# B.Sc. I

## Paper II Organic Chemistry

# BOND PARAMETERS

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# BOND PARAMETERS

BOND LENGTH
BOND ANGLE
BOND ENERGY

BOOK BY
M.M.N. TANDON

# BOND LENGTH

**BOND LENGTH**

Distance between two atomic nuclei is called bond length.

The distance is very small.

Units of measurements are ANGSTROM UNITS[$1°A = 10^{-8}cm = 10^{-10}m$]

**COVALENT BOND LENGTH**

Depends upon

1. Size of atomic radii (single bond) - (a) Polar nature of bond
   (b) Resonance
   (c) Bond order
2. Type of bond - (a) Single bond
   (b) Double bond
   (c) Triple bond-

# BOND LENGTH

**EXAMPLES:**

Covalent radii of carbon

C − = 0.77°A

C = =0.67°A

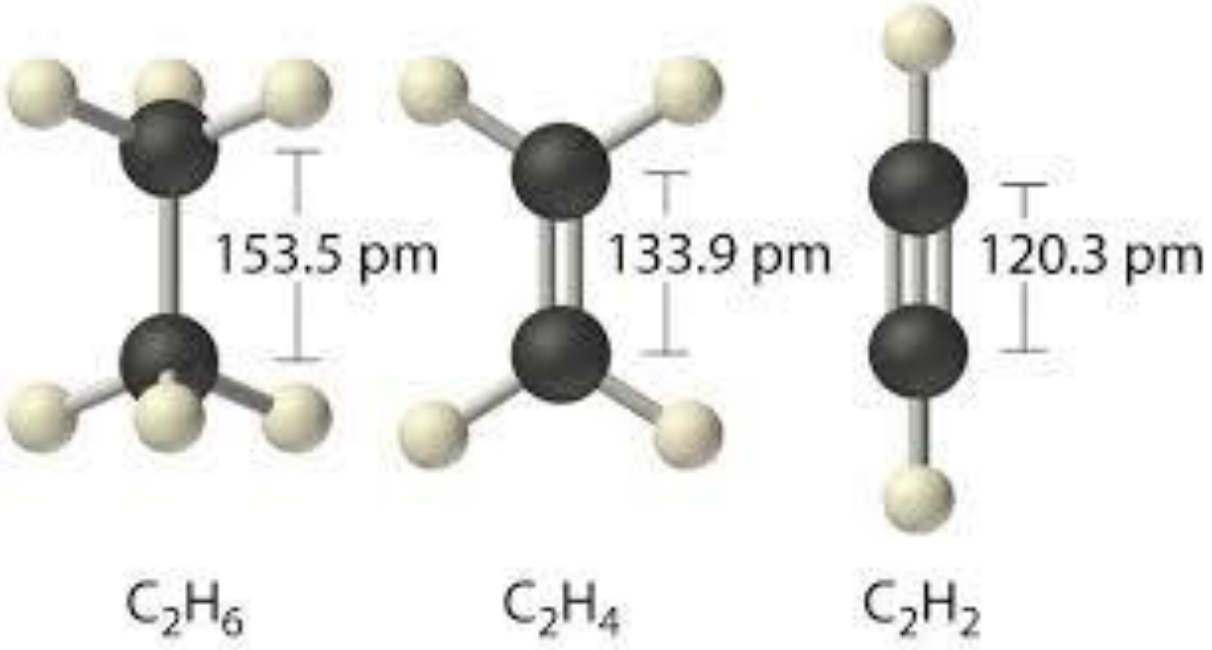
C ≡ =0.60°A

Bond length

C − C = 1.54°A (Single bond)

