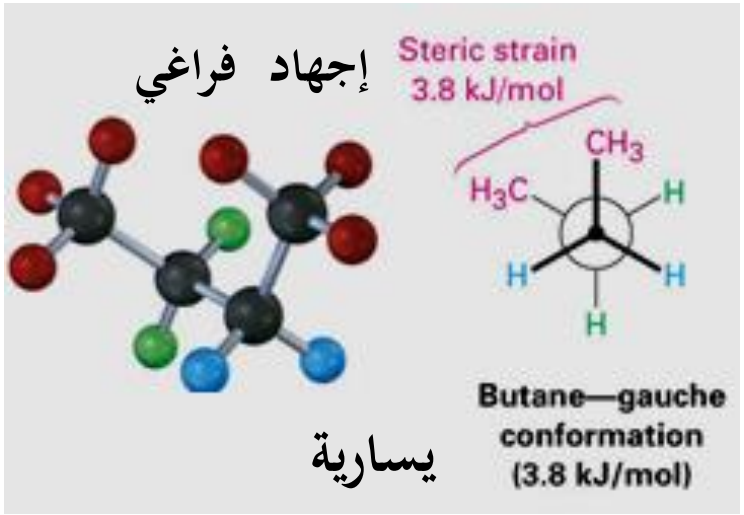


الهيئات في البوتان: الهيئة الضدية والهيئة اليسارية(الإجهاد الفراغي)

