Boiling Points of Some Isomers of Alkanes of similar Molecular Mass

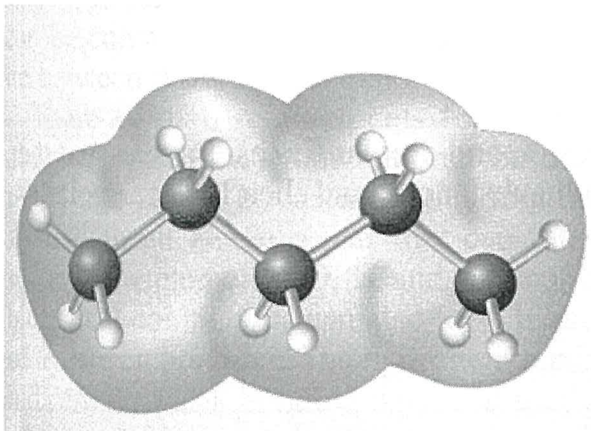
What forces cause substances like octane, carbon dioxide, the halogens and even the noble gases to condense and solidify? An attractive force must be acting between these non-polar molecules and atoms, or they would remain gaseous under any conditions. The intermolecular force primarily responsible for the condensed states of non-polar molecules is the **dispersion force**, or **London force** (after Fritz London).

Dispersion forces are very weak and are caused by momentary oscillations of electron density. Even when localized to bonding or lone pairs, electrons are in constant motion throughout their prescribed regions and we often consider them as “clouds” of negative charge. A nearby electric field can distort an electron cloud, drawing electron density toward a positive charge or repelling it from a negative one. In effect, the field *induces* a distortion in the electron cloud. For a non-polar molecule, this distortion results in a *temporary* dipole moment. Thus dispersion forces are *induced dipole-induced dipole forces.* This process occurs throughout the sample and, at low enough temperatures, keeps the particles together. Dispersion forces increase in strength with the number of electrons because larger electron clouds are more polarisable than smaller electron clouds. Dispersion forces are the weakest of the *intermolecular forces* and affect all molecules.

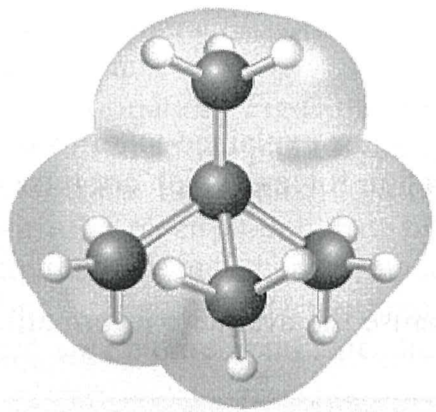
As alkanes get longer their electron clouds get larger and more polarisable, making the dispersion forces larger (stronger) and raising the boiling point (butane -0.5 ^{0}C, pentane 36.1 ^{0}C, hexane 68.7^{0}C, heptane 98.4 ^{0}C and octane 125.7 ^{0}C).

For molecules with comparable numbers of electrons, the shape of the molecule makes an important secondary contribution to the magnitude (size) of the dispersion forces.

The isomers pentane and 2,2-dimethylpropane (C_5H_{12}) have a total of 42 electrons each. 2,2-dimethylpropane is more compact than pentane resulting in its electron cloud being less polarisable than the electron cloud of pentane, hence 2,2-dimethylpropane has smaller dispersion forces accounting for a boiling point 9.5 ^{0}C while that of pentane is 36.1 ^{0}C. Less energy is required to break smaller (weaker) dispersion forces than is required to break larger (stronger) dispersion forces.