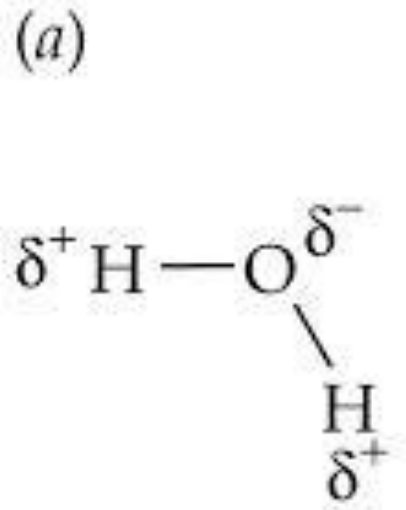
C = C = 1.34°A (Double bond)

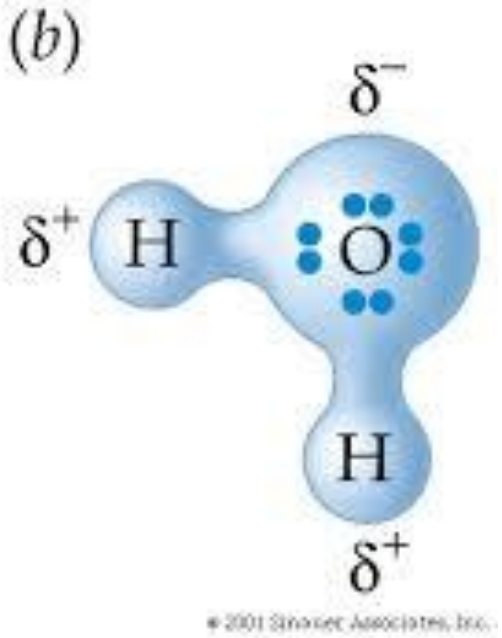
C ≡ C = 1.20°A (Triple bond)



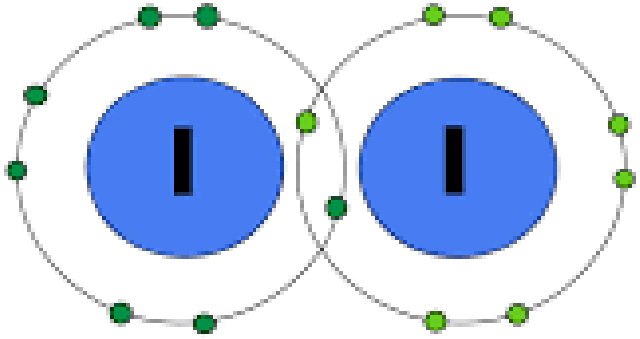
# (a) POLAR NATURE OF BOND CHANGES THE BOND LENGTH

