

Polyhalides : Structure and Bonding

- I_3^-

Bond length – 2.67 \AA

Symmetrical Triiodides

Tetraphenylarsonium iodides $[(C_6H_5)_4As]I_3$ 2.9 \AA

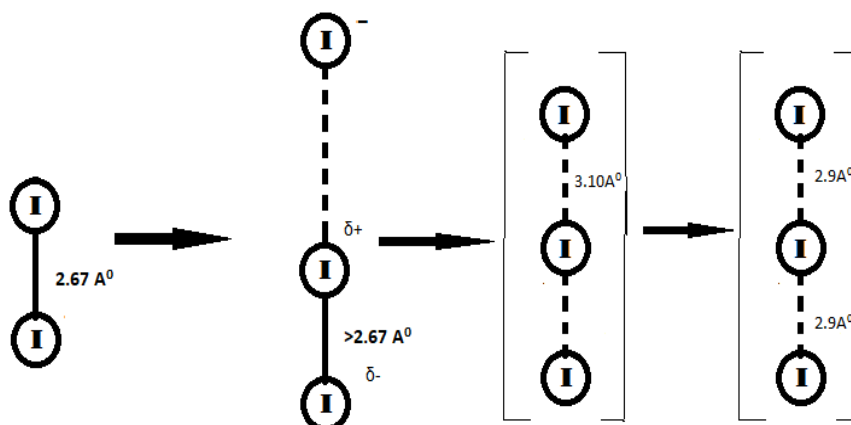
and Unsymmetrical triiodide

CsI_3 (3.03 and 2.83 \AA)

NH_4I_3 (3.10 and 2.82 \AA)

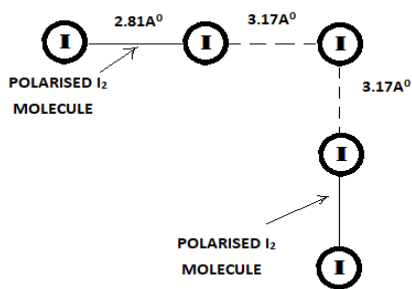
As I_2 approaches I^- there is distortion of electron cloud in I_2

A dipole is introduced in Iodine molecule. The induced dipole attracts I^- the magnitude of polarisation determines strength of bond in Triiodide



Pentaiodide I_5^-

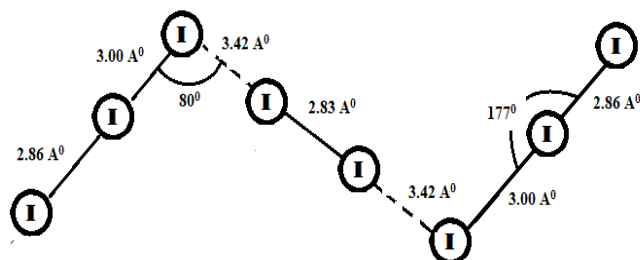
- Two iodine molecules co-ordinated by Iodide. Two unsymmetrical triiodides sharing common iodine atom. The bond lengths are 2.82 and 3.17 \AA
- Bond length as in unsymmetrical triiodides



Tetraiodide I_4^-

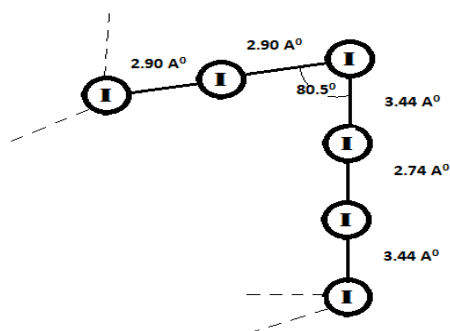
CsI_4 has a dimeric form. It has the molecular formula $(I_4^-)_2$ or I_8^- . I_3^- added to I_5^-

Tetraiodide ion has a Z-arrangement.