$CH_3\overset{3}{C}H_2-\overset{2}{C}H_2CH_3$

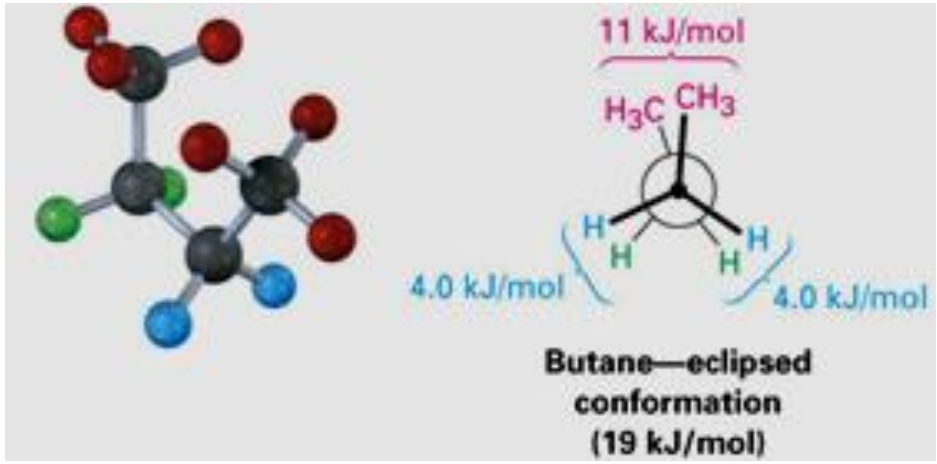


ضدية

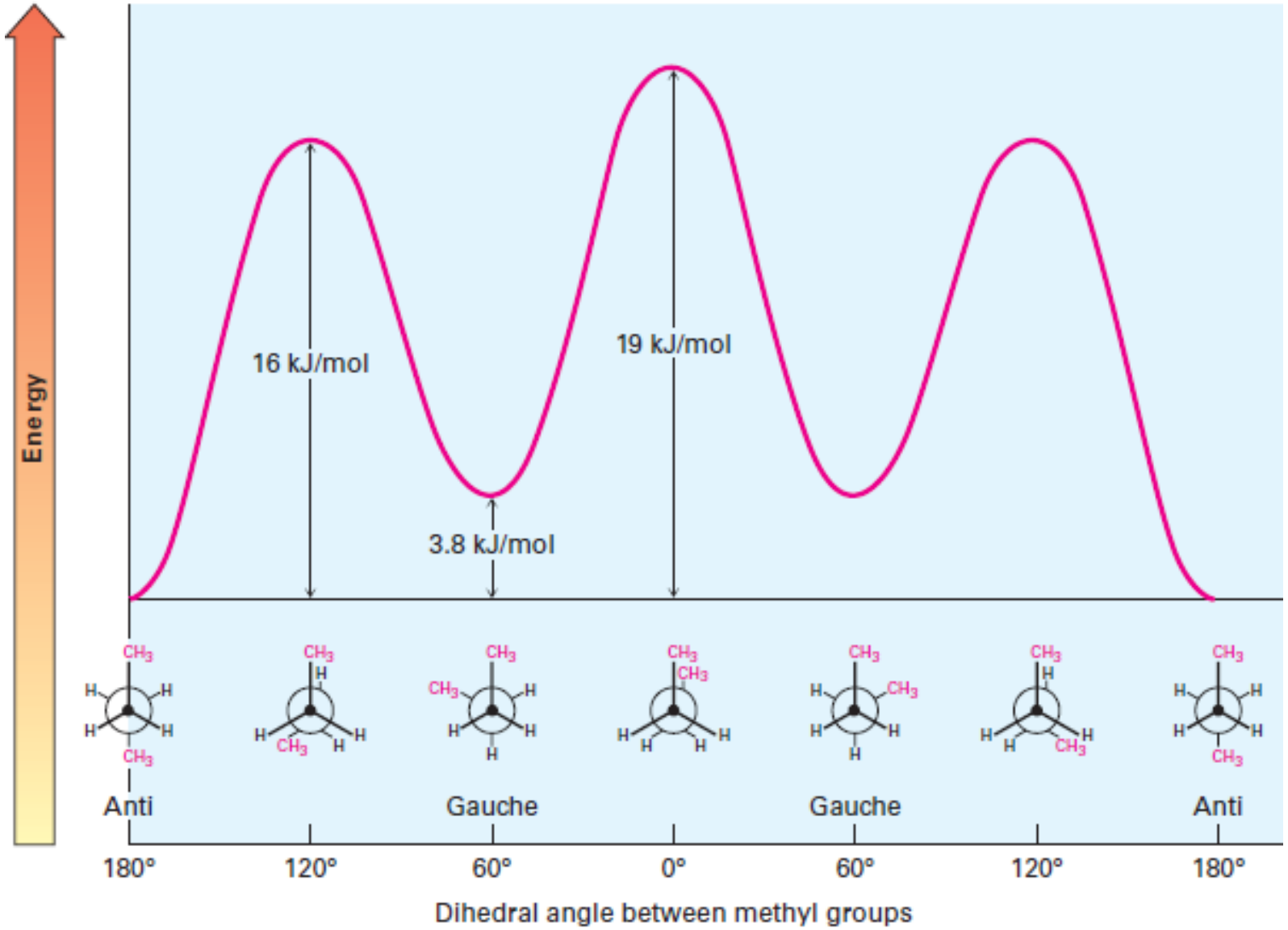


إجهاد فراغي

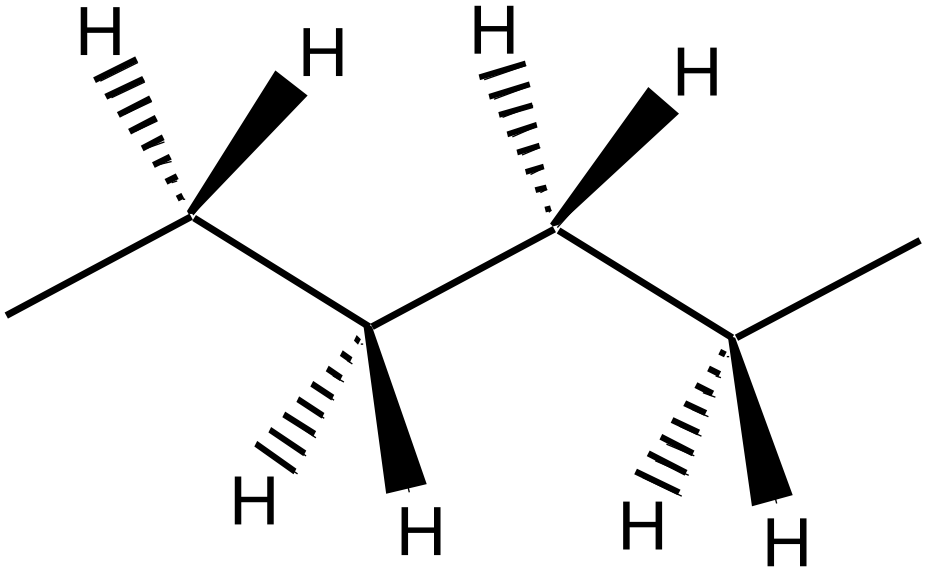
يسارية



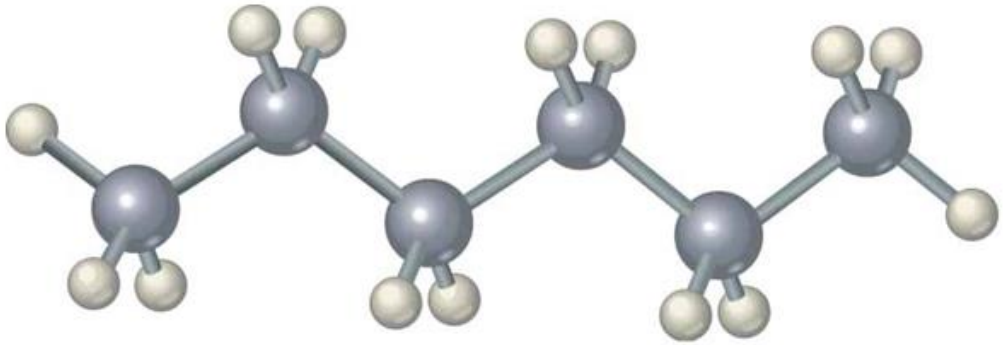
مخطط الطاقة


Energy
16 kJ/mol
19 kJ/mol
3.8 kJ/mol
Anti
Gauche
Gauche
Anti
180°
120°
60°
0°
60°
120°
180°
Dihedral angle between methyl groups

تمثيل السلسلة الكربونية المستقيمة بالهيئة الأكثر ثباتا



الهيئة المتباعدة بشكل Zigzag



Hexane

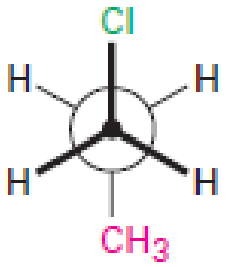
Drawing Newman Projections Worked Example 3.4

Sight along the C1 – C2 bond of 1-chloropropane, and draw Newman projections of the most stable and least stable conformations.

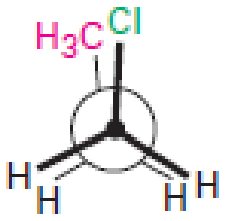
Strategy

The most stable conformation of a substituted alkane is generally a staggered one in which large groups have an anti relationship. The least stable conformation is generally an eclipsed one in which large groups are as close as possible.

Solution



Most stable (staggered)



Least stable (eclipsed)

Problem 3.15

Make a graph of potential energy versus angle of bond rotation for propane, and assign values to the energy maxima

Problem 3.16

Sight along the C2 –C1 bond, 2-methylpropane (isobutane) and (a) draw a Newman projection of the most stable conformation.

(b) draw a Newman projection of the least stable conformation.

(c) make a graph of energy versus angle of rotation around the C2 –C1 bond.

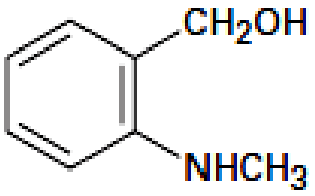
(d) Since an H ⟷ H eclipsing interaction costs 4.0 kJ/mol and an H ⟷ CH3 eclipsing interaction costs 6.0 kJ/mol, assign relative values to the maxima and minima in your graph.