**POLAR**

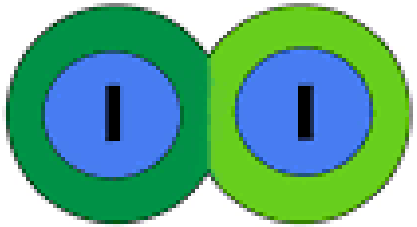



**nonpolar**



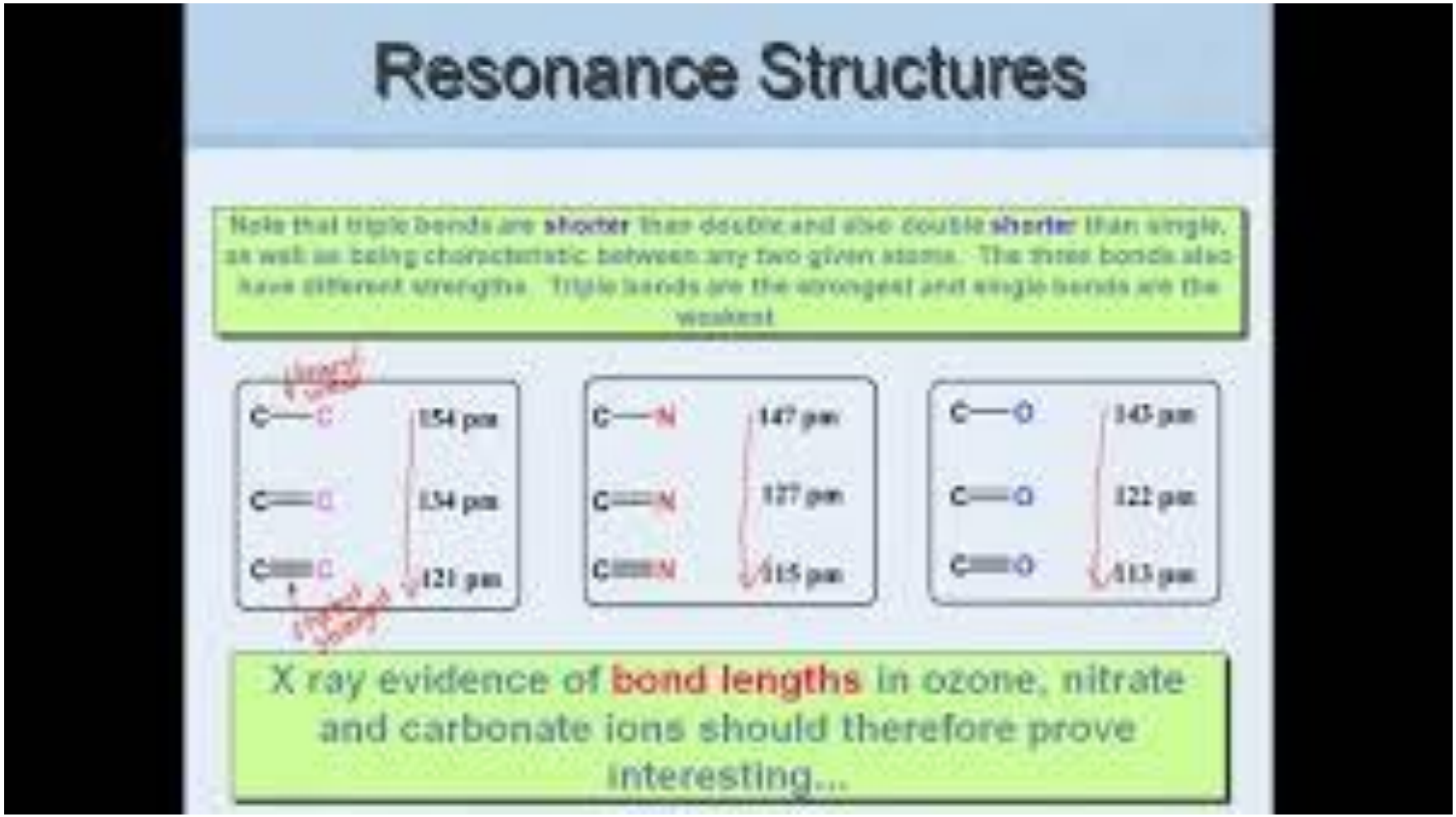

**electronegativity of iodine is 2.5**




**electron density is equally spread out**

# RESONANCE SHORTENS BOND LENGTH

Resonance results in partial double bond character in the molecule
Resonance increases the bond strength of single bonds because the bond length after resonance decreases.