pentane, C_5H_{12}



2,2-dimethylpropane, C_5H_{12}

Compound	Formula	Formula mass	Boiling point ^0C	Comments
Isomers of butane (4 carbon alkanes)				
Butane	C_4H_{10}	58.1	- 0.5	Largest dispersion forces due to the least compact nature of the isomer.
2-Methyl propane	C_4H_{10}	58.1	- 11.7	Smaller dispersion forces due to the more compact nature of the isomer.
Isomers of pentane (5 carbon alkanes)				
Pentane	C_5H_{12}	72.1	36.1	Largest dispersion forces due to the least compact nature of the isomer.
2-Methyl butane	C_5H_{12}	72.1	27.9	Smaller dispersion forces due to the more compact nature of the isomer.
2,2-Dimethyl propane	C_5H_{12}	72.1	9.5	Smallest dispersion forces due to the most compact nature of the isomer.
Isomers of hexane (6 carbon alkanes)				
Hexane	C_6H_{14}	86.2	68.7	Largest dispersion forces due to the least compact nature of the isomer.
2-Methyl pentane	C_6H_{14}	86.2	60.3	Smaller dispersion forces due to the more compact nature of the isomer.
3-Methyl pentane	C_6H_{14}	86.2	63.3	Smaller dispersion forces due to the more compact nature of the isomer.
2,2-Dimethyl butane	C_6H_{14}	86.2	49.7	Smallest dispersion forces due to the most compact nature of the isomer.
2,3-Dimethyl butane	C_6H_{14}	86.2	58.0	Smaller dispersion forces due to the more compact nature of the isomer.

CARBON CHEMISTRY

ISOMERISM: Compounds possessing the same composition and the same molecular mass, but differing in at least one of their physical or chemical properties, are said to be isomeric and each is an isomer of the others.

STRUCTURAL ISOMERISM:

Chain - due to different arrangements of e.g. carbon atoms in the molecule

Number of Alkane Isomers				
Formula	**Number of isomers**		**Formula**	**Number of isomers**
C_6H_{14}	5		$C_{10}H_{22}$	75
C_7H_{16}	9		$C_{15}H_{32}$	4,347
C_8H_{18}	18		$C_{20}H_{42}$	366,319
C_9H_{20}	35		$C_{30}H_{62}$	4,111,846,763

Position - due to differences in the position of some group or atom in carbon chain or ring.
Functional group - due to differences in type of compound as in CH_3OCH_3 (ether) and CH_3CH_2OH (alcohol)

GEOMETRICAL or CIS - TRANS:

Due to different arrangements of dissimilar atoms or groups attached to two carbon atoms attached by a double bond. The presence of the double bond restricts the free rotation of the C atoms joined by it, and permits the existence of two forms.

fumaric acid

H — C — COOH
‖
HOOC — C — H

maleic acid

H — C — COOH
‖
H — C — COOH

PROBLEMS ON ISOMERISM

1. Draw the structural formulae for all the $C_2H_3Cl_3$ compounds and assign them IUPAC or systematic names.

2. Draw the structural formulae of the isomers of chlorobutane and assign them IUPAC or systematic names.

3. Give the empirical formula, the molecular formula, and draw the structural formulae of the isomers of butene and assign them IUPAC or systematic names.

4. Draw the structural formulae and name the isomers of $C_3H_6Cl_2$.

5. Draw the structure of a cyclic saturated hydrocarbon. Is the formula of the cyclic compound typical of an alkane? Are the chemical properties of the cyclic compound typical of an alkane?

6. Draw the structures of, and name all possible isomers of, C_5H_{12}.

7. Draw the structure of 1-pentene.
Draw the structures of the isomers of 1-pentene and name each one of them.

8. For each of the following compounds

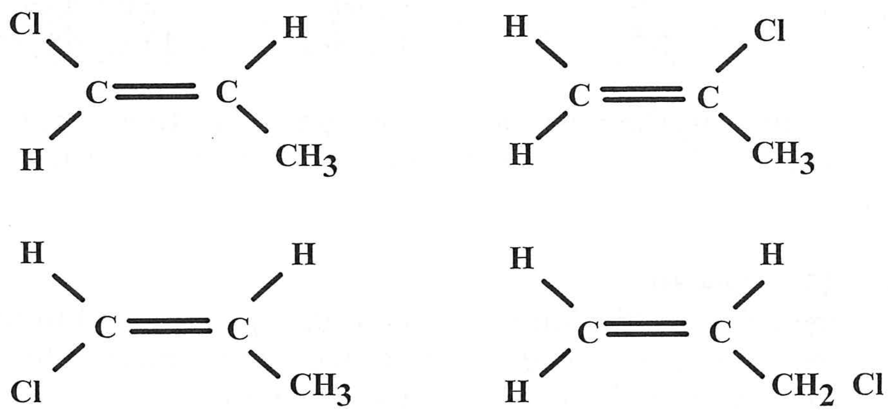
1. draw its structural formula
2. write the molecular formula

