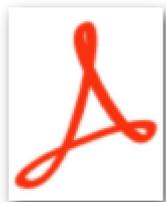# File:Chapter 8 - INNOVATIVE METHODS FOR THE PREDICTION OF AROMATIC ANTI-AROMATIC AND NON-AROMATIC BEHAVIOUR OF SIMPLE ORGANIC COMPOUNDS pp 81-91.pdf

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Chapter_8_-_INNOVATIVE_METHODS_FOR_THE_PREDICTION_OF_AROMATIC_ANTI-AROMATIC_AND_NON-AROMATIC_BEHAVIOUR_OF_SIMPLE_ORGANIC_COMPOUNDS_pp_81-91.pdf (0 × 0 pixels, file size: 172 KB, MIME type: application/pdf)

Summary

Description	In this organic chapter 8, formulae-based mnemonics have been highlighted by classifying the negative charge on carbon atom (localized or delocalized) within the ring system in an innovative and time economic way. Here, I have tried to hub two (02) time economic mnemonics by including two (02) formulae for the prediction of aromatic and antiaromatic behavior of simple organic compounds. This chapter includes innovative formulae involving calculation of 'A' value by just manipulating the no of π bonds within the ring system and delocalized negative charge of carbon if any (DNC) with one (01). The organic compound having cyclic, planar, conjugated with an even number of 'A' value will be treated as aromatic and with an odd number of 'A' value will be treated as an anti aromatic in nature. This chapter encourages students to solve multiple choice type questions (MCQs) on aromaticity of organic compounds and its related properties at different competitive examinations in a time economic ground.
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Chapter-8
INNOVATIVE METHODS FOR THE PREDICTION OF AROMATIC, ANTI AROMATIC AND NON-AROMATIC BEHAVIOUR OF SIMPLE ORGANIC COMPOUNDS

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In this organic chapter 8, formulae-based mnemonics have been highlighted by classifying the negative charge on carbon atom (localized or delocalized) within the ring system in an innovative and time economic way. Here, I have tried to hub two (02) time economic mnemonics by including two (02) formulae for the prediction of aromatic and antiaromatic behavior of simple organic compounds. This chapter includes innovative formulae involving calculation of 'A' value by just manipulating the no of π bonds within the ring system and delocalized negative charge of carbon if any (DNC) with one (01). The organic compound having cyclic, planar, conjugated with an even number of 'A' value will be treated as aromatic and with an odd number of 'A' value will be treated as an anti aromatic in nature. This chapter encourages students to solve multiple choice type questions (MCQs) on aromaticity of organic compounds and its related properties at different competitive examinations in a time economic ground.

The conventional methods, on the detection of planarity of organic compounds by the prediction of hybridization state of carbon atoms in simple organic compounds and their relative aromaticity, are time-consuming [1-7]. Keeping this in mind, in this innovative pedagogical chapter 8, some innovative mnemonics have been introduced along with their omission behaviors, applications, and problems in the different competitive examinations to make aromaticity metabolic, time economic and interesting [8-11].

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METHODOLOGY

1. Prediction of hybridization state of carbon atoms in different organic compounds:

A. Classification of Negative Charge on carbon in organic compounds

The negative charge on the carbon atom of any organic compounds can be generally classified into two types as delocalized negative charge (DNC) and localized negative charge (LNC) as follows:

i)Delocalized negative charge (DNC): When the negative charge on the carbon atom of the ring system of organic compounds undergo delocalization through conjugation then, it is treated as delocalized negative charge (DNC). Negative charge bearing carbon atom of the ring system of the organic compound, when, directly attached with single bonds only from all ends with a ring system, then it is considered as DNC containing carbon atom and its negative charge is to be treated as delocalized negative charge (DNC).