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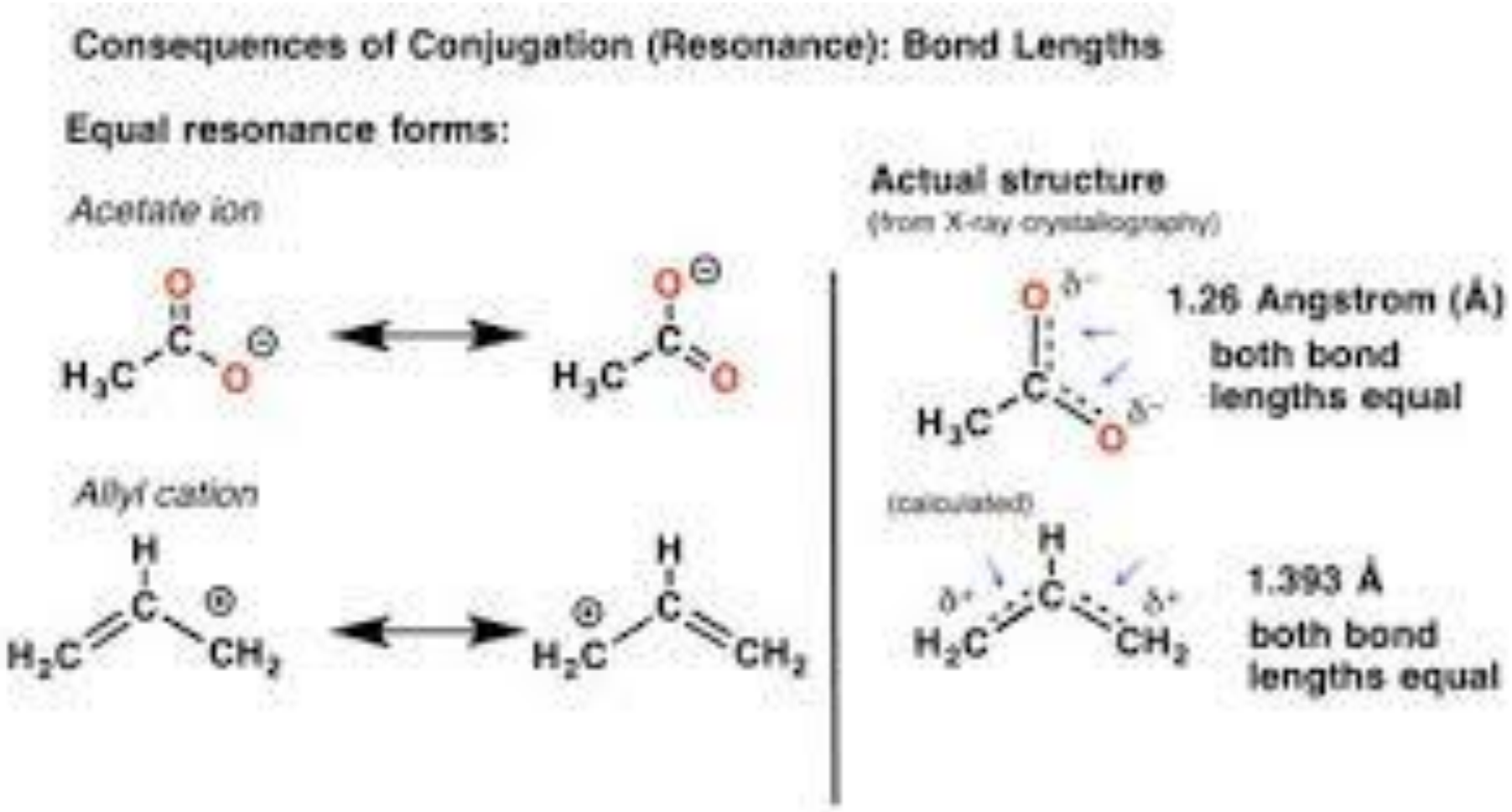

