Bent Bond

Bent bond, also known as banana bond is a term in chemistry that refers to a type of covalent chemical bond with geometry somewhat reminiscent of a banana. The term itself is a general representation of electron density or configuration resembling a similar "bent" structure within small ring molecules or as a representation of double or triple bonds within a compound that is an alternative to the sigma and pi bond model. Bent bond is formed by the oblique overlap of atomic orbitals as a result of which the resultant bond bulges out in a circular fashion.

Bent bonds are a special type of chemical bonding in which the ordinary hybridization state of two' atoms making up a chemical bond are modified with increased or decreased s-orbital character in order to accommodate a particular geometry. Bent bonds are found in strained organic compounds such as cyclopropane, oxirane and aziridine. This bond model concept is used to explain the structure of cyclic and substituted double bonds.
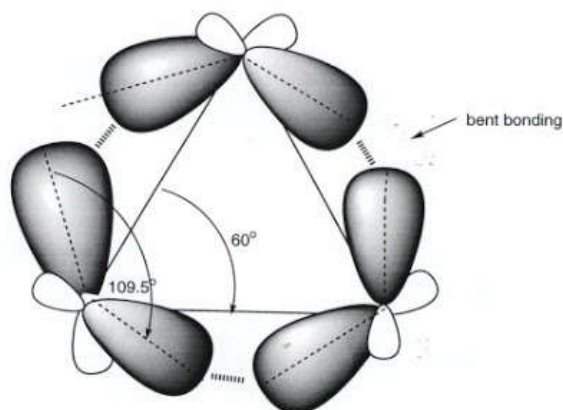

Fig.1a. Depiction of the banana bond in cyclopropane

Concept of Bent Bond

Bent bond is the model which is closely related to the subject of structures of substituted double bonds. Such bond concept could be applied in two ways:

1. The first relates to the ring strain of small cyclic molecules. Although rehybridization occurs as ring size is decreased. e.g., in cyclopropane carbon is sp^3 hybridized. In such types of compounds, it is not possible for C-atoms to assume the 109.5°bond angles with standard hybridization. Increasing the p-character makes it possible to reduce to bond angles to 60°. At the same time' the carbon to hydrogen bonds gain more a-character and shorten as shown in Fig 1a & b.
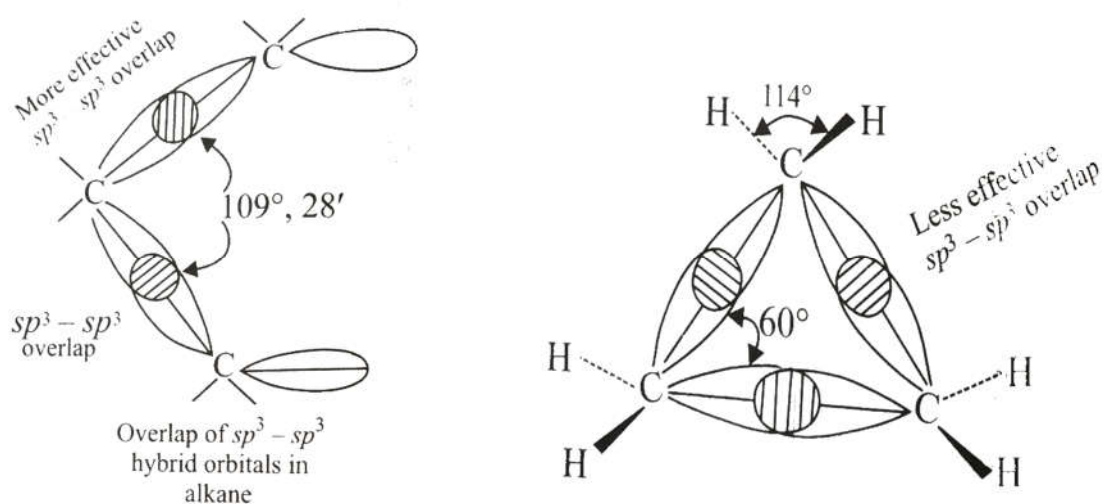

Fig.1b. Depiction of the banana bond in cyclopropane

In cyclopropane the maximum electron density between two C-atoms does not corresponds to the internuclear axis, hence the name bond bent. In cyclopropane the interorbital angle is 104: This bonding can be observed experimentally by X-rays diffraction of certain cyclopropane derivatives; deformations density is outside the line of centers between carbons.