Eg. In cyclopropenyl anions, cyclopentadienyl anions and cycloheptatrienyl anions, (**Fig. 2.14, Fig. 2.15, Fig. 2.16),** the negative charge on C atom is to be treated as DNC, because it is directly attached with single bonds directly from all side of the ring system.
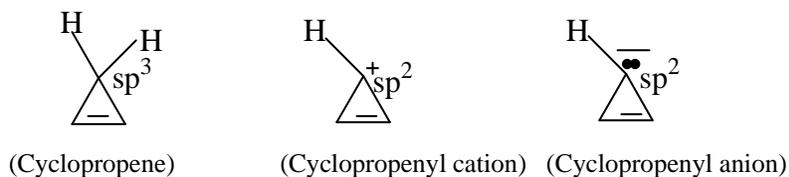

(Cyclopropene)   (Cyclopropenyl cation)   (Cyclopropenyl anion)

Fig. 2.14: Structure of Cyclopropene, Cyclopropenyl cation, and Cyclopropenyl anion

(Cyclopentadienyl anion)   (Cyclopentadienyl cation)   (Cyclopentadiene)

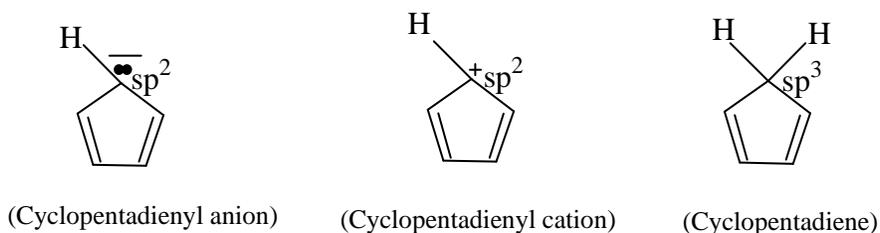**Fig. 2.15: Structure of Cyclopentadienyl anion, Cyclopentadienyl cation, and Cyclopentadiene**

(Cycloheptatrienyl anion)   (Cycloheptatrienyl cation)   (Cycloheptatriene)
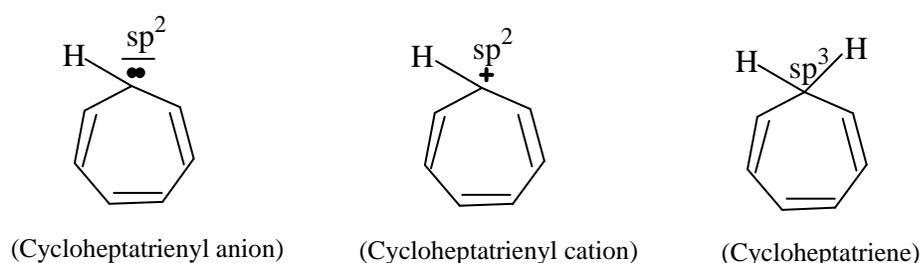
Fig. 2.16: Structure of Cycloheptatrienyl anion, Cycloheptatrienyl cation, and Cycloheptatriene

ii)Localized negative charge (LNC): When the negative charge on the carbon atom of the ring system of organic compounds does not undergo delocalization through conjugation then it is to be treated as Localized negative charge (LNC). Negative charge bearing carbon atom of the ring system of the organic compound when directly attached with single and double bonds with the ring system is to be considered as LNC containing carbon atom and its negative charge is to be treated as localized negative charge (LNC).

Ex. In phenyl carbanion, negative charge on carbon atom is treated as LNC, because it is directly attached with one double bond to other carbon atom within the phenyl ring.

B) Planarity of organic compounds

Planarity is one of the vital characteristics for the prediction of aromatic, antiaromatic and nonaromatic behavior of organic compounds. For aromatic and antiaromatic behavior, the compound must be planar, whereas, nonplanar organic compounds are to be treated as nonaromatic in nature.

Planarity of organic compounds depends on the nature of the hybridization state of carbon atoms present in them. When all carbon atoms of organic compounds are in same (sp^2) hybridization state, then, they are treated as planar but when there is a mixing of sp^2 and sp^3 hybridization state within the carbon atoms of organic compounds, then, they are to be treated as nonplanar. Prediction of hybridization state of organic compounds discussed in **chapter 2** and its comparative study with conventional formula has been discussed in **chapter 3**.

2. Conventional methods for Identifying Aromatic and Anti-Aromatic behavior of organic compounds:

It was first devised by Huckel in 1931[1].

i) Aromatic nature of organic compound

a.Cyclic b. Planer, where, all bonded atoms are in the same plane (having sp^2 hybridized) c. A conjugated molecule with conjugated π-electron system d. Contains $(4n + 2)$ π electrons, where, n is a positive integer (n=0,1,2,3 etc.)

ii) Anti Aromatic nature of organic Compound:

a.Cyclic b. Planer, where, all bonded atoms are in the same plane (having sp^2 hybridized) c. A conjugated molecule with conjugated π-electron system d. Contains $4n\pi$ electrons, where, n is a positive integer (n = 0,1,2,3 etc.).

iii) Non-Aromatic Nature of organic Compound:

If a compound violates any one of the above three conditions (a or b or c) then it is nonaromatic in nature.