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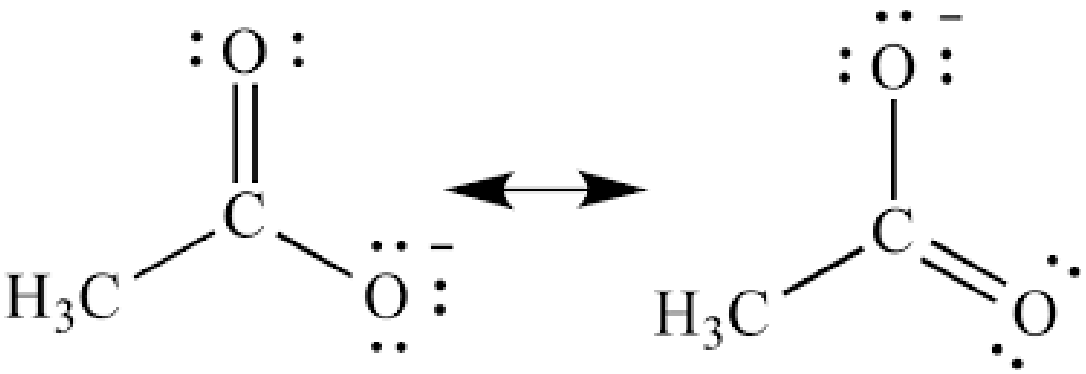
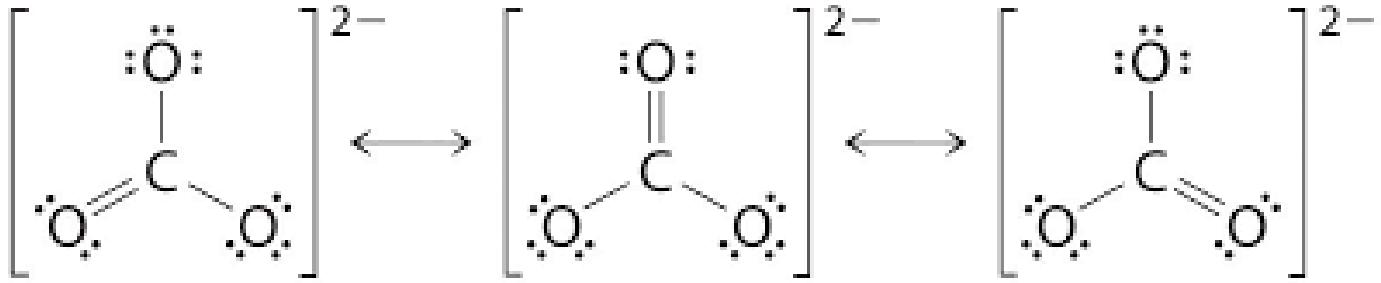
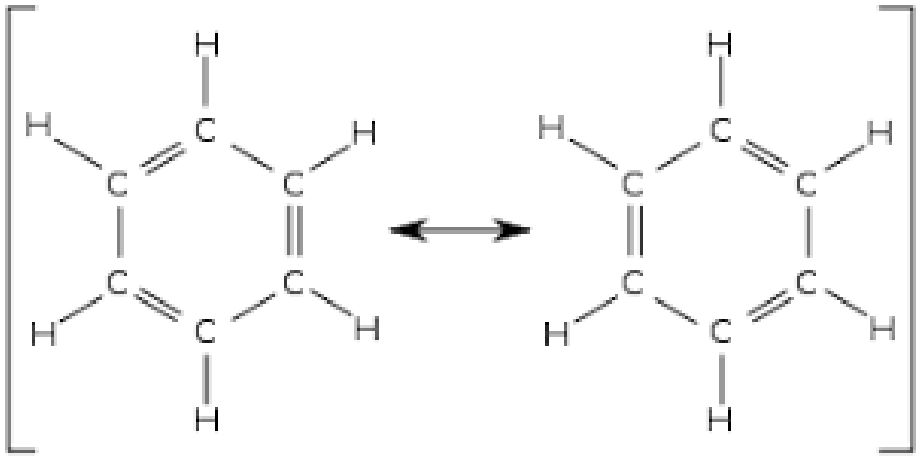


**[C – O] = 1.54** °A

**[C = O] = 1.34** °A





**BOND LENGTH = 1.39** °A

# (c) BOND ORDER

Bond order is the number of chemical bonds between a pair of atoms and indicates the stability of a bond.

For example, in diatomic nitrogen, N≡N, the bond order is 3; in acetylene, H−C≡C−H, the carbon-carbon bond order is also 3, and the C−H bond order is 1.

Bond order and bond length indicate the type and strength of covalent bonds between atoms.

Bond order and length are inversely proportional to each other: when bond order is increased, bond length is decreased.

# BOND ANGLE

**COVALENT BOND ANGLE:**

Bond angle is the angle formed by two bonds.

Angle between the central atom and the terminal atoms of a molecule is the bond angle.

