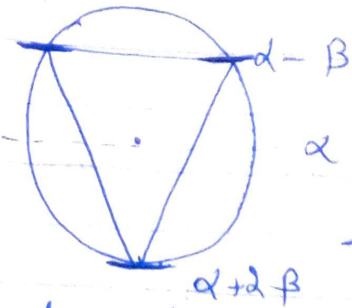
Huckel's Rule Frost Circle



Cyclopropenyl system

→ Draw a regular polygon with one vertex down.

→ Draw a circle passing thru all the vertices.

→ Draw horizontally dashed line at the level of each vertex.

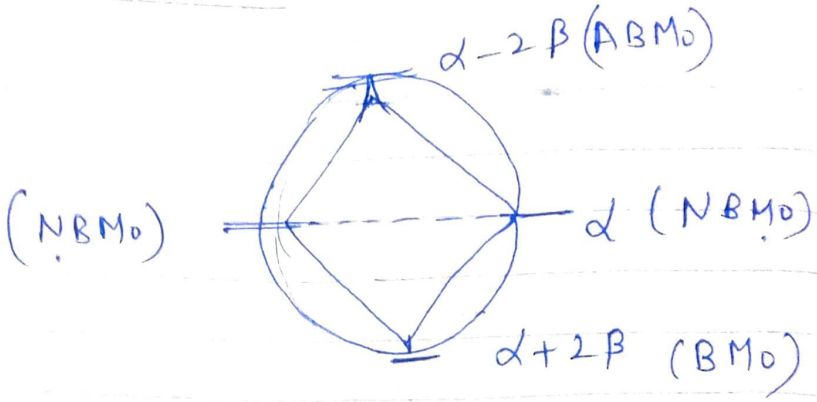
→ The resulting diagram gives energy levels, determined geometrically with energy α at the level of the centre of the circle.

→ The horizontal diameter represents the energy of a carbon p orbital and so if any energy levels are present on this line, they must be non bonding.

→ M.O. below Non bonding M.O. = Bonding M.O.
M.O. above " " " " = Anti-Bonding M.O.

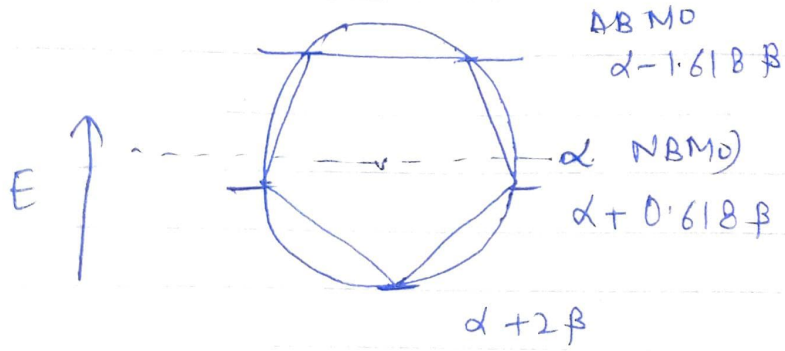
→ Insertion of the ring with polygon will make the position of M.O.

