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Summary

Description	In this chapter, formulae-based mnemonics have been highlighted by classifying the lone pair of electrons (localized or delocalized) 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 heterocyclic 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 lone pair electron (DLP) with one (01). The heterocyclic compound having cyclic, planar, 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 antiaromatic in nature. In case of a multi hetero atom based heterocyclic compound, containing both delocalized lone pair electron (DLP) and localized lone pair electron (LLP) based heteroatoms, Aromatic and Anti Aromatic behavior should be predicted with respect to DLP based hetero atom only. But when heterocyclic compounds contain both LLP based hetero atoms then Aromaticity should be predicted with respect to that heteroatom which contains the lowest possible position number as per IUPAC nomenclature or any one of the heteroatom.
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Chapter-9

INNOVATIVE METHODS FOR THE PREDICTION OF AROMATIC, ANTI-AROMATIC AND NON-AROMATIC BEHAVIOUR OF HETEROCYCLIC COMPOUNDS

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In this chapter, formulae-based mnemonics have been highlighted by classifying the lone pair of electrons (localized or delocalized) 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 heterocyclic 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 lone pair electron (DLP) with one (01). The heterocyclic compound having cyclic, planar, 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 antiaromatic in nature. In case of a multi hetero atom based heterocyclic compound, containing both delocalized lone pair electron (DLP) and localized lone pair electron (LLP) based heteroatoms, Aromatic and Anti Aromatic behavior should be predicted with respect to DLP based hetero atom only. But when heterocyclic compounds contain both LLP based hetero atoms then Aromaticity should be predicted with respect to that heteroatom which contains the lowest possible position number as per IUPAC nomenclature or any one of the heteroatom. The conventional methods on the detection of planarity of organic compounds through the prediction of hybridization state of carbon atoms in simple organic compounds and their relative aromaticity are time consuming[1-6]. Keeping this in mind, in this innovative pedagogical chapter 9, some innovative mnemonics have been introduced by classifying a lone pair of electrons as LLP and DLP, along with their omission behaviors, applications, and problems in different competitive examinations to make aromaticity of heterocyclic compounds, metabolic, time economic and interesting[7].

1.Hückel, Erich, “Quantentheoretische Beiträge zum Benzolproblem I. Die Elektronenkonfiguration des Benzols undverwandter Verbindungen”, *Z.Phys.* 70 (1931): 204–86.
2. I.L. Finar, *Organic Chemistry 2* (Pearson: 2002), 606-637.
3. R.T. Morrison, and R.N. Boyd, *Organic Chemistry* (1992), 1059-1061.
4. T.W.Graham Solomons and C.B. Fryhle *Organic Chemistry* (Wiley, India: 2012), 655-658.
5. J.G. Smith, *Organic Chemistry* (2008), 616-619.
6. Jerry March, *Advanced Organic Chemistry: Reaction, Mechanisms, and Structure* (JOHN WILEY & SONS: 2005), 45.
7.A.Das, "Lone Pair Electron Discriminate Hybridization with Aromatic and Anti Aromatic behavior of Heterocyclic Compounds-Innovative Mnemonics”, *World Journal of Chemical Education* 6(April 2018):95-101,doi:10.12691/wjce-6-2-4, http://pubs.sciepub.com/wjce/6/2/4/.

METHODOLOGY

1.Prediction of the hybridization state of the heteroatom in different heterocyclic compounds:

A) Classification of Lone Pair of Electrons in heterocyclic compounds

Lone Pair of electrons can be generally classified into two types as Delocalized lone pair electron (DLP) and Localized lone pair electron (LLP) as follows:

i)Delocalized lone pair electron (DLP): When the lone pair of electron of heteroatom undergo delocalization through conjugation then it is to be treated as a delocalized lone pair electron (DLP). The heteroatom (atom containing lone pair electron) which is directly attached with single bonds only from all ends is to be considered as DLP based heteroatom and its lone pair is to be treated as (DLP).

Eg. In Pyrrole **(Fig.2.18)**, **the** lone pair of N atom is to be treated as DLP because it is directly attached with three single bonds only.

ii)Localized lone pair electron (LLP): When the lone pair electron of the heteroatom does not undergo delocalization through conjugation then it is to be treated as Localized lone pair electron (LLP). The heteroatom (atom containing lone pair electron) which is directly attached with single and double bonds with the ring system is to be considered as LLP containing a hetero atom and its lone pair is to be treated as a localized lone pair electron (LLP).

Eg. In Pyridine **(Fig.2.18),** the lone pair of N atom is to be treated as LLP because it is directly attached with double and single bonds with the ring system.