**FACTORS AFFECTING/CHANGING BOND ANGLE**

1. **Hybridization**
2. **Lone pair of electrons**
3. **Electronegativity of central atom**
4. **Electronegativity of terminal atom**

# 1. HYBRIDIZATION

Hybridization is the idea that a number of atomic orbitals of different shapes and energies, fuse to form same number of new hybridized orbitals, equal in energy and similar in shape, which in turn, influences molecular geometry and bonding properties.

**1. Hybridization (% of 's' character) -**

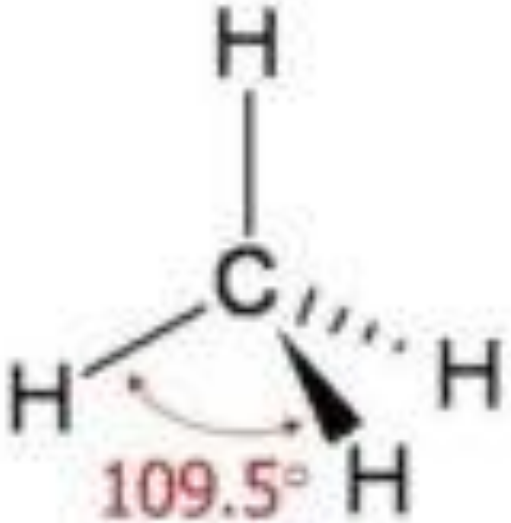
(a) In saturated hydrocarbons (single bond), the hybridization is sp3 [25 % s character = 109°28']

(b) In unsaturated hydrocarbons (double bond), the hybridization is sp2 [33 % s character = 120°]

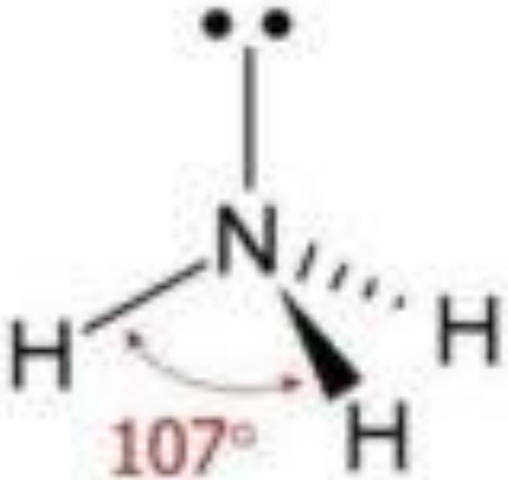
(a) In unsaturated hydrocarbons (triple bond), the hybridization is sp [50% s character = 180°]

# 2. LONE PAIR OF ELECTRONS

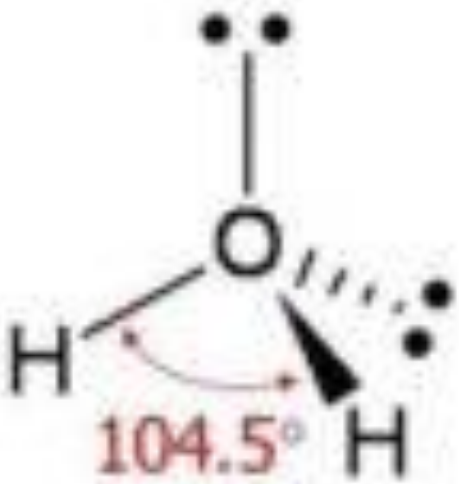
**Lone pair of electrons at the central atom repels the shared pair (bonded pair) of electrons towards the terminal atoms.**
**Due to this, the bonds are displaced slightly towards each other, resulting in a decrease of bond angle.**
**More the lone pair of electrons, smaller is the bond angle.**