2. The second use of bent bonds is as an alternative interpretation of multiple bonding. Multiple bonding can be explained by considering the example of ethylene. In this molecule, the sigma bond is formed by head-on overlap of

sp^2-hybrid orbital of C-atoms and Pi bond is formed by the parallel overlap of remaining p-orbitals on each of C-atoms.

(a) C_2H_4 σ-bonded framework   **(b) C_2H_4 π bonding**
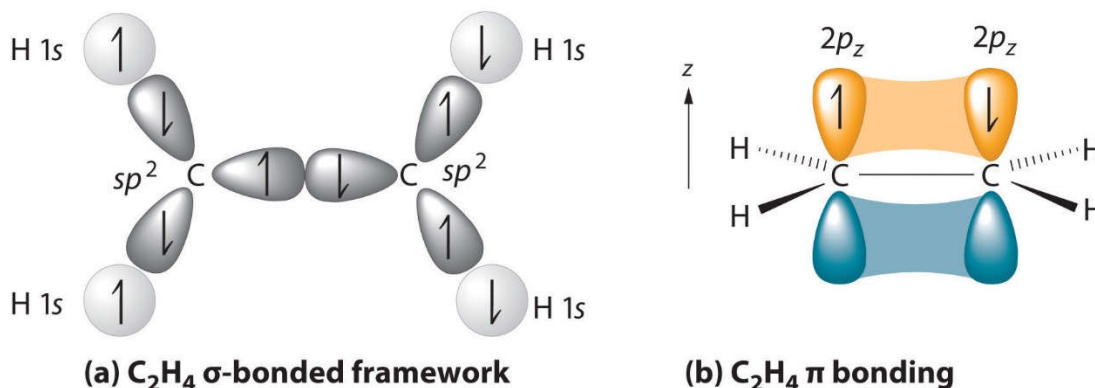
Fig.2. Sigma and pi bonds formation in ethylene molecule

There are two methods for interpreting the bonding in multiple bonded compounds. The first method of interpreting multiple bonds is the σ-π picture, which was developed in the context of MOT. The second method has been advocated by L. Pauling in VBT, but neither is limited to either MOT or VBT.
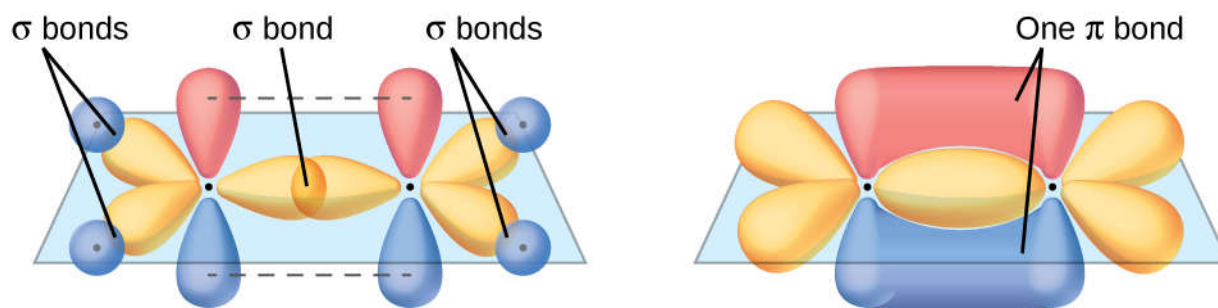

Fig.3. Sigma and pi bonds formation in ethylene molecule

The double bond in ethylene molecule consists of a sigma bond formed by the head-on overlap of trigonal hybrids (*sp^2*) on each C-atom and a π-bond is formed by the sideways overlap of the remaining p-orbitals on each C-atom in Fig 3.