B) Planarity of Heterocyclic Compounds

Planarity is one of the vital features for prediction aromatic, antiaromatic and nonaromatic behavior of heterocyclic compounds or other organic compounds. For aromatic and antiaromatic behavior the compound must be planar, whereas, the nonplanar compound is nonaromatic in nature. Planarity of heterocyclic compounds depends on the nature of the hybridization state of carbon and heteroatoms present in it. When all atoms (carbon and hetero) in the heterocyclic compounds having sp^2 hybridized then it is planar but when there is a mixing of sp^2 and sp^3 hybridization state then it is treated as nonplanar.

C) The conventional method for prediction of hybridization state of the heteroatom in heterocyclic compounds:

Hybridization state for a molecule can be calculated by the formula P = 1/2 (V+MA−C+A),

Where, V = Number of valance electrons in the central atom, MA = Number of surrounding monovalent atoms, C = Cationic charge, A = Anionic charge, P = power of the hybridization state of the central atom

D)Innovative method for predicting hybridization state of the heteroatom to forecast planarity of different heterocyclic compounds:

Prediction of sp^2 and sp^3 Hybridization state

Power on the Hybridization state of the heteroatom (P_{Hyb}) = (T_{SLLP}) – 1

where, P_{Hyb} = Power on the Hybridization state of the heteroatom, T_{SLLP} = (Total no of σ bonds around each central atom + Localized lone pair electron), here, S = number of σ bonds around each central atom, LLP = Localized lone pair of electron. If the power of the hybridization state (P_{Hyb}) will be 03, 02 and 01 then the hybridization state will be sp^3, sp^2, and sp respectively. All single (-) bonds are the σ bond, in a double bond (=), there is one σ and one π. In addition to these, each localized lone pair electron (LLP) can be treated as one σ bond [7].

2. Identifying Aromatic and Anti-Aromatic behavior of organic compounds

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

A) Conventional methods:

i) Aromatic nature of organic compound

1.Cyclic molecule,

2.Planer molecule in which all bonded atoms lie in the same plane (having sp^2 hybridized)

3.Conjugated molecule with conjugated π-electron system,

4.Contains (4n + 2) π electrons, where, n is a positive integer (n = 0,1,2,3 etc.)

ii) Anti Aromatic nature of organic Compound:

1. Cyclic molecule,
2. Planer molecule in which all bonded atoms lie in the same plane (having sp^2 hybridized)
3. A conjugated molecule with a conjugated π-electron system,

4. 4nπ 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 (1 or 2 or 3) then it is nonaromatic in nature.

B) Innovative methods for Aromatic and Anti-Aromatic behavior of heterocyclic compounds

The present study will be an innovative mnemonic involving calculation of ‘A' value by just manipulating the no of π bonds within the ring system and delocalized lone pair electron (DLP) with one (01).

The heterocyclic compound having cyclic, planar, conjugated (i.e. all the carbon atoms having the same state of hybridization, sp^2) 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 antiaromatic in nature.

i) Prediction of Aromatic behavior:

In the first case, the 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 = πb+DLP+1(constant)], here, πb = number of π bonds within the ring system and DLP = Delocalized lone pair of electron (lone pair of electron of heteroatom which can undergoes delocalization).

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 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 = πb+DLP+1(constant)], here, πb = number of π bonds within the ring system and DLP = Delocalized lone pair of electron (lone pair of electron of heteroatom which can undergoes delocalization).

If the value of ‘A’, for a certain organic compound comes out as an odd number then this compound will treat as an anti-aromatic compound.

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

Any compound that lacks one or more of the above features i.e. it may be acyclic / non-planar /nonconjugated, is to be treated as nonaromatic. But in this case, ‘A' value may be even or odd number.

It is always to be noted that in case of same heteroatoms based heterocyclic compounds, containing both DLP and LLP same heteroatoms, Aromatic and Anti Aromatic behavior should be predicted with respect to DLP based hetero atom only. In case of a multi hetero atom based heterocyclic compound, containing both DLP and LLP heteroatoms, Aromatic and Anti Aromatic behavior should be predicted with respect to DLP based hetero atom only. But when heterocyclic compounds contain both LLP based hetero atoms then Aromaticity should be predicted with respect to that heteroatom which contains the lowest possible position number as per IUPAC nomenclature or any one of the heteroatoms.

RESULTS AND DISCUSSION

1. Prediction of the hybridization state (sp^2 & sp^3) of the heteroatom in heterocyclic compounds can be well explained in the following way

Hybridization state of heteroatom in heterocyclic compounds can be calculated from the total number of σ bonds around heteroatom and number of localized lone pair of electrons (T_{SLLP}) on the heteroatom and subtract one (01) from this total value of T_{SLLP} to get the hybridization state (sp^2 & sp^3) of the heteroatom in the heterocyclic compounds.