METHANE




AMMONIA

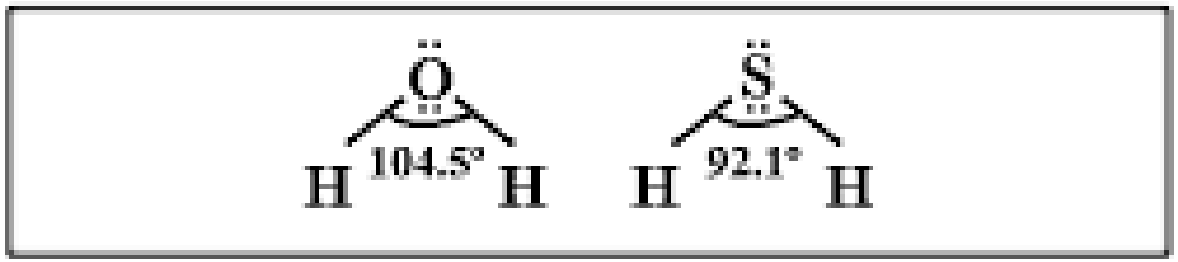



WATER

# 3. ELECTRONEGATIVITY OF CENTRAL ATOM

If terminal atoms remain same and the electronegativity of the central atom increases the bonded electrons would be pulled towards the central atom. The electron concentration near the central atom will increase [↑] and repulsion between bonding pair – bonding pair will increase [↑], therefore the deviation will be more and bond angles will also increase [↑]. Therefore, more electronegative is the central atom, greater is the bond angle.

Bond angle in $H_2O$(104.5°) is higher than the bond angle of $H_2S$ (92.1°). The difference is due to:




A. O is diatomic and S is tetra-atomic

B. difference in electronegativity of S and O

C. difference in oxidation states of S and O

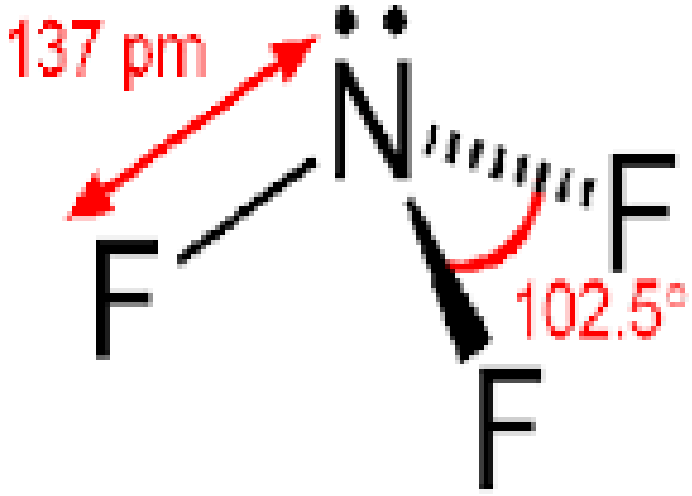
D. difference in shapes of hybrid orbitals of S and O

# 4. ELECTRONEGATIVITY OF TERMINAL ATOMS

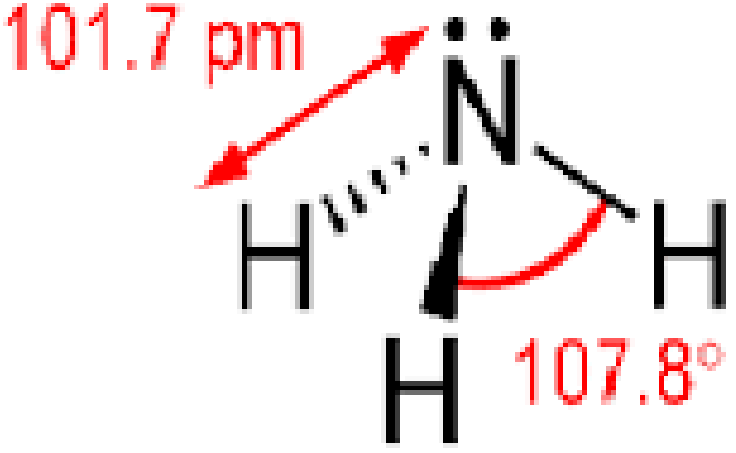
If the central atom remains the same and terminal atoms are different then as electronegativity difference between the central and terminal atom increases [↑], bond angles will decrease.