A. 2-chloropentane
B. 1-chloro-2-methylbutane
C. 1-chloro-3-methylbutane
D. 1-chloro-2,2-dimethylpropane
E. 3-chloropentane
F. 2-chloro-2-methylbutane

How are all the compounds related ?

9. Consider the following structures

(1) (2)

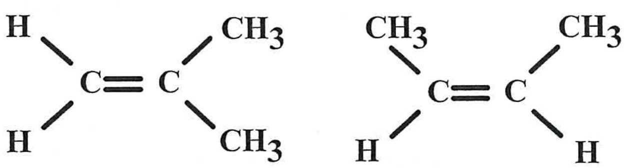


(3) (4)

Which are isomers ?

A. 1 and 2 only
B. 1, 2 and 3 only
C. 2, 3 and 4 only
D. 1 and 3 only
E. 1, 2, 3 and 4

10. Two organic structures shown here represent :



A. the same compound C_4H_8
B. a pair of geometric isomers
C. a pair of cis - trans isomers
D. structural isomers
E. answers B and C are both correct.

11. Which of the following structures is NOT an isomer of the other three?

A. 2-methyl-2-pentene
B. cyclohexane
C. 1-hexene
D. hexane

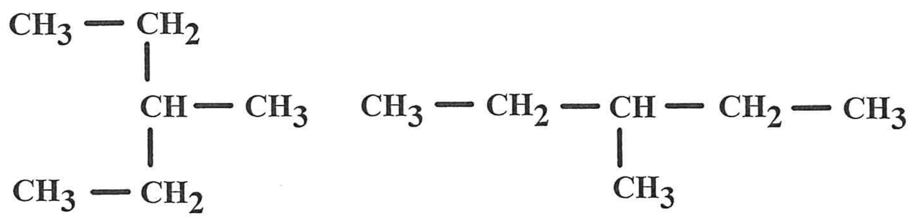
12. Which of the following compounds exhibit(s) geometrical isomerism ?

I	CH3CH=CHCH3	II	(CH3)2C=CH2
III	(CH3)2C=C(CH3)2	IV	CH3CH=C(CH3)CH2CH3

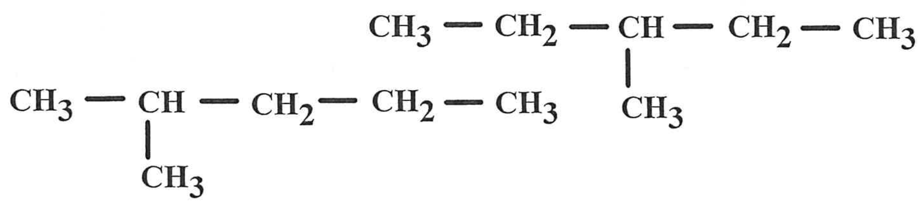
A. I, II and III only B. I and III only C. II and IV only
D. IV only E. I and IV only

13. Do the following pairs of structures represent isomers or are they just different ways of drawing the same molecule? Name the compounds below.

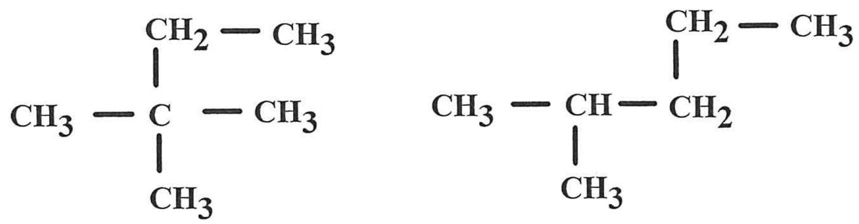
A.



B.