3. Innovative methods for Aromatic and Anti-Aromatic behavior of simple organic compounds

The present innovative mnemonics involving two formulae for calculation of 'A' value by just manipulating the number of π bonds within the ring system and delocalized negative charge of carbon atoms (DNC) as the number of electron pair (e^- p) within the ring system with constant one (01).

Organic compounds, having cyclic, planar (i.e. all the carbon atoms having the same state of hybridization, sp^2), conjugated with an even number of 'A' value will be treated as aromatic in nature and with an odd number of 'A' value will be treated as an anti aromatic in nature.

i) Prediction of Aromatic behavior:

The organic compound must be cyclic, planar (i.e. all the carbon atoms having same state of hybridization) and conjugated with even number of A value, where, $A = \pi b + e^- p (DNC) + 1$ (constant), here, πb = number of π bonds within the ring system and $e^- p$ (DNC) = number of electron pair within the ring system (delocalized negative charge on carbon atoms of ring system). Here, each delocalized negative charge (DNC), treated as one electron pair ($e^- p$). If the value of 'A', for a certain organic compound comes out as an even number then this compound will be treated as aromatic compound.

ii) Prediction of Anti-aromatic behavior:

In the second case, the organic compound, must be cyclic, planar (i.e. all the carbon atoms having same state of hybridization) and conjugated with odd number of A value, where, $A = \pi b + e^- p (DNC) + 1$ (constant),

here, πb = number of π bonds within the ring system and $e^- p$ (DNC) = number of electron pair within the ring system (delocalized negative charge on carbon atoms of ring system). Here, each delocalized negative charge (DNC), treated as one electron pair ($e^- p$). If the value of 'A', for a certain organic compound comes out as an odd number then this compound will be treated as antiaromatic.

iii) General Condition for Non-aromatic behavior of Organic Compounds:

Any compound that lacks one or more of the first three features (cyclic/conjugated/planar), that is, it may be acyclic/non-planar/nonconjugated, is to be treated as nonaromatic.

Innovative Formula: Evaluation of A Value to predict Aromatic and Anti Aromatic Nature

$$A = \pi b + e^- p \text{ (DNC)} + 1 \text{(constant)} = \text{even no} = \text{Aromatic}$$

$$A = \pi b + e^- p \text{ (DNC)} + 1 \text{ (constant)} = \text{odd no} = \text{Anti Aromatic}$$

where, πb = number of π bonds within the ring system, $e^- p$ (DNC) = number of electron pair within the ring system (delocalized negative charge on carbon atoms of ring system). Here, each delocalized negative charge (DNC), treated as one electron pair ($e^- p$).

RESULTS AND DISCUSSION

1. Innovative method for prediction of the hybridization state (sp^2 & sp^3) of carbon atoms in organic compounds

Prediction of the hybridization state (sp^2 & sp^3) of carbon atoms in organic compounds has been **discussed in chapter 2.**

2. Innovative methods for prediction of Aromatic and Anti-Aromatic behavior of simple organic compounds

Innovative *Formula:* **Evaluation of A Value to predict Aromatic and Anti Aromatic Nature**

$$\mathbf{A = \pi b + e^- p \text{ (DNC)} + 1\text{(constant)} = \text{even no} = \text{Aromatic}}$$

$$\mathbf{A = \pi b + e^- p \text{ (DNC)} + 1 \text{ (constant)} = \text{odd no} = \text{Anti Aromatic}}$$

where, πb = number of π bonds with in the ring system, $e^- p$ (DNC) = number of electron pair within the ring system (delocalized negative charge on carbon atoms of ring system). Here, each delocalized negative charge (DNC), treated as one electron pair ($e^- p$).

Any compound that lacks one or more of the first three features i.e., it may be acyclic/non-planar/non conjugated is to be treated as nonaromatic.

Ex.a. In cyclopropene, cyclopentadiene, and cycloheptatriene (**Fig.2.14, Fig.2.15, Fig.2.16),** the vertex carbon atom is in sp^3 hybridization state (discussed in chapter 3). Here in all cases, the presence of one sp^3 hybridized vertex carbon atom along with other sp^2 hybridized carbons makes cyclopropene, cyclopentadiene, and cycloheptatriene nonplanar and thus nonaromatic.