The orbitals will resemble the MOs (molecular orbitals). The two bonds are not equivalent, since they differ in energy as well as symmetry. In accordance with the

principle of maximum overlap, one should expect the sigma bond to be stronger than the pi-bond. If we assume that the sigma bond in an ethylene molecule has the same strength as that in ethane molecule, it would have the bond energy of about 347 kJ mol^{-1}. The experimental value of the bond dissociation energy of ethylene (breaking sigma and pi bonds) is 598 kJ mol^{-1}, indicating about 251 kJ mol^{-1} for the pi-bond. The difference of some. 96 kJ mol^{-1} between the sigma and Pi bonds can be attributed to the poor overlap of the latter.

According to Pauling approach the C-atom is considered to be hybridized tetrahedrally (*sp³* to the first approximation in all compounds, saturated or unsaturated, multiple bonds are considered to be formed from the oblique overlap of these hybrid orbital as shown in following Fig.4. The resulting bonds are called bent bonds or banana bonds. Since the two bonds are equivalent, it is possible to assume that each bent bond has an energy of 299 kJ mol^{-1}.
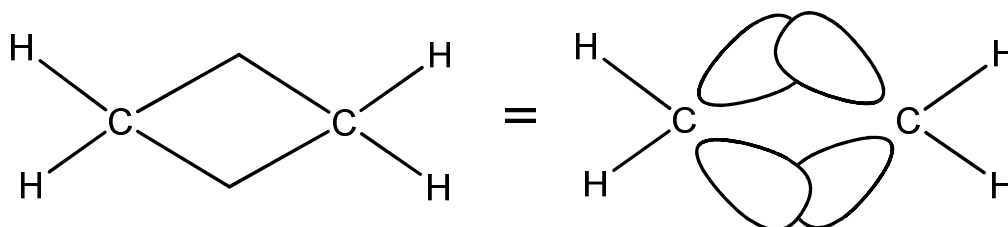

Fig.4. Bent bond representation of ethylene molecule

Four Electrons Three Centre Bond

Generally there are two types of covalent bonds.

- *First* one is the ordinary two centre, two electron (2c - 2e) bond, formed by the overlap of a p-orbital of the central atom with a a-orbital of an outer atom,

- *Second* one is the three centre-four electron (3c -4e) bond, formed from a p-orbital of the central atom and the a-orbital of two outer atoms. For

example, three centre form electron (3c – 4e) bond model approach is based on the two main ideas:

(i) Use of the outer d-orbitals of the central atom of non-transition metal ion is so slight that these may be neglected altogether.

(ii) Presence of bond angles close to 900 and 1800 in AB_4 molecules suggests that orbitals perpendicular to one another are being used.

For molecules with an octet, or less, of electrons in the valence shell of the central atom, the hybridization employing sp, sp^2 and sp^3 orbitals remain valid. For· example, Be atom in $BeCl_2$ is sp hybridized, B in BF_3 is sp^2 hybridized and C in CH_4 is sp^3 hybridized. The 3c – 4e model has been proposed for molecules in which five or more electron pairs on the central atom must be accounted for chemical bonding. In molecules of AB_4E type (SeF_6, the central atom A is considered to use p_x and p_y orbitals to bond the two B-atoms (F), while the remaining two B atoms (F) are bound using p_z orbital to form a 3c – 4e bond. The remaining electron pair on the central atom is postulated to be occupying a pure s-orbital and have no stereo chemical role. Similarly AB_3E_2 type (ClF_3) molecule also has 3c – 4e bonding.