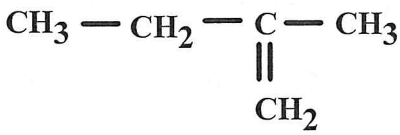
C.

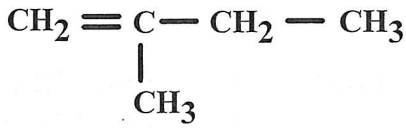


Draw the structures of, and name all possible isomers of, C_5H_8.

15. Do the following pairs of structures represent isomers or are they just different ways of drawing the same molecule? Name the compounds below.

A.



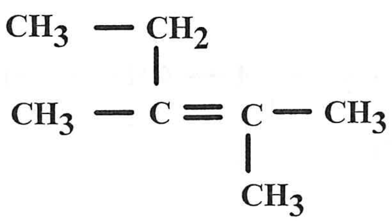


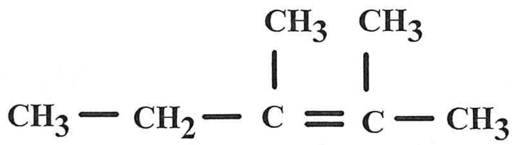
B.

$$CH_3-CH_2-CH_2-C\equiv C-CH_3$$

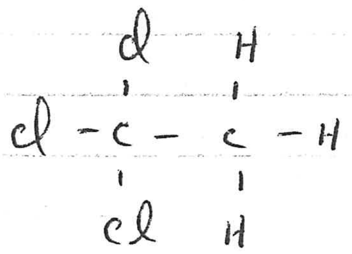
$$CH_3-CH_2-C\equiv C-CH_3$$

C.

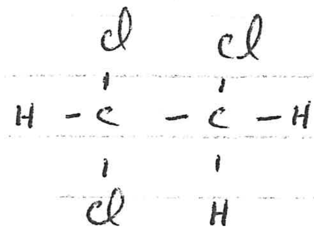




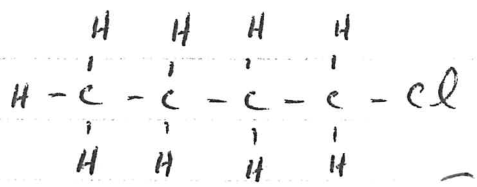
Answers to Problems on Isomerism

1. 

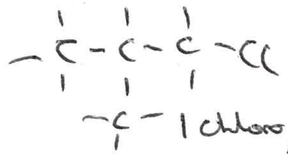
1,1,1 TRICHLOROETHANE



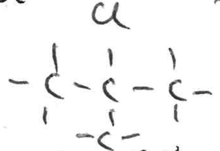
1,1,2 TRICHLOROETHANE

2. 

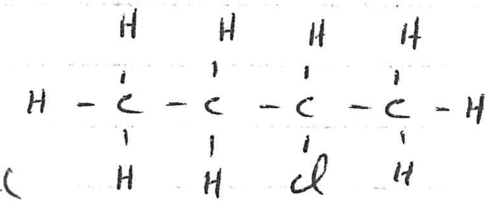
1-CHLOROBUTANE



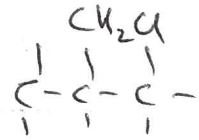
1 chloro, 2 methyl propane



2 chloro, 2 methyl propane

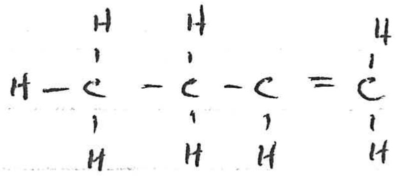


2 - CHLOROBUTANE

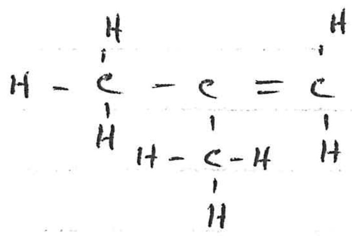


2 Chloromethyl propane

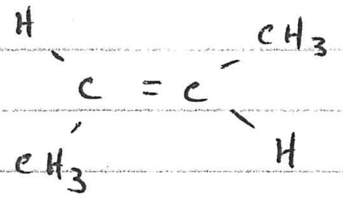
3. EMPIRICAL FORMULA : CH_2 MOLECULAR FORMULA C_4H_8