I_7^- Heptataiodide

- $[(C_2H_5)_4N]I_7$

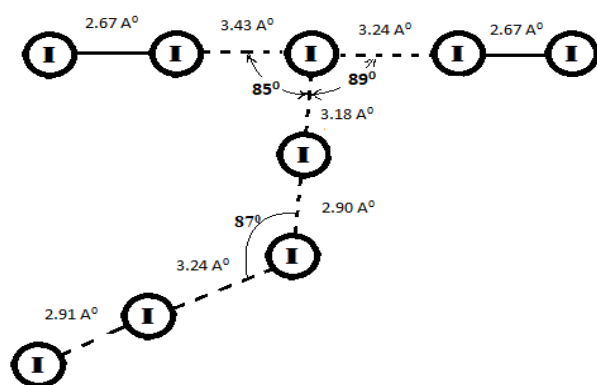


- Infinite 3-dimensional framework of molecules (2.74 \AA)

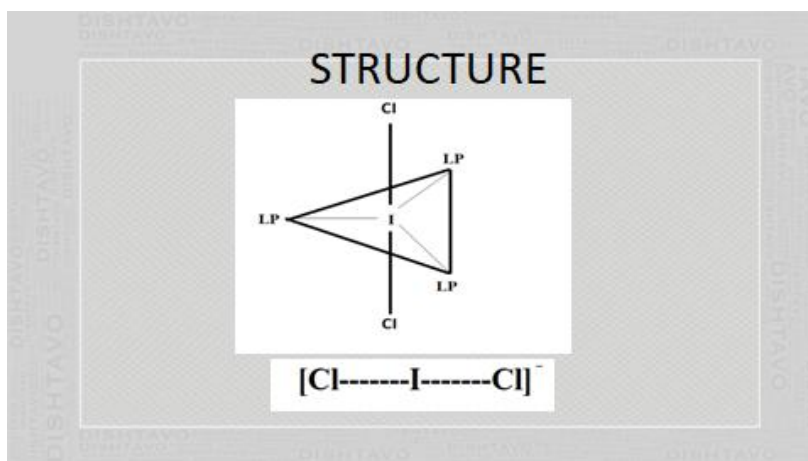
- Symmetrical triiodide ions (2.9\AA) are co-ordinated through long bonds (3.44\AA) to Iodide ion.

Structure of I_9^-

- Complex Structure
- $\text{I}_7^- + \text{I}_2$ or $\text{I}_5^- + 2\text{I}_2$. It has irregular structure, with bond lengths $2.67, 2.90, 3.18, 3.24, 3.43$ and 3.49\AA

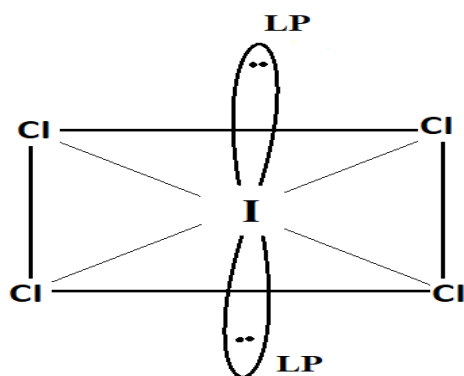


Structure of Dichloroiodate ion



- Structure of ICl_2^- is distorted trigonal pyramidal. ICl_2^- has sp^3 d-hybridized state, having trigonal bipyramidal shape. Distorted due to the presence of lone pair of electron on I-atom. The three lone pairs are in the equatorial positions, leaving the Cl and I in a linear molecular shape, but due to the presence of lone pair of electron on iodine atom the structure is distorted.

- Structure of Tetrachloroiodate ion ICl_4^-



- The central iodine atom has six pairs of electrons but it has just four bonding pairs of electrons.
- Its two lone pairs of electrons occupy the axial positions. These lone pairs repel each other and the four bonding pairs so that the four chlorine atoms occupy the equatorial positions.
- This produces a square planar structure, even though there is an octahedral arrangement of electron pairs.