

VIVEKANANDA COLLEGE

THAKURPUKUR, KOLKATA – 700063

NAAC ACCREDITED 'A' GRADE



Topic: Frost diagram (qualitative drawing)

Course Title: CEMA-CC-1-1-TH

Paper: Organic Chemistry- IA

Semester: I

Name of the Teacher: Sirsendu Gayen

Name of the Department: Chemistry

Frost Circles :

Use of Inscribed Polygon Method to Determine the Relative Energies of π Molecular Orbital's for Cyclic Planar and Completely Conjugated Compounds and to Classify Them as Aromatic and Antiaromatic

According to Hückel's rule, an aromatic compound must have $(4n + 2)$ π electrons that form an uninterrupted π electron cloud. In addition, it must be planar and cyclic. **The bonding π MO (molecular orbitals) of an aromatic compound are fully occupied, while the antibonding and non-bonding π MO are fully unoccupied.**

Whether or not a compound is aromatic may be determined by the so-called Frost circle - a simple method used to estimate the relative π orbital energies of both planar and cyclic compounds with an uninterrupted π electron system.

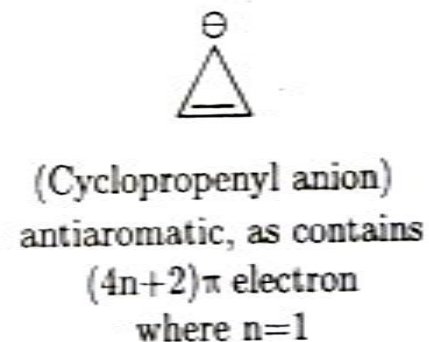
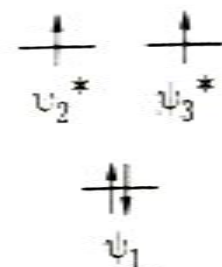
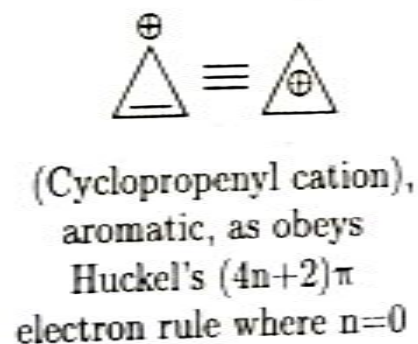
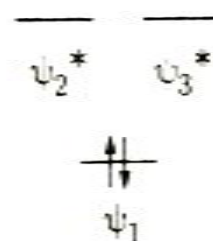
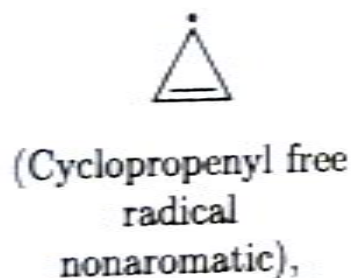
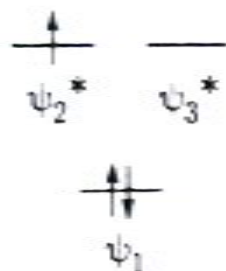
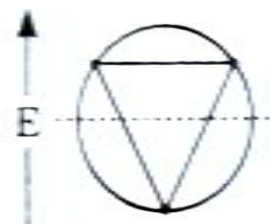
The relative energies of p molecular orbitals in planar cyclic conjugated systems can be determined by a simplified approach developed by A. A. Frost in 1953. This involves the following steps:

- 1) Draw a circle
- 2) Place the ring (polygon representing the compound of interest) in the circle with one of its vertices pointing down. Each point where the polygon touches the circle represents an energy level.
- 3) Draw a **horizontal line** passing through the centre of the circle.
- 4) Place the correct number of electrons in the orbitals, starting with the lowest energy orbital first, in accordance with Hund's rule.