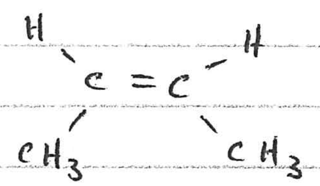
BUTENE



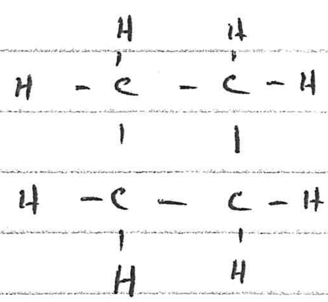
2 - METHYL - PROPENE



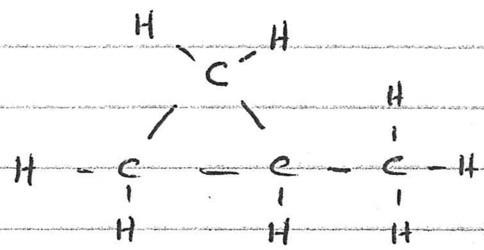
TRANS - 2 - BUTENE



CIS - 2 - BUTENE

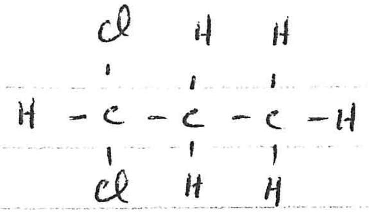


CYCLOBUTANE

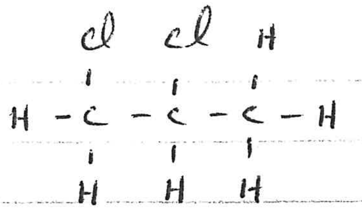


METHYL CYCLOPROPANE

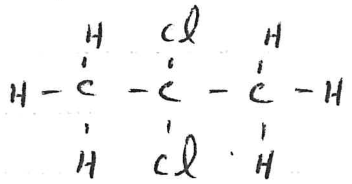
4.



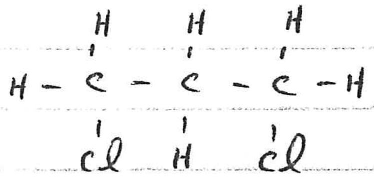
1,1 - DICHLOROPROPANE



1,2 - DICHLOROPROPANE



2,2 - DICHLOROPROPANE

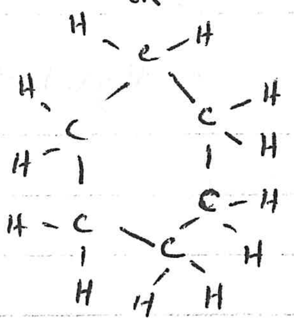


1,3 - DICHLOROPROPANE

5.

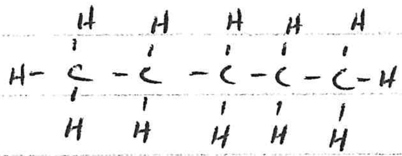
NO, THE FORMULA IS NOT TYPICAL OF AN ALKANE. IT IS TYPICAL OF AN ALKENE

OR

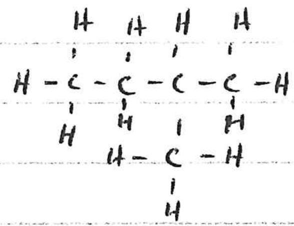


THE CHEMICAL PROPERTIES HOWEVER ARE TYPICAL OF AN ALKANE AS IT CONTAINS C - C SINGLE BONDS i.e. IT IS A SATURATED HYDROCARBON

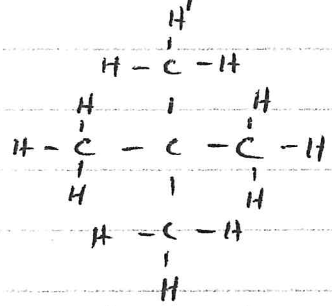
6.