Adequate examples on prediction of the hybridization state of hetero atom in heterocyclic compounds containing one, two or more same or different number of hetero atoms from the corresponding T_{SLLP} value (total number of σ bonds around the central atom + localized lone pair of electrons on the central atom) of the central atom have been explored in **Table 2.3.**

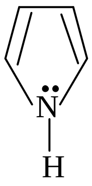
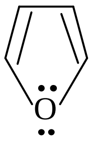
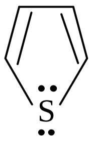
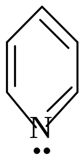
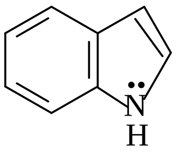
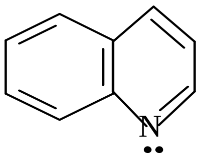
2. Innovative mnemonic for Aromatic and Anti-Aromatic behavior of heterocyclic compounds

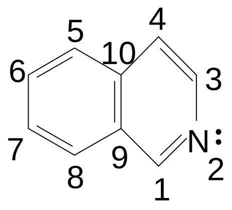
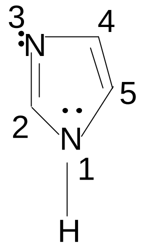
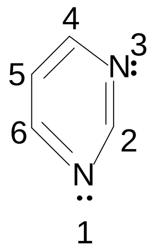
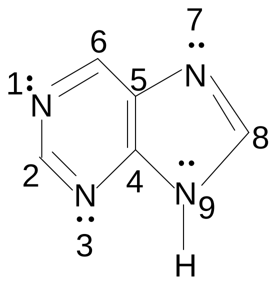
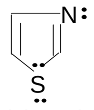
The present chapter will be an innovative mnemonic involving calculation of ‘A' value by just manipulating the no of π bonds within the ring system and delocalized lone pair electron (DLP) with one (01)[7]**.**

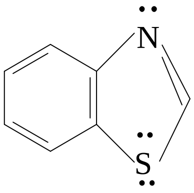
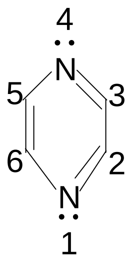
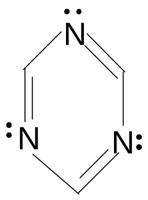
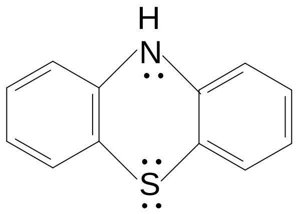
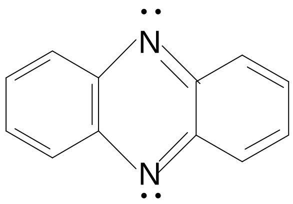
The heterocyclic compound, having cyclic, planar, conjugated (i.e. all the carbon atoms having the same state of hybridization, sp^2), with an even number of ‘A' value will be treated as aromatic in nature and with an odd number of ‘A' value will be treated as an antiaromatic in nature.

Hybridization states of different heterocyclic compounds with the help of LLP have been presented in Table 9.7a and their aromatic behaviors with the help of DLP have been illustrated in Table 9.7b.

Table-9.7a Hybridization state of Heteroatom in Heterocyclic Compounds with the help of LLP

Heterocyclic Compounds (Planar/nonplanar)	Number of σ bonds around the hetero atom (from single and double bonds) (T_S)	Number of localized Lone Pair of e^{-}s (LLP)	Total Number of σ bonds around the hetero atom (T_{SLLP})	Power on the Hybridization state of the heteroatom **(P_{Hyb}) = (T_{SLLP}) – 1** (Corresponding Hybridization state)
 Pyrrole (Planar)	03	0 (the lone pair of electron undergo delocalization, DLP with the ring system)	03	02 (sp^2 N)
 Furan (Planar)	02	01 (out of two lone pairs of electrons, one undergo delocalization, DLP and other remain as LLP)	03	02 (sp^2 O)
 Thiophene (Planar)	02	01 (out of two lone pairs of electrons of S one undergo delocalization, DLP and other remain as LLP)	03	02 (sp^2 S)
 Pyridine (Planar)	02	01	03	02 (sp^2 N)
 Indole (Planar)	03	0	03	02 (sp^2 N)
 Quinoline (Planar)	02	01	03	02 (sp^2 N)

 Isoquinoline (Planar)	02	01	03	02 (sp^2 N)
 Imidazole (Planar)	03 (N1) 02 (N3)	0 (N1) 01 (N3)	03 03	02 (sp^2 N1) 02 (sp^2 N3)
 Pyrimidine (Planar)	02 (N1) 02 (N3)	01 (N1) 01 (N3)	03 03	02 (sp^2 N1) 02 (sp^2 N3)
 Purine (Planar)	02 (N1) 02 (N3) 02 (N7) 03 (N9)	01 (N1) 01 (N3) 01 (N7) 0 (N9)	03 03 03 03	02 (sp^2 N1) 02 (sp^2 N3) 02 (sp^2 N7) 02 (sp^2 N9)
 Thiazole (Planar)	02 (N) 02 (S)	01 (N) 01 (S) (out of two lone pairs of electrons on S, one undergo delocalization, DLP and other remain as LLP)	03 03	02 (sp^2 N) 02 (sp^2 S)