The MO theory explains the 3c - 4e bond as follows. The illustrate the idea, let us take the example of XeF_2, the valence shell configuration of Xe and F are *X: $5s^2$ $5p^6$*, and *F: $2s^2$, $2p^5$*. If the bonds lie in the x-direction, this *$2p_x$* orbitals of each fluorine bearing the unpaired electron and the filled *$5p_x$* orbital of Xenon will participate in forming three centre sigma MO_S. Similarly, the *$2p_y$* orbitals of fluorine along with $5p_y$ orbital of Xenon will form three-centre Pi-MOs. Thus, by using the *p_z* orbitals of the fluorine and Xenon we get another set of Pi-MOs. The corresponding π_y and

π_z MOs are degenerate as usual. Here the Pi-system is of no interest from the stand point of stability of the molecule, as the bonding, non-bonding and antibonding Pi-MOs are completely filled in and yield the Pi-band order 'zero. (Fig 4).
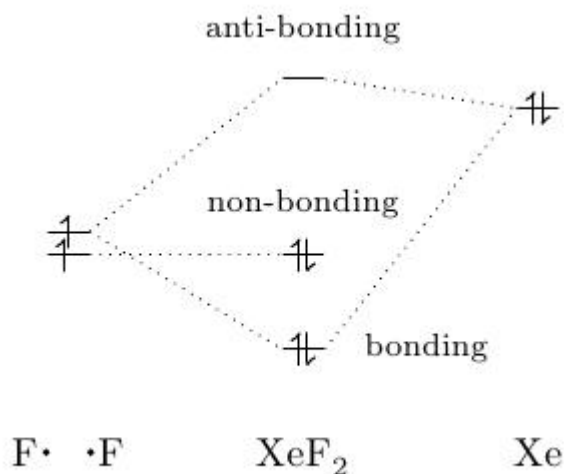

Fig.4. The MO picture of XeF_2 molecule

Bridge Bond and Electron Deficient Compounds

Bridge bond is a type of chemical bond in which one atom is linked between the two atoms. There are some cases in which the number of available valence electrons is not sufficient to display the normal electron pair bonds (2c - 2e) among all the constituent atoms. In other words the molecules in which there are not enough electrons to form covalent bonds between the atoms are called electron deficient molecules. The occurrence of electron deficient covalent bonds is a common feature of some elements of group 13 of the periodic table. For example $(BH_3)_2$, $[Al(CH_3)_3]_2$ are electron deficient molecules. since they do not contain enough electrons to form the two-electron bonds between the atoms.
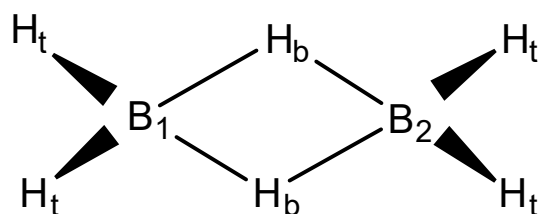
Fig 5a. Structure of Diborane

Diboranee (B_2H_6) is the best example to understand the bridge bond. Electron diffraction studies have shown that B_2H_6 has a hydrogen bridged structure as shown in Fig.5a & b in which two irregular BH_3 tetrahedral have one edge in common, Thus two boron atoms represented as B_1 and B_2 and four hydrogen atoms (called terminal H-atoms and are represented as H_a-atoms) lie in the plane of the .paper (coplanar) while the remaining two H-atoms (called bridging H-atom and hence represented as H_b-atom) are located centrally above and below the plane of the paper. These bridging H-atom prevent the notation between the two B-atoms. Specific heat measurements also confirm that notation is hindered.
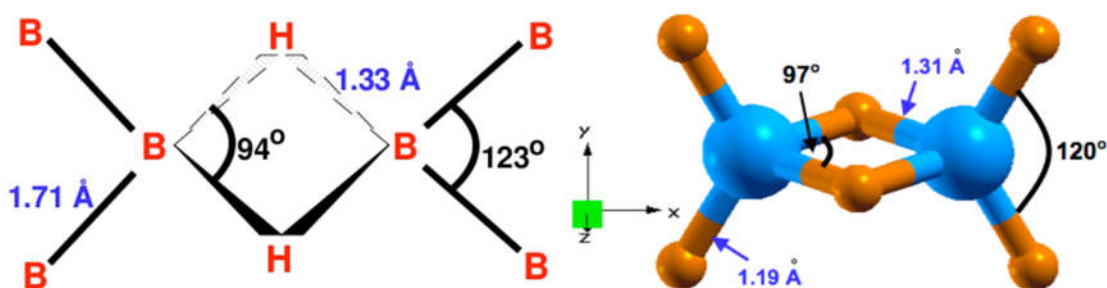