Cyclobutadiene

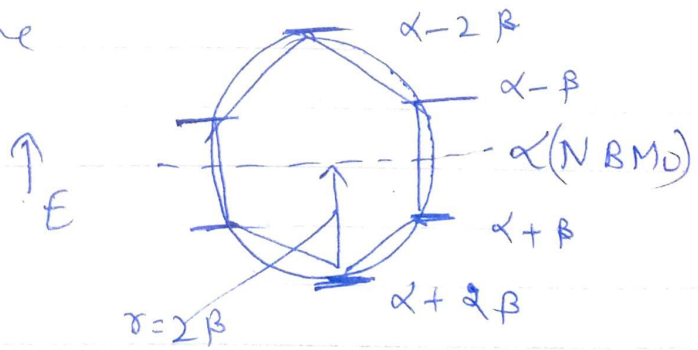


Relative energies of M.O's of cyclobutadiene derived from frost circle

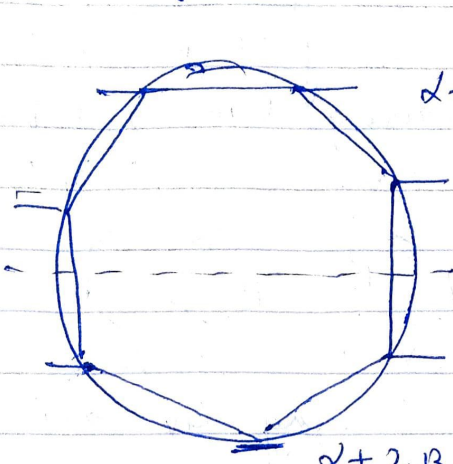
Cyclopentadienyl ~~ca~~ system



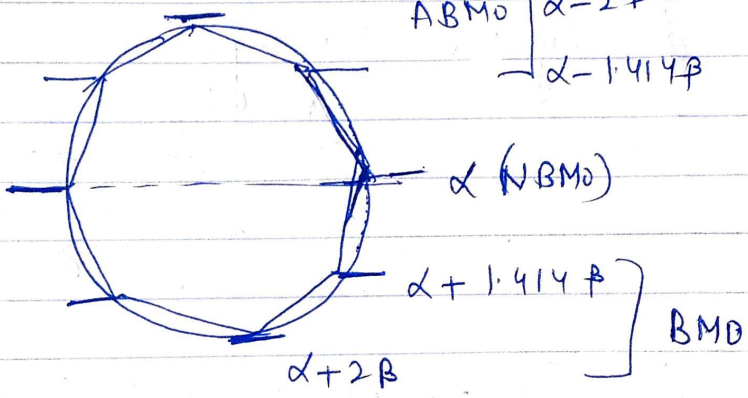
Benzene



Cycloheptatrienyl system



Cyclo octatetraene system

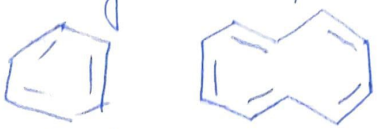


From the frost circle (i.e. from HMOT for monocyclic conjugated system) following generalisation can be made to construct the π-MO of conjugated monocyclic systems having even or odd number of carbons in the ring.

Generalyalion are:

i) Conjugated monocyclic systems can be classified into four categories for construction of π mol. orbitals.

a) System having (4n+2) carbon atoms in the ring n = 1, 2, 3, 4 etc.

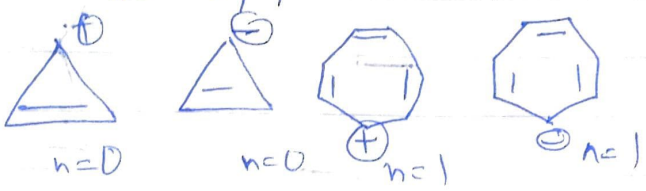


n = 1 n = 2.

b) System having 4n carbon atoms in the ring.

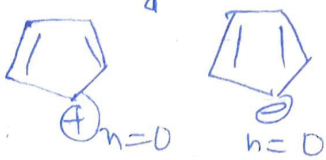
n = 1 n = 2

c) System having (4n+3) carbon atoms in ring n = 0, 1, 2 ....



n = 0 n = 0 n = 1 n = 1

d) System having (4n+5) carbon atoms in the ring.



n = 0 n = 0

ii) There is always one M.O. lower in energy than all others. $(\alpha + 2\beta)$

iii) If there is even no. of carbon atoms (4n+2 or 4n), there is a single M.O. highest in energy $(\alpha - 2\beta)$

iv) All M.O. appear in degenerate pair except one lowest in energy & for even numbered system, one highest in energy.

v) System with 4n carbon atoms have 3 types of M.O.

a) BMO b) NBMO c) ABMO

Other systems have only 2 types of M.O.

a) BMO c) ABMO

vi) NBMO of 4n system → only one degenerate pair.

vii) No. of BMO's is always odd in all the case

viii) System with even no of carbon atoms

No. of BMO = ABMO.

System with odd no. of carbon atoms

No. of BMO ≠ No. of ABMO.

For 4n+3 = No. of ABMO > BMO

For 4n+5 = No. of BMO > ABMO

ix) No. of e^- in any MO = 2 as per Aufbau & Hund rule.