 Benzothiazole (Planar)	02 (N) 02 (S)	01 (N) 01 (S) (out of two lone pairs of electrons on S, one undergo delocalization, DLP and other remain as LLP)	03 03	02 (sp^2 N) 02 (sp^2 S)
 Pyrazine (p-diazine) (Planar)	02 (N1) 02 (N1)	01 (N1) 01 (N1)	03 03	02 (sp^2 N1) 02 (sp^2 N4)
 Cyanidine (Planar)	02 (N1, N3, and N5)	01 (N1, N3, and N5)	03	02 (sp^2 N1, N3, N5)
 Phenothiazine (Planar)	03 (N) 02 (S)	0 (N) 01 (S) (out of two LP of S, one undergo delocalization(DLP), and others remain as LLP)	03 03	02 (sp^2 N) 02 (sp^2 S)
 Phenazine (Planar)	02 (both N)	01 (both N)	03	02 (sp^2 both N)

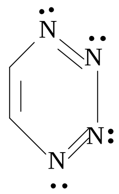
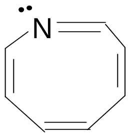
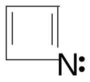
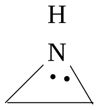
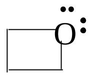
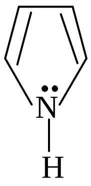
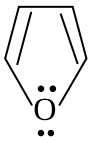
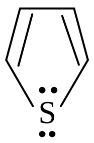
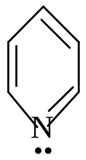
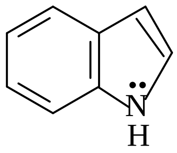
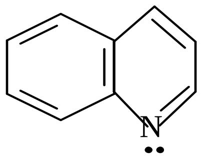
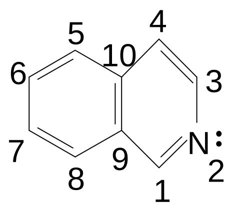
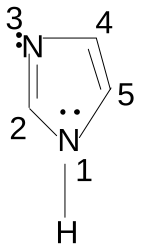
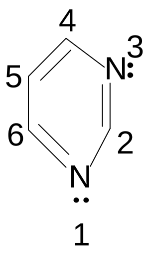
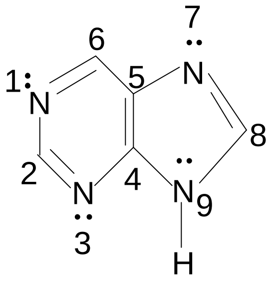
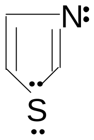
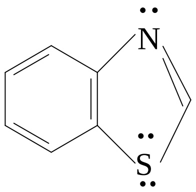
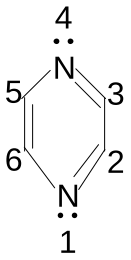
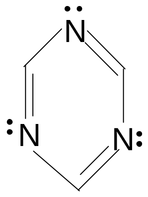
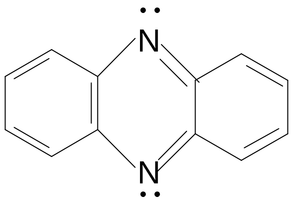
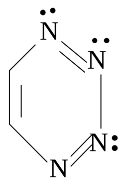
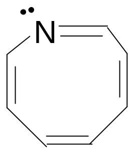
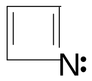
 1,2,3,4-tetrazine (Planar)	02 (N1,N2,N3,N4)	01 (N1,N2,N3,N4)	03	02 (sp^2 All N)
 Azocine (Planar)	02	01	03	02 (sp^2 N)
 Azetine (Planar)	02	01	03	02 (sp^2 N)
 Aziridine (non-planar)	03	01	04	03 (sp^3 N)
 Oxetan (non-planar)	02	02	04	03 (sp^3 O)

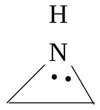
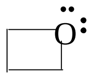
Table 9.7b Aromaticity of Heterocyclic Compounds with the help of DLP

Hetero Cyclic Compound (Cyclic, Planar, Conjugated)	πb value [πb =number of π bonds within the ring system]	DLP	A value [A = πb + DLP + 1(constant)] (even No /odd No)	Remark on Nature of compound (Aromatic/Anti Aromatic)
 Pyrrole	2	1	2 + 1 + 1 = 4 (even No)	Aromatic
 Furan	2	1 (Here out of two lone pairs on O only one LP take part in delocalization)	2 + 1 + 1 = 4 (even No)	Aromatic