Fig 5b. Hydrogen bridge structure of B_2H_6

It is obvious that length of B_1-H_t bond = B_2-H_t bond which is equal to 119.A°, This bond length is almost equal to that for a single bond given by the sum of the single-bond normal covalent radii, of boron and hydrogen i.e., $r_B + r_H$ which is equal to $0.85 + 0.30 == 1.15A^0 > r_B + r_H = 1.15A^0$ indicating the presence of fractional bond.

Facts about the Bridge Structures

Following facts support the bridge structure in diborane molecule.

1. 'Nuclear magnetic resonance (NMR) and Raman spectra have shown that four hydrogen namely H_t-atom are of one type while the remaining two namely H_b-atoms are of different types.

2. Specific heat measurements have shown that the two ends of the molecule cannot be rotated against each other. This hindered notation clearly indicates that the two bridging hydrogen' atoms lie in a plane at right angles to that of boron atom and four terminal hydrogen atom.

3. The terminal and bridging position of the H-atoms has also been confirmed by its chemical reactivity. When diborane is reacted with methyl borane (BMe_3), we get tetraethyl borane $(CH_3)_4$ B_2H_4 whose structure is given as;
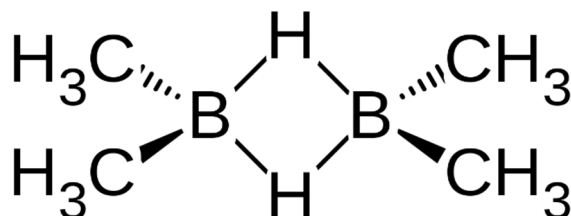

Fig 6. Tetramethyl borane

MO Theory and Bridge Bond

Bridge bond is also known as three-centre two electron (3c – 2e) bond. In B_2H_6, each B-atom is *sp³* hybridized. Among the four *sp³* hybrid orbitals, one is remaining vacant. Each boron utilizes two *sp³* hybrid orbital to form two normal electron pair (2c - 2e) terminal B - H_t bonds. Thus, the electron pair in each terminal B - H, bond is localized between the nuclei in the bonding molecular orbital (2c –

2e) formed through combination of Is-orbital of the terminal hydrogen and *2sp³* hybrid orbitals of the B-atom (Fig 7).
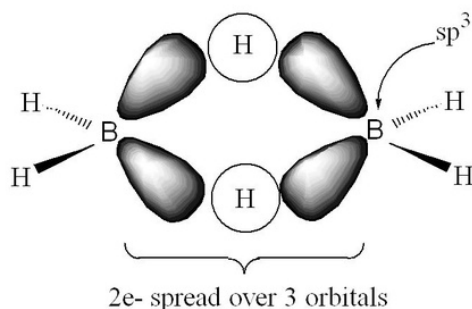

Fig 7. Three centers two electron bond (3c – 2e)