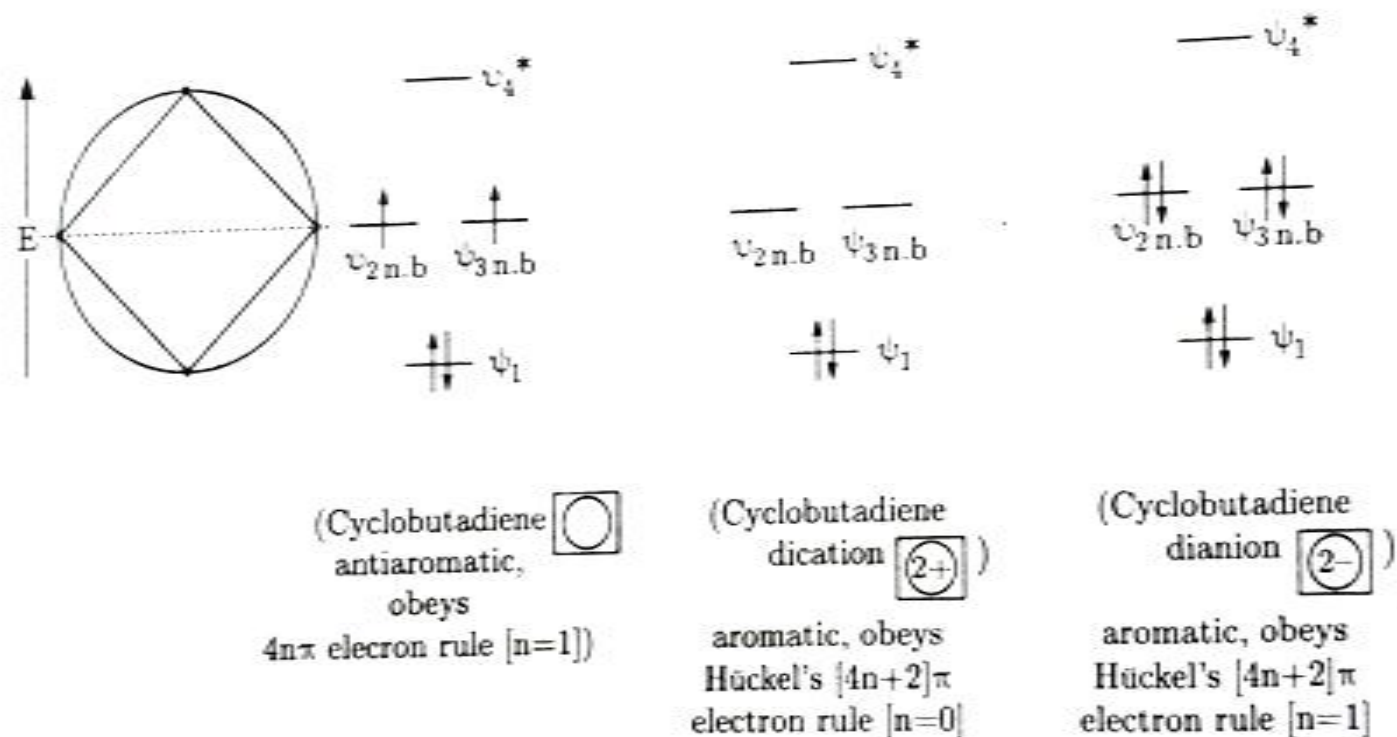
*** The total number of corners is equal to the number of π molecular orbitals. Corners touches below the horizontal line are bonding MOs, those above are antibonding MOs and those on the line are nonbonding Mos.**

*** The non bonding MOs have same energy content as those of participating atomic orbitals, while bonding MOs possess lower energy and antibonding MOs contain higher energy compared to atomic orbitals.**

Frost's circle presentation of three membered cyclic systems:

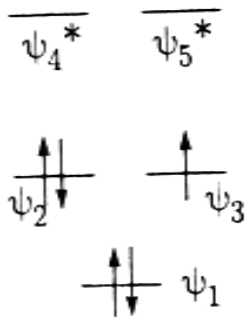
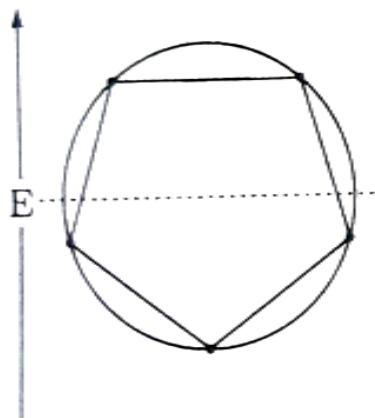