 Thiophene	2	1 (Here out of two lone pairs on O only one LP take part in delocalization)	2 + 1 + 1 = 4 (even No)	Aromatic
 Pyridine	3	0	3 + 0 + 1 = 4 (even No)	Aromatic
 Indole	4	1	4 + 1 + 1 = 6 (even No)	Aromatic
 Quinoline	5	0	5 + 0 + 1 = 6 (even No)	Aromatic
 Isoquinoline	05	0	5 + 0 + 1 = 6 (even No)	Aromatic
 Imidazole	02	01 (N1)	2 + 1 + 1 = 4 (even No)	Aromatic
 Pyrimidine (m-diazine)	03	0 (N1)	3 + 0 + 1 = 4 (even No)	Aromatic

 Purine	04	01 (N9)	4 + 1 + 1 = 6 (even No)	Aromatic
 Thiazole	02	01 (S)	2 + 1 + 1 = 4 (even No)	Aromatic
 Benzothiazole	04	01 (S)	4 + 1 + 1 = 6 (even No)	Aromatic
 Pyrazine (p-diazine)	03	0	3 + 0 + 1 = 4 (even No)	Aromatic
 Cyanidine	03	0	3 + 0 + 1 = 4 (even No)	Aromatic
 Phenazine	07	0	7 + 0 + 1 = 8 (even No)	Aromatic

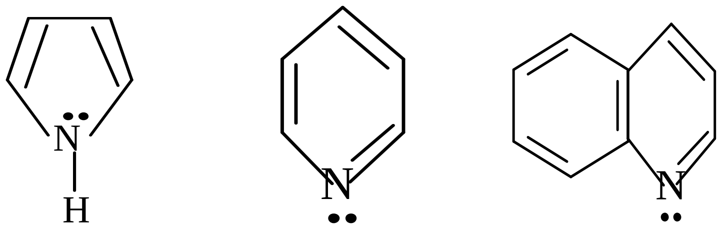
 1,2,3,4-tetrazine	03	0	3 + 0 + 1 = 4 (even No)	Aromatic
 Azocine	04	0	4 + 0 + 1 = 5 (odd No)	Anti aromatic
 Azetine	02	0	2 + 0 + 1 = 3 (odd No)	Anti aromatic

Hetero Cyclic Compound (Cyclic, non-planar)	πb value [πb =number of π bonds within the ring system]	DLP	A value [A = πb + DLP + 1(constant)] (even No/odd No)	Remark on Nature of compound
 Aziridine	-	-	-	Non-Aromatic (nonplanar – sp^3)
 Oxetan	-	-	-	Non-Aromatic (nonplanar – sp^3)

Ex.a. Pyridine is cyclic, planar and conjugated heterocyclic compound. In Pyridine **(Fig.2.18)**, lone pair of ‘N’ atom is to be treated as localized lone pair of electron (LLP), because, it is directly attached with double and single bonds with the ring system, hence, it is considered for calculating the power of the hybridization state, $(P_{Hyb}) = (T_{SLLP}) - 1$, to predict the hybridization state of heteroatom ‘N’ in pyridine. This LLP is not to be under consideration for the prediction of ‘A’ value [A = πb+DLP+1(constant)], in aromaticity, of the heterocyclic compound. Here, in pyridine, around ‘N’, there are two σ bonds and one LLP (localized lone pair electrons). Hence, power of the hybridization state of ‘N’ in pyridine, $(P_{Hyb}) = (T_{SLLP}) - 1 = (2+1)-1 = 2$ (sp^2-N). All rest five carbon atoms are in same hybridization state sp^2, hence, pyridine is planar. Here, A = πb+DLP+1(constant) = 3 + 0 + 1 (constant) = 4 (even no), hence, pyridine is aromatic in nature. Here, πb =

number of π bonds, within the ring system and DLP = Delocalized lone pair electron (a lone pair of electron of heteroatom which is directly attached with single bonds only from all ends with the ring system).

Ex.b. Pyrrole is cyclic, planar and conjugated heterocyclic compound. In Pyrrole **(Fig.2.18)**, the lone pair of N atom is to be treated as DLP, because, it is directly attached with three single bonds only. Hence, it is considered for calculating of ‘A’ value [A = πb+DLP+1(constant)], in aromaticity of heterocyclic compound and is not to be under consideration for calculating the power of the hybridization state, $(P_{Hyb}) = (T_{SLLP}) - 1$, to predict the hybridization state of heteroatom ‘N’ in pyrrole. Here, in pyrrole, around ‘N’, there are three σ bonds and zero LLP (localized lone pair electrons). Hence, power of the hybridization state of ‘N' in pyrrole, $(P_{Hyb}) = (T_{SLLP}) - 1 = (3+0)-1 = 2$ (sp^2-N). All rest four carbon atoms are in same hybridization state sp^2, hence, pyrrole is planar. Here, A = πb+DLP+1(constant) = 2 + 1 + 1 (constant) = 4 (even no), hence, pyrrole is aromatic in nature. Here, πb = number of π bonds, within the ring system and DLP = Delocalized lone pair electron (lone pair electron of heteroatom which is directly attached with single bonds only from all ends with the ring system).