But for the bridging bonds, the three orbitals, i.e., one sp3 hybrid orbital from each boron and Is orbital of the bridging H-atom, undergo LCAO to form three centre molecular orbitals, i.e. bonding MO, nonbonding MO and antibonding MO. The MO energy diagram for B_2H_6 is shown in Fig 8.
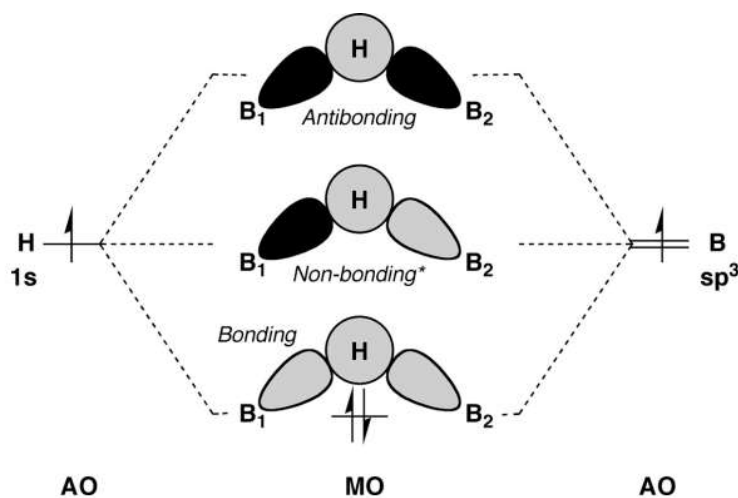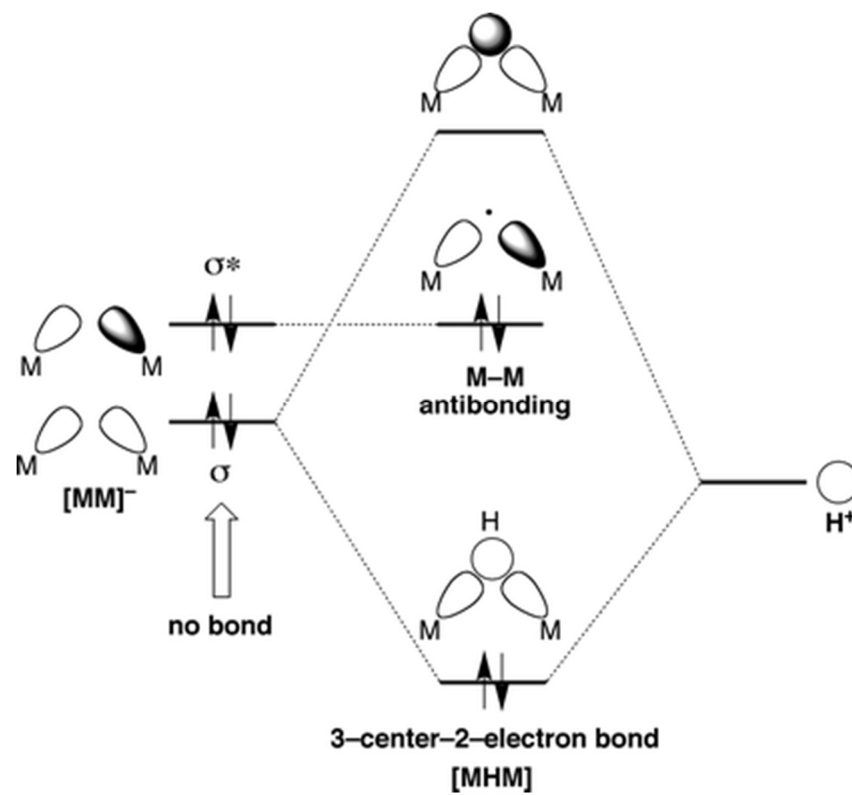

Fig. 8a. MO scheme for one of the B–H–B bridging three center two electron bonds
(This picture is still a simplification of the actual MO scheme)

Fig. 8b. MO energy diagram of B_2H_6 molecule