Frost's circle presentation of four membered cyclic systems:

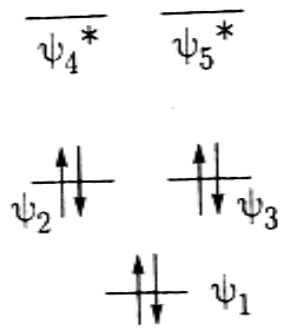


Although *cyclobutadiene dianion* is *aromatic*, it could *not* be *synthesised* as a strong *coulombic repulsion* is present in the doubly negatively charged species.

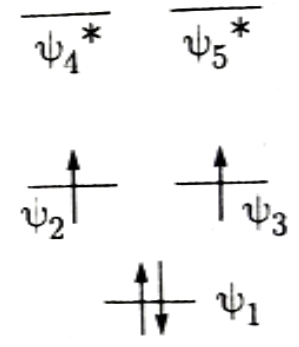
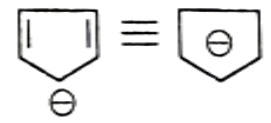
Frost's circle presentation of five membered cyclic systems:



Cyclopentadienyl
free radical
nonaromatic



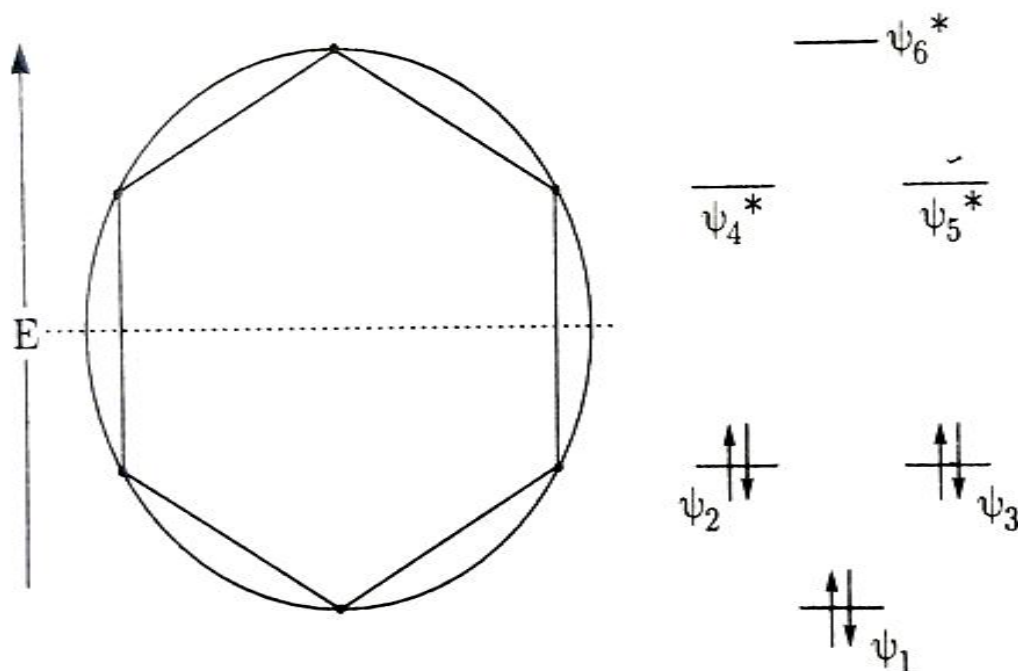
Cyclopentadienyl
anion; aromatic
obeys Hückel's
(4n+2) π electron
rule (n=1)