Pyrrole Pyridine Quinoline

Fig. 2.18: Structure of pyrrole, pyridine, and quinoline

Ex.c. Quinoline is cyclic, planar and conjugated heterocyclic compound. In quinoline **(Fig.2.18)**, lone pair of ‘N’ atom is to be treated as localized lone pair of electron (LLP), because, it is directly attached with double and single bonds with the ring system, hence, it is considered for calculating the power of the hybridization state, $(P_{Hyb}) = (T_{SLLP}) - 1$, to predict the hybridization state of heteroatom ‘N’ in quinoline. This LLP is not to be under consideration for the prediction of ‘A’ value [A = πb+DLP+1(constant)], in aromaticity, of the heterocyclic compound. Here, in quinoline, around ‘N', there are two σ bonds and one LLP (localized lone pair electrons). Hence, power of the hybridization state of ‘N’ in quinoline, $(P_{Hyb}) = (T_{SLLP}) - 1 = (2+1)-1 = 2$ (sp^2-N). All rest carbon atoms are in same hybridization state sp^2, hence, quinoline is planar. Here, A = πb+DLP+1(constant) = 5 + 0 + 1 (constant) = 6 (even no), hence, quinoline is aromatic in nature. Here, πb =

number of π bonds, within the ring system and DLP = Delocalized lone pair electron (the lone pair of electron of heteroatom which is directly attached with single bonds only from all ends with the ring system).

Ex.d. Aziridine **(Fig.2.19)**, is cyclic, nonplanar, nonconjugated heterocyclic compound. Here, 'N' atom is surrounded by three σ bonds and one LLP (localized lone pair electrons). Hence, power of the hybridization state of 'N' in aziridine, $(P_{Hyb}) = (T_{SLLP}) - 1 = (3+1)-1 = 3$ (sp^3-N). Hence, it is nonplanar and non-aromatic.

Aziridine Oxetan

Fig.2.19: Structure of aziridine and oxetan

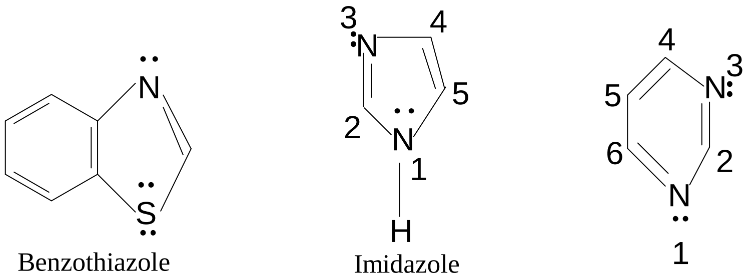
Ex.e. Oxetan **(Fig.2.19)**, is cyclic, nonplanar, nonconjugated heterocyclic compound. Here, 'O' atom is surrounded by two σ bonds and two LLP (localized lone pair of electrons). Hence, power of the hybridization state of 'O' in oxetan, $(P_{Hyb}) = (T_{SLLP}) - 1 = (2+2)-1 = 3$ (sp^3-O). Hence, it is nonplanar and non-aromatic.

OMISSION BEHAVIOR OF HETEROCYCLIC COMPOUNDS WITH RESPECT TO AROMATIC, ANTI-AROMATIC AND NON-AROMATIC BEHAVIOUR

i) Heterocyclic compound, containing both DLP and LLP heteroatoms:

In case of a multi hetero atom based heterocyclic compound, containing both DLP and LLP heteroatoms, Aromatic and Anti Aromatic behavior should be predicted with respect to DLP based hetero atom only.

Ex.a. Benzothiazole **(Fig. 9.28)**, is a multi hetero atom based heterocyclic compound, containing both DLP and LLP hetero atoms. Here, for N, DLP = 0, LLP = 1 and for S, DLP = 1, LLP =1, so, in this case 'A' value should be calculated with respect to S only not N. Here, A = 4 + 1 + 1 = 6 (even no) = Aromatic.