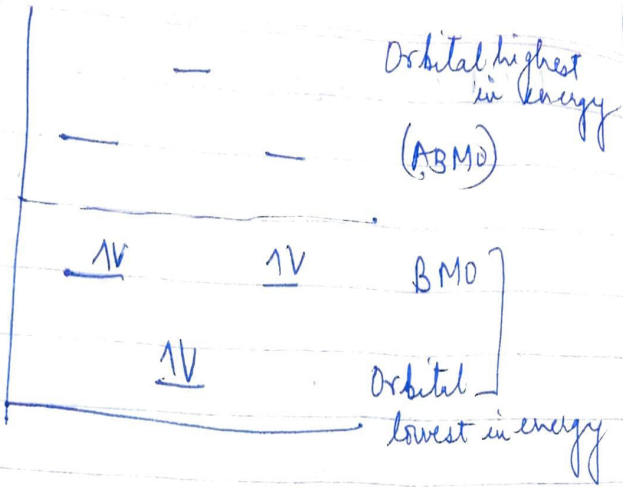
The above generalisations can be used for constructing π-mol. orbitals of monocyclic conjugated systems.

4n+2

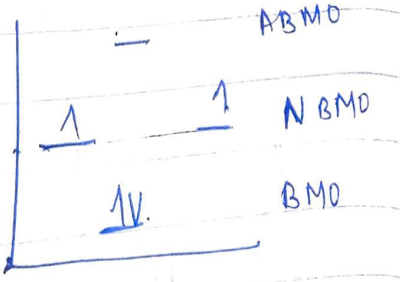
1) Benzene ∴ Total no. of M.O = 4×1+2 = 6

- One BMO lowest in energy (Point iv)
- One ABMO highest in energy.

Rem. orbitals 4n+2−2 = 4n i.e. 4 (2 BMO, 2 ABMO) (in form of pairs)



2) 4n (System) :-
Cyclobutadiene
3 types of MO: BMO, ABMO, NBMO (One degenerate pair)
∴ BMO = 1
ABMO = 1.



b) Cyclooctatetraene :- (8)
1 pair of NBMO = 2 MO.
Rem. 6.
One lowest in energy & one highest in energy.
Rem = 4
2 BMO & 2 ABMO

3) $(4n+3)$ System :-

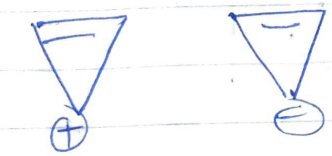
Cyclopropenyl ion $n=0$

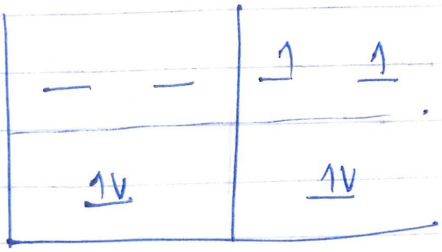
M.O. = 3

1 M.O. lowest in energy
& 1 pair of degenerate AB MO.

$3+4n-3 = 4n$ [2n bonding, 2n anti bonding] $n=0$, $n=0$

$n=0$



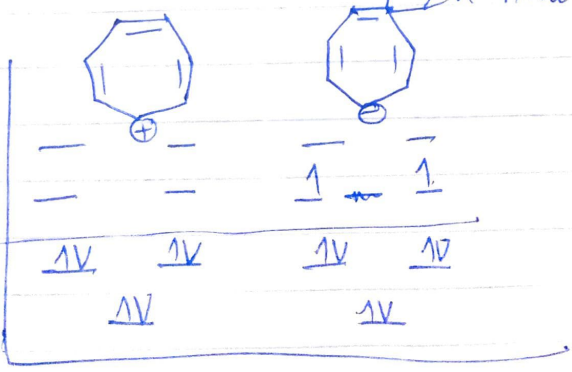


Cycloheptatrienyl ion :-

$4n+3 = 4\times1+3 = 7$ M.O.

One M.O. lowest in energy & 1 pair of degenerate AB MO,

$4n+3-3 = 4n$ [$n=1$: 2n bonding = 2, 2n Anti bond. = 2]



4) $(4n+5)$ (Cyclopentadienyl ion)

=

One B.M.O. lowest in energy.

~~2 ABMO (degenerate) highest energy~~

~~No. of degenerate B.M.O, always one pair more than no. of degenerate ABMO.~~

No. of remaining orbitals

$5 + 4n - 1 = 4n + 4$

$n = 0$

[2 π BMO
2 π ABMO]