Cyclopentadienyl
cation, antiaromatic
follows 4n π
electron rule (n=1),

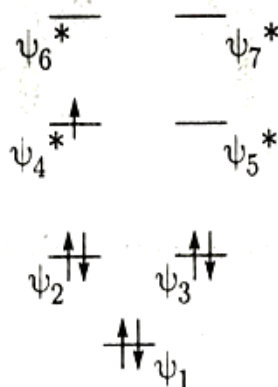
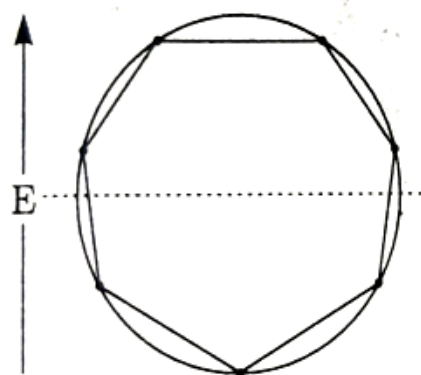


Frost's circle presentation of six membered cyclic systems:

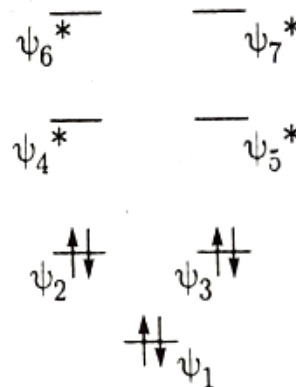


Benzene is aromatic
as it follows Hückel's
($4n+2$) π electron rule ($n=1$)
Aromatic sextet is full here,
and so benzene shows
unusual stability

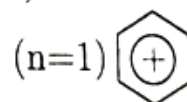
Frost's circle presentation of seven membered cyclic systems:



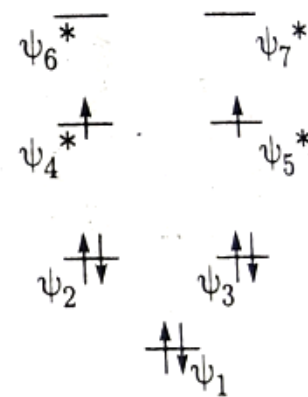
Cycloheptatrienyl
free radical,
nonaromatic



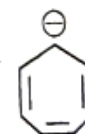
Cycloheptatrienyl
cation, aromatic,
obeys Hückel's
(4n+2)π electron rule