Ex.b. In cyclopropenyl anion, cyclopentadienyl anion and cycloheptatrienyl anion (**Fig. 2.14, Fig. 2.15, Fig. 2.16),** vertex carbon atom bearing negative charge is in sp^2 hybridization state (discussed in chapter 3). Here in all cases, negative charge of vertex carbon atom is treated as delocalized negative charge (DNC) and can be counted during prediction of A value and not to be counted for the prediction of the hybridization state. The presence of all sp^2 hybridized carbons in cyclopropenyl anions, cyclopentadienyl anions and cycloheptatrienyl anions makes them planar. Here, A value for cyclopropenyl anion = πb + e⁻ p (DNC) + 1(constant) = 1+1+1 = 3 (odd no) = Anti Aromatic; A value for cyclopentadienyl anion = πb + e⁻ p (DNC) + 1(constant) = 2+1+1 = 4 (even no) = Aromatic and A value for cycloheptatrienyl anion = πb + e⁻ p (DNC) + 1(constant) = 3+1+1 = 5 (odd no) = Anti Aromatic.

Ex.c. In cyclopropenyl cation, cyclopentadienyl cation and cycloheptatrienyl cation (**Fig. 2.14, Fig. 2.15, Fig. 2.16),** vertex carbon atom bearing positive charge is in sp^2 hybridization state (discussed in chapter 3). The presence of all sp^2 hybridized carbons in cyclopropenyl cations, cyclopentadienyl cations and cycloheptatrienyl cations makes them planar. Here, A value for cyclopropenyl cation = πb + e⁻ p (DNC) + 1(constant) = 1+0+1 = 2 (even no) = Aromatic; A value for cyclopentadienyl cation = πb + e⁻ p (DNC) + 1(constant) = 2+0+1 = 3 (odd no) = Anti Aromatic and A value for cycloheptatrienyl cation = πb + e⁻ p (DNC) + 1(constant) = 3+0+1 = 4 (even no) = Aromatic.

In cyclobutadiene and cyclooctatetraene (**Fig. 2.17),** all carbon atoms are in sp^2 hybridized (discussed in chapter 3), which makes them planar. Here, A value for cyclobutadiene = πb + e⁻ p (DNC) + 1(constant) = 2+0+1 = 3 (odd no) = Anti Aromatic and A value for cyclooctatetraene = πb + e⁻ p (DNC) + 1(constant) = 4+0+1 = 5 (odd no) = Anti Aromatic.
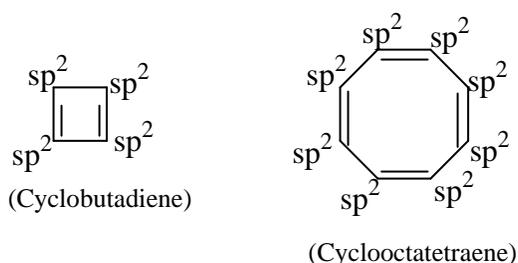

Fig. 2.17: Structure of Cyclobutadiene and Cyclooctatetraene

Adequate examples of aromatic, anti-aromatic and non-aromatic behavior of simple organic compounds have been described in **Table 8.6**.

Table 8.6: Aromatic, anti-aromatic and non-aromatic behavior of organic compounds