PENTANE

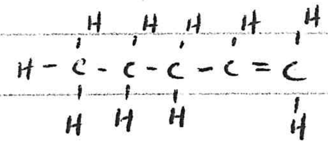


2 - METHYLBUTANE

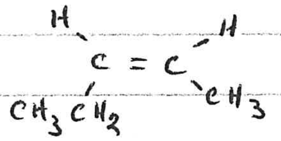


2,2 - DIMETHYLPROPANE

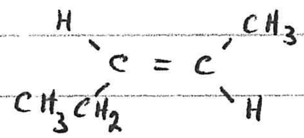
7.



PENTENE



CIS - 2 - PENTENE



TRANS - 2 - PENTENE

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_3$

2 METHYL - 2 - BUTENE

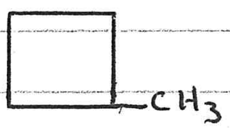
$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2CH_3$

2 - METHYLBUTENE

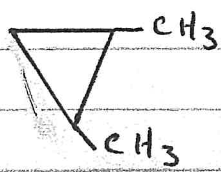
$CH_2=CH\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$

3 - METHYLBUTENE

CYCLOPENTANE



METHYLCYCLOBUTANE



1,2 DIMETHYLCYCLOPROPANE

AND 1,1 DIMETHYLCYCLOPROPANE

8. A. $CH_3CHCH_2CH_2CH_3$
$\quad\quad\;|$
$\quad\quad Cl$

B. $Cl-CH_2CHCH_2CH_3$
$\quad\quad\quad\;|$
$\quad\quad\quad CH_3$

C. $Cl-CH_2CH_2CHCH_3$
$\quad\quad\quad\quad\;|$
$\quad\quad\quad\quad CH_3$

D. $\quad\quad\quad\; CH_3$
$\quad\quad\quad\quad\;|$
$Cl-CH_2-C-CH_3$
$\quad\quad\quad\quad\;|$
$\quad\quad\quad\quad CH_3$

E. $CH_3CH_2CHCH_2CH_3$
$\quad\quad\quad\;|$
$\quad\quad\quad Cl$

F. $\quad\;\; Cl$
$\quad\quad\;|$
$CH_3C-CH_2CH_3$
$\quad\quad\;|$
$\quad\quad CH_3$

THEY ARE ALL STRUCTURAL ISOMERS OF FORMULA $C_5H_{11}Cl$

9. E. ALL HAVE MOLECULAR FORMULA C_3H_5Cl
1 & 3 ARE CIS/TRANS ISOMERS

10. D. THE FIRST COMPOUND IS 2-METHYL PROPENE
THE SECOND COMPOUND IS CIS-2-BUTENE

11. D. 12 E.

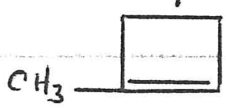
13. A. NO, JUST DIFFERENT WAYS OF DRAWING THE SAME MOLECULE
3-METHYL-PENTANE
B. YES, THEY ARE ISOMERS
2-METHYL PENTANE AND 3-METHYLPENTANE
C. YES, THEY ARE ISOMERS
2,2-DIMETHYLBUTANE AND 2-METHYLPENTANE

14. $CH_3CH_2CH_2C\equiv CH$ PENTYNE

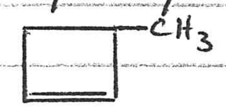
$CH_3CH_2C\equiv CCH_3$ 2-PENTYNE

$\quad\quad CH_3$
$\quad\quad\;|$
$CH_3CHC\equiv CH$ 3 METHYL BUTYNE

CYCLOPENTENE



METHYLCYCLOBUTENE



3METHYLCYCLOBUTENE

15. A. NO, JUST DIFFERENT WAYS OF DRAWING SAME MOLECULE 2-METHYLBUTENE
B. NO, THEY HAVE DIFFERENT MOLECULAR FORMULAE
2-PENTYNE (C_5H_8) AND 2-HEXYNE (C_6H_{10})
C. NO, JUST DIFFERENT WAYS OF DRAWING 2,3-DIMETHYL-2-PENTENE