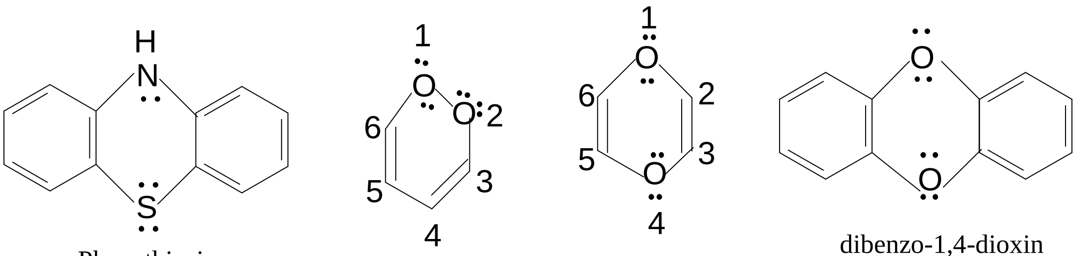
Benzothiazole Imidazole Pyrimidine

Fig. 9.28. Structure of Benzothiazole, Imidazole, and Pyrimidine

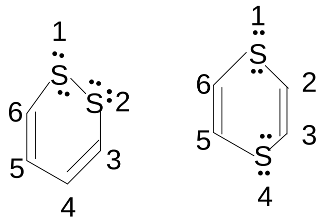
But when heterocyclic compounds contain both LLP based hetero atoms then Aromaticity should be predicted with respect to that heteroatom which contains the lowest possible position number as per IUPAC nomenclature or any one of the heteroatom. **Ex.b.** Imidazole **(Fig. 9.28)** is a multi hetero atom based heterocyclic compound in which, N1 is DLP based heteroatom and N3 is LLP based heteroatom. In this case, Aromaticity should be predicted with respect to the DLP based hetero atom N1. For N1, A = πb+DLP+1(constant) = 2+1+1 = 4 (even No) = Aromatic. **Ex.c.** Pyrimidine **(Fig. 9.28)** is a multi hetero atom based heterocyclic compound in which, both N1 & N3 are in the same environment based heteroatoms (LLP based heteroatoms). In this case, Aromaticity should be predicted with respect to N1 (lowest possible position number as per IUPAC nomenclature). For N1, A = πb+DLP+1(constant) = 3+0+1 = 4 (even no) – Aromatic.

ii)Heterocyclic compounds containing different DLP based heteroatoms (one contains vacant d orbitals):

Ex.d. Phenothiazine **(Fig. 9.29)**, there are two DLP based hetero atoms N and S. In between N and S, since S having vacant d orbitals, so, in this case, ‘A' value will be predicted with respect to DLP based S heteroatom which contains vacant d orbitals only. Here, A = πb + DLP + 1(constant) = 6 +1+1 = 8 (even no) = Aromatic.



Phenothiazine 1,2-dioxin 1,4-dioxin dibenzo-1,4-dioxin



1,2-dithiin 1,4-dithiin

Fig.9.29. Structure of phenothiazine, 1,2-dioxin, 1,4-dioxin, dibenzo-1.4-dioxin and 1,2-dithiin and 1,4-dithiin

iii) Heterocyclic compounds containing same DLP based heteroatom having no d orbitals:

Omission behavior of some heterocyclic compounds such as 1,2-dioxin, 1,4-dioxin, and dibenzo-1.4-dioxin **(Fig. 9.29),** will be observed when there, is at least two heteroatoms (same or different) but both the hetero atoms do not have any d orbitals (such as O etc.) and they are in a DLP based environment in the ring system. These molecules have been studied with advanced molecular orbital techniques known as ‘ab initio calculations’. ‘Ab initio quantum chemistry methods’ are computational chemistry methods based on quantum chemistry[8].

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[8] Levine, Ira N. “Quantum Chemistry”. *Englewood Cliffs, New Jersey: Prentice Hall.* (1991): 455–544

In the case of 1,2-dioxin, 1,4-dioxin and dibenzo-1.4-dioxin **(Fig. 9.29),** there is DLP based O atoms in all the molecules but still, they will be nonaromatic due to the prevention of significant free electron delocalization (makes nonconjugated). The π electrons from the carbon bonds and the lone pair electrons on the oxygen atoms do not overlap to a significant degree due to the absence of vacant d orbitals in both O atoms in each case (pπ-dπ overlap is not possible here in conjugation). It makes these molecules nonconjugated and thus allows the molecules to become nonaromatic instead of aromatic (A value = even No).

In the heterocyclic compounds, where, there is two DLP based N atoms instead of two DLP based O atoms or there is one DLP N atom along with one DLP O atom, the same phenomena of nonaromatic behavior will be observed. Because, both N and O atoms do not have any vacant d orbitals, and hence pπ-dπ overlap is not possible here in conjugation.

iv)Heterocyclic compounds containing same DLP based heteroatoms having vacant d orbitals:

1,4-dithiin and 1,2-dithiin heterocyclic compounds **(Fig. 9.29)** are antiaromatic, here both S atoms, having vacant d orbitals, contain one DLP and one LLP and here both DLP of both S atoms participate in the delocalization. Hence, for the prediction of ‘A' value, consider both DLP (DLP = 2). Here, A = πb + DLP + 1 (Constant) = 2 + 2 + 1 = 5 (odd No) = Anti Aromatic.