Organic Compound (Cyclic, Planar/Cyclic, non-planar)	πb value [πb = number of π bonds within the ring system]	e⁻p value [e⁻p = number of delocalized electron pair outside or adjacent to the ring system]	A value [A = πb + e⁻p + 1(constant)] (even no/odd no)	Nature of compound (aromatic/anti-aromatic/non aromatic)
Benzene or [6] annulene (Cyclic, Planar)	3 π bonds	0	3 + 0+1 = 4 (even no)	Aromatic
Naphthalene (Cyclic, Planar)	5 π bonds	0	5 + 0 +1 = 6 (even no)	Aromatic
Anthracene (Cyclic, Planar)	7 π bonds	0	7 + 0 + 1 = 8 (even no)	Aromatic
Cyclopropene (Cyclic, non planar due to one sp³ hybridized carbon atom)	1 π bond	0	1 + 0 + 1 = 2 (even no)	Non-aromatic
Cyclopropenyl cation (Cyclic, Planar)	1 π bond	0	1 + 0 + 1 = 2 (even no)	Aromatic
Cyclopropenyl anion (Cyclic, Planar)	1 π bond	1 (For one negative charge on carbon which undergoes delocalization)	1 + 1+ 1 = 3 (odd no)	Anti-aromatic
Cyclobutadiene or [4] annulene (Cyclic, Planar)	2 π bonds	0	2 + 0 + 1 = 3 (odd no)	Anti aromatic
Cyclopentadiene (Cyclic, non planar due to one sp³ hybridised carbon atom)	2 π bonds	0	2 + 0 + 1 = 3 (odd no)	Non-aromatic
Cyclopentadienyl cation (Cyclic, Planar)	2 π bonds	0	2 + 0 + 1 = 3 (odd no)	Anti-aromatic
Cyclopentadienyl anion (Cyclic, Planar)	2 π bonds	01(For one negative charge on carbon which undergo delocalization)	2 + 1 + 1 = 4 (even no)	Aromatic
Cyclooctatetraene or [8] annulene (Cyclic, Planar)	4 π bonds	0	4 + 0 + 1 = 5 (odd no)	Anti-aromatic
Cyclooctatrienyl cation (Cyclic, non-planar due to one sp³ hybridized carbon atom adjacent to positive charge)	3 π bonds	0	3 + 0 + 1 = 4 (even no)	Non aromatic

OMISSION BEHAVIOR OF AROMATIC AND NON-AROMATIC ORGANIC COMPOUNDS:

There are some compounds, which do not follow the above rules of A value. Huckel's also cannot explain the aromatic or non-aromatic behavior of these compounds. These compounds have been represented below.

Cyclodecapentaene **(Fig.8.25)**, is non aromatic due to the interaction of the hydrogen of 1 and 6, it is non planar, although, here, $A = \pi b + e^- p$ (DNC) + 1(constant) = 5 + 0 + 1 = 6 (even number).

Pyrene **(Fig.8.25)**, is a polycyclic aromatic hydrocarbon consisting of four fused benzene rings, resulting in a flat aromatic system. It has 8 π bonds and zero (0) DNC. Here, A = 8 + 0 + 1 = 9 (odd number). But still, it is aromatic instead of antiaromatic because double bonded C_{15}-C_{16} does not take part in resonance.
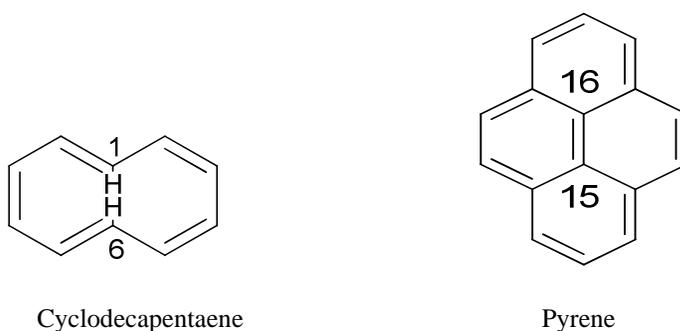

Cyclodecapentaene   Pyrene

Fig. 8.25. Geometry of Cyclodecapentaene and Pyrene

APPLICATIONS OF AROMATICITY IN ORGANIC CHEMICAL EDUCATION

Aromaticity has various applications as follows:

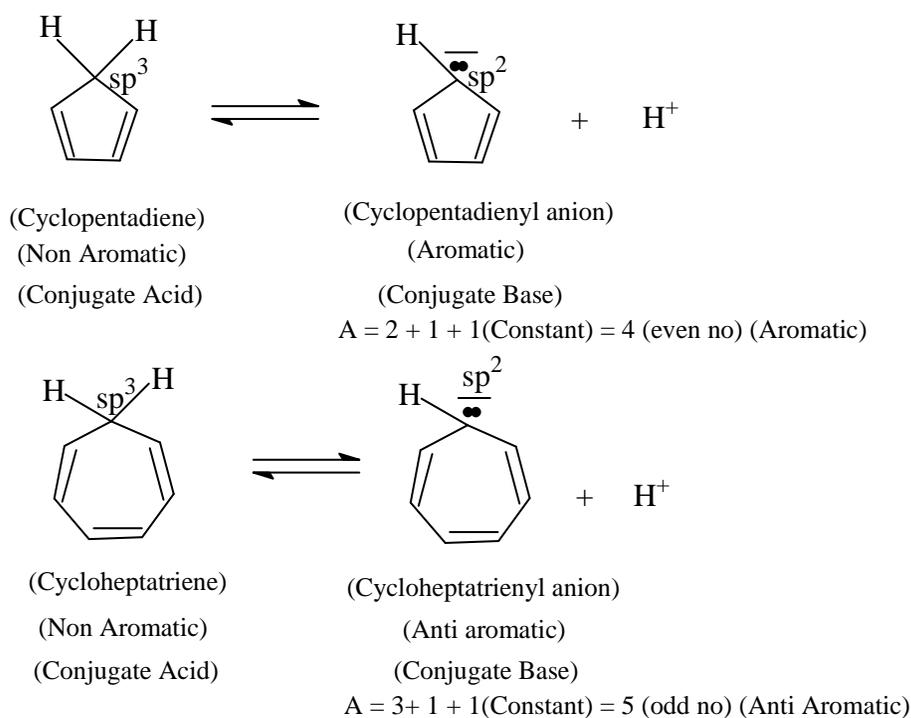**i) Predicting stability and reactivity order of organic compounds with aromaticity**

Stability of organic compounds follows the order, Aromatic > nonaromatic> antiaromatic. Since reactivity is inversely proportional to the stability, therefore, reactivity follows the order, anti-aromatic > nonaromatic> aromatic.

Ex.a. cyclopropenyl cation (Aromatic) > cyclopropene (Non aromatic) > cyclopropenyl anion (Anti aromatic) (Stability) and reactivity order is cyclopropenyl cation (Aromatic) < cyclopropene (Non aromatic) < cyclopropenyl anion (Anti aromatic).

ii)Predicting acidic character of organic compounds with aromaticity

Cyclopentadienyl anion, the conjugate base of cyclopentadiene, is aromatic, whereas, cycloheptatrienyl anion, the conjugate base of cycloheptatriene, is antiaromatic. Since, Stability of organic compounds, follows the order,

Aromatic > nonaromatic> antiaromatic, therefore, the conjugate base of cyclopentadiene is much more stable than the conjugate base of cycloheptatriene, which is depicted below.

(Cyclopentadiene)
(Non Aromatic)
(Conjugate Acid)

(Cyclopentadienyl anion)
(Aromatic)
(Conjugate Base)
A = 2 + 1 + 1(Constant) = 4 (even no) (Aromatic)

(Cycloheptatriene)
(Non Aromatic)
(Conjugate Acid)

(Cycloheptatrienyl anion)
(Anti aromatic)
(Conjugate Base)
A = 3+ 1 + 1(Constant) = 5 (odd no) (Anti Aromatic)

Hence, in the first case, due to the stability of the conjugate base, cyclopentadienyl anion, the equilibrium shifted towards the forward direction, which increases the concentration of H^+ (proton) as well as the acidity of cyclopentadiene over cycloheptatetraene. Therefore, cyclopentadiene is much more acidic than cycloheptatetraene.

iii) Predicting stability and reactivity order of organic compounds in aromaticity using molecular orbital theory (MOT)

Factors affecting the stability of organic compounds in aromaticity with the help of molecular orbital theory (MOT):

- **Stability α Number of filled bonding molecular orbitals (BMOs)**

- **For the same number of filled BMOs, Stability α 1 / Number of electrons in antibonding molecular orbitals (ABMOs)**

Ex. a. Decreasing order of stability among cyclopropenyl anion, cyclopropenyl radical and cyclopropenyl cation is as follows: cyclopropenyl cation > cyclopropenyl radical > cyclopropenyl anion. This is due to the presence of the different number of electrons in antibonding molecular orbitals (ABMOs) of the cyclopropenyl anion, cyclopropenyl cation and cyclopropenyl radical, where, in all cases, the number of filled bonding molecular orbital (FBMO) be same and is one (**Fig.8.26**). Since

reactivity is inversely proportional to the stability, therefore, reactivity follows the order cyclopropenyl cation < cyclopropenyl radical < cyclopropenyl anion. Becoz, with an increasing number of electrons in higher energetic antibonding molecular orbitals (ABMOs) increases reactivity and thus decreases the stability of organic compounds.