Greater electronegativity of terminal atom will pull the shared electrons away from the central atom.

Repulsive effect of electrons will decrease and bond angle will decrease.

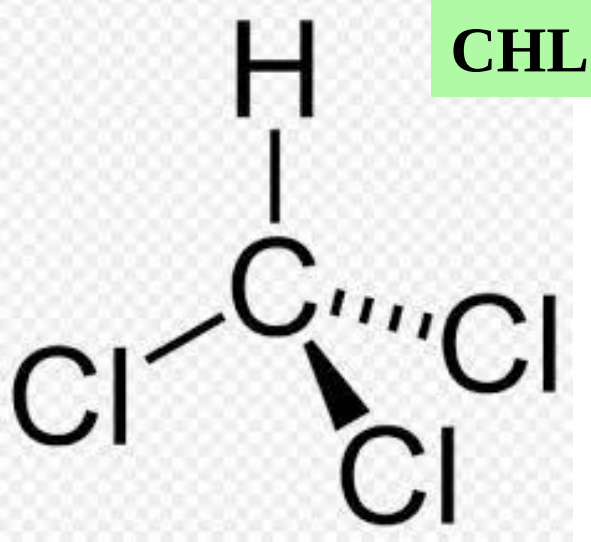



The shared pair of electrons are nearer to fluorine hence less repulsion and bond angle is small.



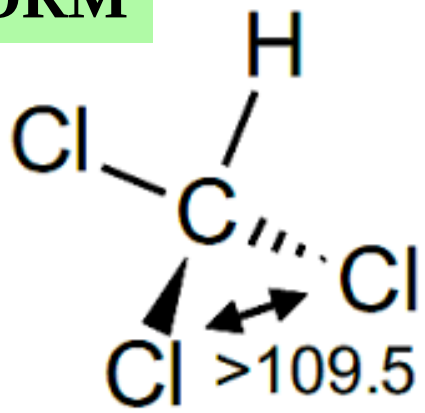

The shared pair of electrons are near to nitrogen, hence more repulsion and bond angle will be large.

# 4. NUMBER OF ELECTRONEGATIVE TERMINAL ATOMS



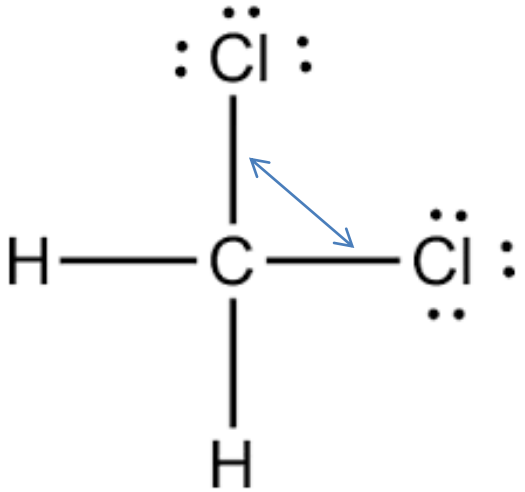

**CHLOROFORM**

CHCl3




**112 °**

**METHYLENE CHLORIDE**




**111 °**

CH2Cl 2

# BOND ENERGY

1. ENERGY REQUIRED TO BREAK A BOND - DISSOCIATION ENERGY
2. ENERGY REQUIRED TO FORM A BOND - BOND ENERGY

| | | |
|---|---|---|
| $CH_3 - H$ | 102 k cal | Primary H |
| $CH_3CH_2 - H$ | 97 kcal | Primary H |
| $(CH_3)_2\ CH-H$ | 94 kcal | Secondary H |
| $(CH_3)_3\ C-H$ | 89.4 kcal | Tertiary H |

| | |
|---|---|
| H−H | 103.4 k cal |
| C−H | 98.8 kcal |
| C−C | 83 kcal |
| C =C | 145 kcal |
| C ≡C | 192 kcal |
| C −O | 80 kcal |
| C=O | 166 kcal |