APPLICATIONS OF AROMATICITY IN ORGANIC CHEMICAL EDUCATION

Aromaticity has various applications as follows:

i) Predict the basic character of heterocyclic compounds:

The delocalized lone pair of electrons (DLP) on the nitrogen atom of heterocyclic compounds in Aromaticity decreases basic nature of heterocyclic compounds, whereas, localized lone pair electrons (LLP) on the nitrogen atom of heterocyclic compounds increases basic character of heterocyclic compounds as follows:

Ex.a.: In between pyridine (LLP = 01, DLP = 0) and pyrrole (DLP = 01, LLP = 0), pyridine is much more basic than pyrrole. Because, the lone pair of N in pyrrole is in delocalized (DLP) through resonance, so, this lone pair can't be donated for protonation, whereas, the lone pair of N in pyridine is localized (LLP) and hence ready for donation. Hence, pyridine is more basic than pyrrole. **Ex.b.**: In between pyridine (LLP = 01, DLP = 0) and indole (DLP = 01, LLP = 0), pyridine is more basic than indole. Because, the lone pair of N in indole is in delocalized (DLP) through resonance, so, this lone pair can't be donated or protonated, whereas, the lone pair of N in pyridine is localized (LLP) and hence ready for donation. Hence, pyridine is more basic than indole.

Ex.c.: In between furan (LLP = 01, DLP = 01) and pyrrole (DLP = 1, LLP = 0), furan is much more basic due to presence of higher electronegative oxygen atom (E.N. = 3.5) than nitrogen (E.N. = 3.0), which decreases the delocalization tendency of lone pair of electrons for resonance and thus increases the electron density on the heteroatom oxygen in furan.

ii) Predict Stability and reactivity of different heterocyclic compounds with the help of Aromaticity:

By predicting the nature of heterocyclic compound on the basis of aromatic, antiaromatic or non-aromatic nature, different kind of problems, regarding stability and reactivity can easily be solved. Order of stability is aromatic > nonaromatic> antiaromatic and order of reactivity is Anti-aromatic > nonaromatic> aromatic, since, stability is inversely proportional to reactivity.

PROBLEMS ON AROMATICITY

Q.1. Which one of the following chemical system is nonaromatic? (Karnataka NEET 2013)

a)Benzene b)Naphthalene c)Thiophene d)Cyclopentadiene

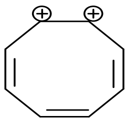
Ans: (d) Cyclopentadiene (sp^3 hybridized C atom makes it nonplanar, hence, non-aromatic)

Q.2. The nonaromatic compound among the following is? (AIEEE 2011)

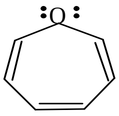
a) Cyclopentadiene b) Thiophene c) Naphthalene d) None

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

Q.3. The correct statement about following species is (NET 2018)



A

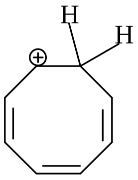


B

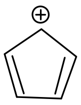
a) Both A and B are aromatic b) A is aromatic and B is antiaromatic c) A nonaromatic and B is antiaromatic d) A is aromatic and B is homoaromatic

Ans: b) A is aromatic and B is antiaromatic [for species A, DNC = 0, ‘A’ value = 3+0+1 = 4 (even number - aromatic) & for species B, LLP =1, DLP = 1, ‘A’ value = 3+1+1 = 5 (odd number - antiaromatic)]

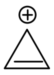
Q.4. Among the carbocations given below (NET 2011)



A



B



C

a)A is homoaromatic, B is antiaromatic and C is aromatic b)A is aromatic, B is antiaromatic and C is homoaromatic c)A is antiaromatic, B is aromatic and C is homoaromatic d)A is homoaromatic, B is aromatic and C is antiaromatic

Ans: a)A is homoaromatic, B is antiaromatic and C is aromatic [sp^3 hybridized carbon atom in A makes it homoaromatic, for B, ‘A’ value = 2+0+1 = 3 (odd number - antiaromatic) & for species C, ‘A’ value = 1+0+1 = 2 (even number - aromatic)]

Q.5. Which one of the following pairs is more basic?

Question	Answer
i) Pyridine and Pyrrole	Ans: i) pyridine > pyrrole
ii) Pyridine and Indole	ii) pyridine > indole
iii) Furan and Pyrro	iii) Furan > Pyrrole

Conclusion

It may be expected that these time economic innovative mnemonics will help the student of chemical education from Undergraduate to Post-Graduate level to predict hybridization state of the heteroatom, and identification of aromatic and antiaromatic behavior of heterocyclic compounds with respect to the classification of a lone pair of electrons present in the heteroatom of heterocyclic compounds. Experiments, *in vitro*, on 100 students, showed that by using these formulae students can save up to 5-10 minutes' time in the examination hall.

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