Ex. b. Decreasing order of stability among cyclopentadienyl anion, cyclopentadienyl radical and cyclopentadienyl cation is as follows:

cyclopentadienyl anion (FBMOs = 3) > cyclopentadienyl radical (FBMOs = 2) > cyclopentadienyl cation (FBMOs = 1).

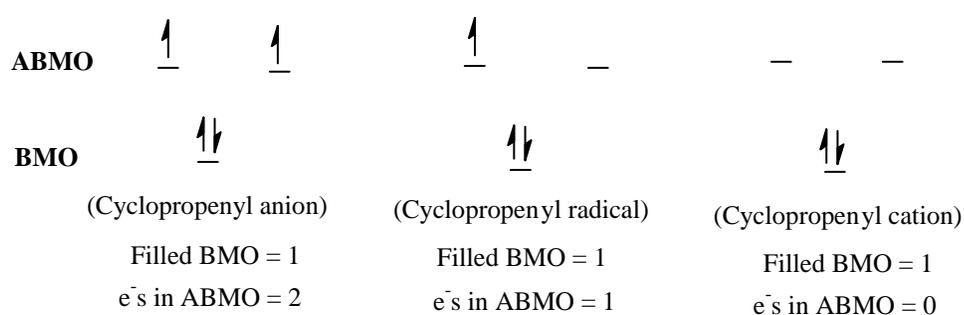Here, FBMOs = filled bonding molecular orbitals (**Fig.8.27**).

Fig.8.26: Molecular orbital diagram of the cyclopropenyl anion, cyclopropenyl radical and cyclopropenyl cation
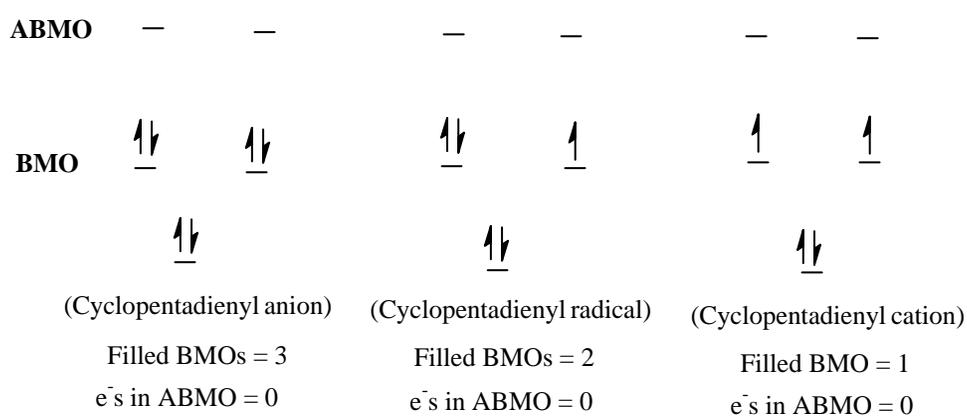

Fig.8.27: Molecular orbital diagram of cyclopentadienyl anion, cyclopentadienyl radical and cyclopentadienyl cation

PROBLEMS ON AROMATICITY

Q.1. Which one of the following chemical system is nonaromatic?

a)Benzene   b)Naphthalene   c)Cyclopropenyl anion   d)Cyclopentadiene

Ans: (d) Cyclopentadiene (sp^3 hybridized C atom makes it nonplanar, hence, non-aromatic)

Q.2. The nonaromatic compound among the following is?

a) Cyclopentadiene   b) Benzene   c) Naphthalene   d) None

Ans: (a) Cyclopentadiene (sp^3 hybridized C atom makes it nonplanar, hence, non-aromatic)

Q.3. Which one is more stable?

a) Cyclopentadienyl anion   b) Cyclopentadiene   c)cyclopentadienyl cation   d) None

Ans: a) Cyclopentadienyl anion (Aromatic)

Conclusion

It may be expected that these two-time economic innovative methods will help the student of chemical education at Undergraduate, Senior Undergraduate and Post-Graduate level to predict the aromatic and antiaromatic behavior of organic compounds along with nonaromatic nature. **Experiments,** *in vitro,* **on 100 students, showed that by using these formulae students can save up to 4-5 minutes' time in the examination hall to find out the aromatic/antiaromatic character of organic compounds. Based on this, I can strongly recommend using these two-time economic innovative mnemonics including two formulae in the field of organic chemistry.**

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