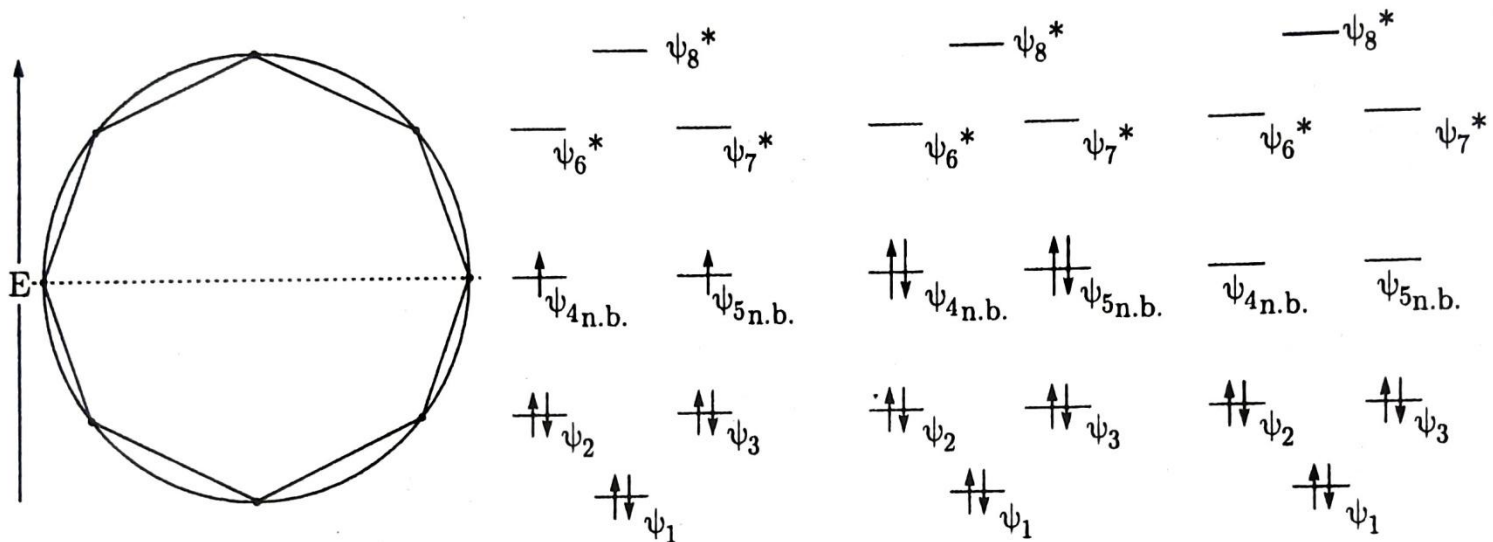
Tropylium cation



Cycloheptatrienyl
anion, should be
antiaromatic;
as it obeys 4nπ
electron rule (n=1)



Frost's circle presentation of eight membered ring



Cyclooctatetraene (COT) is antiaromatic, obeys $4n\pi$ electron rule, ($n=2$). Actually becomes non-aromatic as it attains a non planar structure which is tub shaped.



Unstable upon delocalisation of π electrons

Tub shaped COT stable

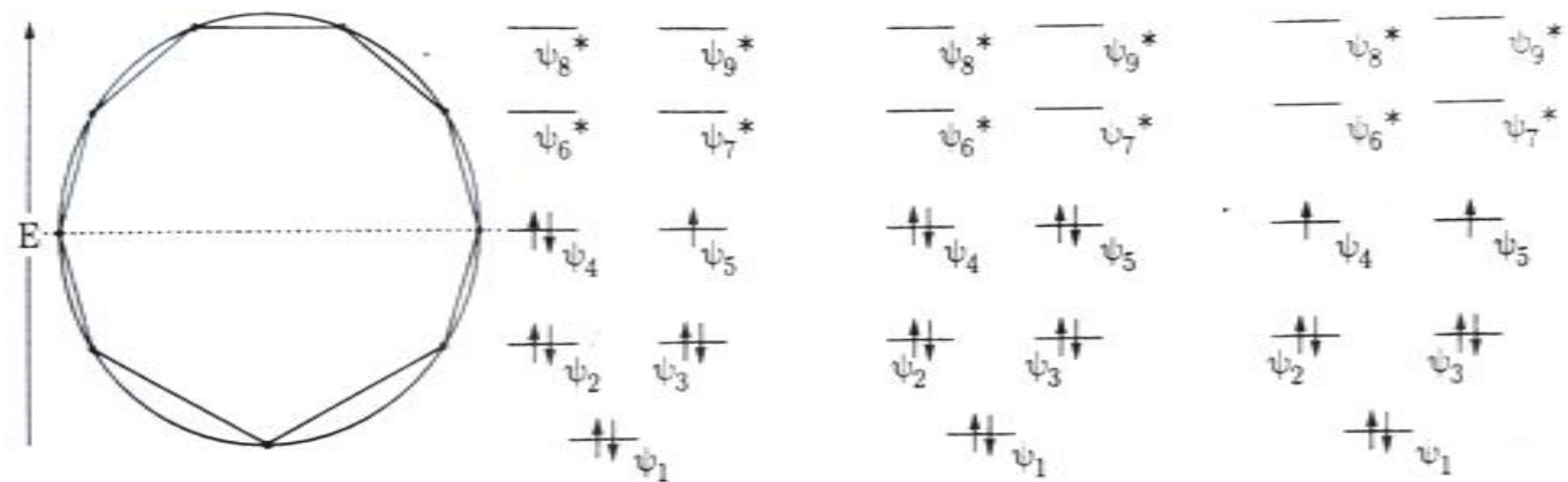
Cyclooctatetraene dianion is aromatic, follows Hückel's $(4n+2)\pi$ electron rule ($n=1$)