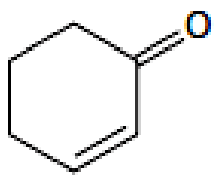
Gazoline

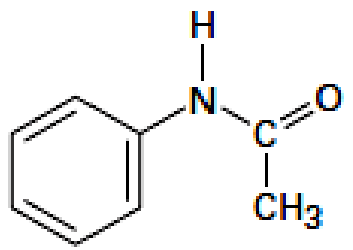
Additional Problems

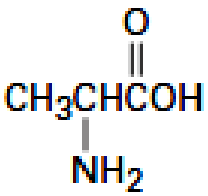
Functional Groups

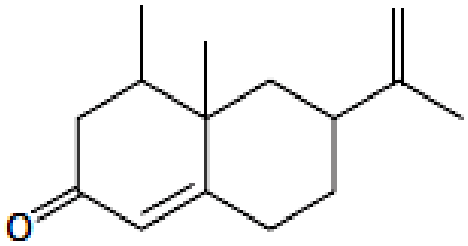
3.22 Locate and identify the functional groups in the following molecules

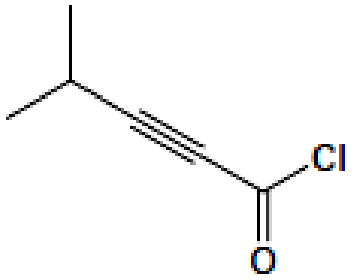
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

Additional Problems

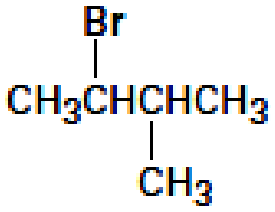
3.25 Predict the hybridization of the carbon atom in each of the following functional groups:

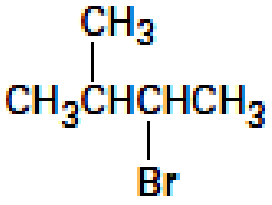
(a) Ketone (b) Nitrile (c) Carboxylic acid

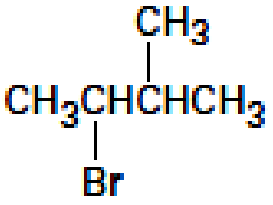
Additional Problems

3.29 In each of the following sets, which structures represent the same compound and which represent different compounds?

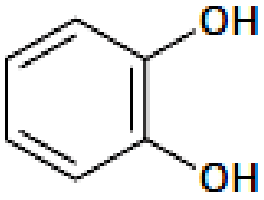
(a)

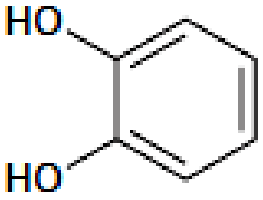


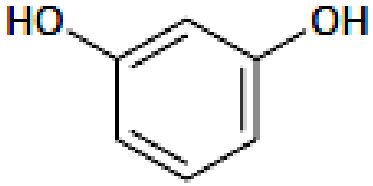




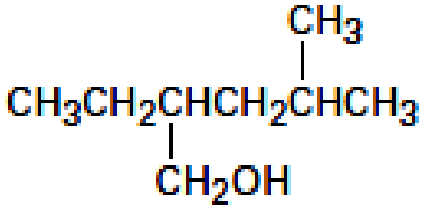
(b)

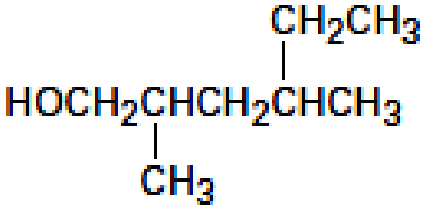


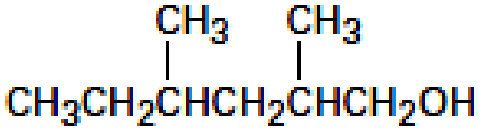




(c)







Additional Problems

3.24 Propose structures for the following:

(a) A ketone, C_4H_8O
(b) A nitrile, C_5H_9N
(c) A dialdehyde, $C_4H_6O_2$
(d) A bromoalkene, $C_6H_{11}Br$
(e) An alkane, C_6H_{14}
(f) A *cyclic* saturated hydrocarbon, C_6H_{12}
(g) A diene (dialkene), C_5H_8
(h) A keto alkene, C_5H_8O