Cyclooctatetraene dication is aromatic, follows Hückel's $(4n+2)\pi$ electron rule ($n=1$)



Frost's circle presentation of nine membered ring

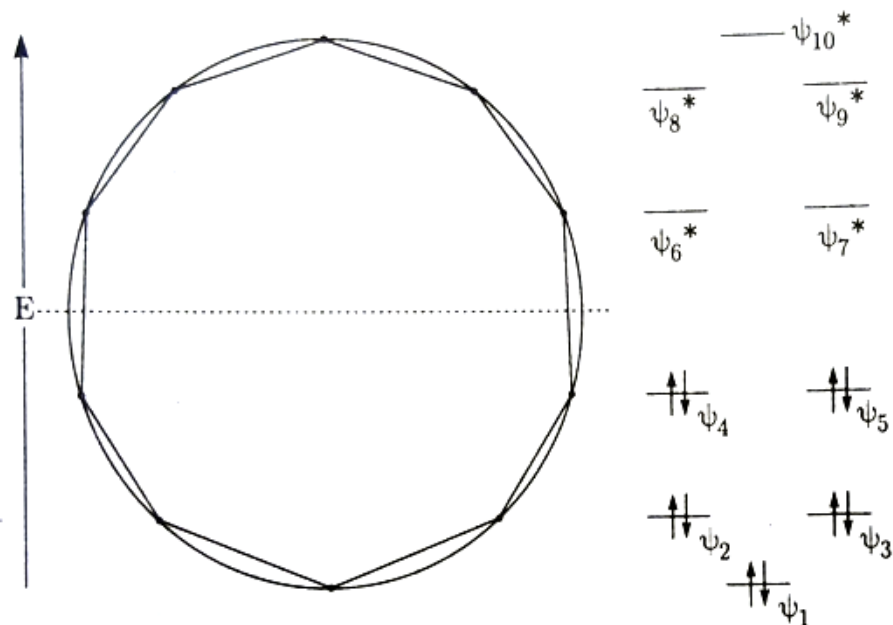


Cyclononatetraenyl
free radical
(non aromatic)

Cyclononatetraenyl
anion *aromatic*, obeys
Hückel's $(4n+2)\pi$
electron rule (n=12)

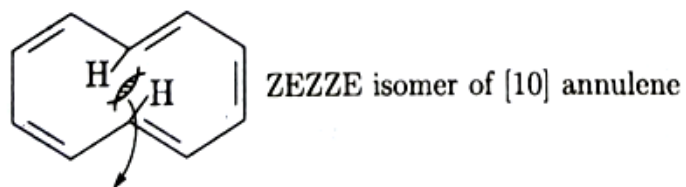
Cyclononatetraenyl
cation *antiaromatic*,
obeys Hückel's
 $4n\pi$ electron
rule (n=2)

Frost's circle presentation of ten membered ring



[10] annulene, should be aromatic as it possesses ten π electrons and hence obeys Hückel's $(4n+2)\pi$ electron rule ($n=2$)

But it is **nonaromatic** as the molecule becomes nonplanar due to trans annular interaction between the inner hydrogens present in ZZZZ isomer of [10] annulene. Other isomers of [10] annulene are even more unstable.



Transannular interaction between the inner hydrogens, which is basically a vander Waals force of repulsion.

References:

* Organic Chemistry, Volume I, Anup Pathak and Anupa Saha, Books & Allied Ltd; 2nd Revised edition

* Organic Chemistry – A Modern Approach, Volume I, Nimai Tewari, McGraw-Hill Education

* http://www.chemgapedia.de/vsengine/vlu/vsc/en/ch/12/oc/vlu_organik/aromaten/aromaten/aromaten_gesamt.vlu/Page/vsc/en/ch/12/oc/aromaten/aromaten/frost/frost.vscm1.html

* <https://www.masterorganicchemistry.com/2017/05/17/frost-circles/#one>