Classification of Negative Charge Discriminate Hybridization with Aromatic and Anti-aromatic Behavior of Organic Compounds - Innovative Mnemonics

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Abstract In this approach, formulae-based mnemonics by using the classification of negative charge (localized or delocalized) have been highlighted by innovative and time economic way to enhance interest of students' who belong to paranoia zone of chemistry for the prediction of hybridization state of carbon atom containing negative charge (one or more) and aromatic, anti-aromatic, non-aromatic behavior of different organic compounds. Here, I have tried to hub three (03) time economic mnemonics by including three (03) formulae for the prediction of hybridization state of carbon atom (containing negative charge), aromatic, anti-aromatic, and non-aromatic behavior of organic compounds. Educators can use these mnemonics in their teaching style in the classroom lectures after discussing conventional methods and its limitation to make chemistry intriguing.   This article encourages students to solve multiple choice type questions (MCQs) on 'Aromaticity of negative charge containing organic compounds' at different competitive examinations in a time economic ground.

Keywords: *σ bonds, delocalized negative charge, localized negative charge, even number, odd number*

1. Introduction

The conventional methods [1-8] for determination of hybridization state of carbon atom containing negative charge in organic compounds along with the prediction of their aromatic, anti-aromatic, and non-aromatic nature is time consuming and mystifying. Keeping this in mind, previously I have introduced formulae-based mnemonics to focus the limitations of conventional formula to predict the hybridization state of center atom in the organic compounds and solved them in the light of innovative formulae [9].

Here, in this innovative article, I have introduced three (03) time economic innovative mnemonics by using three (03) formulae for the prediction of hybridization state of negative charge-based carbon atom and aromatic, anti-aromatic, non-aromatic nature of organic compounds containing negative charge to make aromaticity in organic chemistry metabolic and interesting for students and educators. This study shows the classification of negative charge discriminate prediction of hybridization state with identification of aromatic, anti-Aromatic, non-aromatic nature of organic compounds containing negative charge.

In this article, formulae-based mnemonics have highlighted by counting total number of σ bonds and localized negative charge (T_{SLNC}) and subtract one (01) from this total value (T_{SLNC}) to predict the power of the hybridization state of carbon atoms bearing negative charge in different organic compounds by innovative and time economic way.

This article also includes innovative formulae involving calculation of 'A' value by just manipulating the number of π bonds within the ring system and delocalized negative charge of carbon (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. The compounds which are non-planar due to the mixing of sp^2 and sp^3 hybridization state will be treated as non-aromatic.

2. Formulae Based Methodologies

2.1. Classification of Negative Charge in Organic Compounds

The negative charge on the carbon atom of any ring system can be generally classified into two types of as

delocalized negative charge (DNC) and localized negative charge (LNC) as follows:

a) 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 an organic compound, when, directly attached with single bonds from all ends within the ring system, then it is considered as DNC containing carbon atom and its negative charge is to be treated as DNC.

Ex. In cyclopropenyl anions, cyclopentadienyl anions and cycloheptatrienyl anions (Figure 1a, 1b, 1c)**,** negative charge on C atom is treated as DNC, because it is directly attached with single bonds directly from all side.

b) 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 an organic compound, when, directly attached through single and double bonds with the other carbons in the ring system is considered as LNC containing carbon atom and its negative charge is treated as localized negative charge (LNC).

Ex. In phenyl carbanion (Figure 1d)**,** negative charge on carbon atom is treated as LNC, because it is directly attached with double bond to other carbon atom within the phenyl ring.
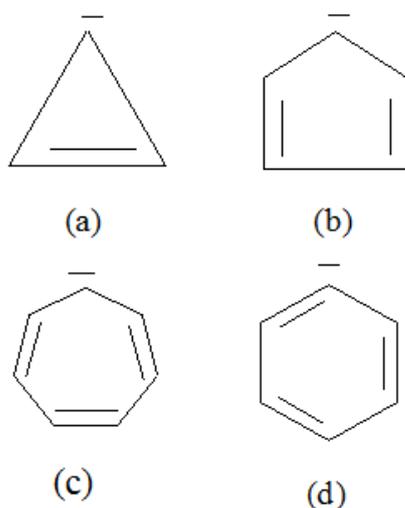

Figure 1. Structure of cyclopropenyl anion (a), cyclopentadienyl anion (b) and cycloheptatrienyl anion (c) and phenyl carbanion (d)

2.2. Planarity of Organic Compounds

Planarity is one of the vital features for prediction aromatic and anti-aromatic with non-aromatic behavior of organic compounds. For aromatic and anti-aromatic behavior, the compound must be planar, whereas the non-planar compounds fall in non-aromatic nature. Planarity of organic compounds depends on the nature of the hybridization state of carbons present in them. When all carbon atoms in an organic compound are sp^2 hybridized then it is planar but when there is a mixing of sp^2 with sp^3 or sp hybridization state then it is treated as non-planar.

2.3. The Conventional Formula for Prediction of Hybridization State Organic Compounds

Hybridization state theory was first devised by Linus Pauling in 1931 [1,2,3].

Hybridization state for a molecule can be calculated by the conventional formula

$$P = 1/2 \left(V + MA - C + A \right),$$

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 or ions.

2.4. Innovative Formula for the Prediction of the Hybridization State of Carbon Atom Bearing Negative Charge in Organic Compounds

Innovative Formula (prediction of sp^2 and sp^3 hybridization state):

Power on the hybridization state of the central atom or ions

$$\left(P_{Hyb} \right) = \left(T_{SLNC} \right) - 1$$

where, P_{Hyb} = power on the hybridization state of the carbon atom bearing negative charge, T_{SLNC} = (Total no of σ bonds around each carbon atom + LNC), LNC = localized negative charge.

2.5. Conventional Methods for Identifying Aromatic and Anti-Aromatic Behavior of Organic Compounds

It was first devised by Huckel in 1931 [4].

i) Aromatic nature of organic compound:

a. Cyclic

b. Planer, where, all bonded atoms are in the same plane (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 (sp^2 hybridized)

c. A conjugated molecule with conjugated π-electron system

d. Contains 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 (a or b or c) then it is nonaromatic in nature.

2.6. Innovative Formulae for Aromatic and Anti-Aromatic Behavior of Organic Compounds Containing Carbon Atom/Atoms Bearing Negative Charge

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) within the ring system with constant one (01).

Organic compounds, having cyclic, planar (i.e. all the carbon atoms having the same hybridization state, 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.

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

$$A = \pi b + DNC + 1 (constant) = even\ no = Aromatic$$

$$A = \pi b + DNC + 1 (constant) = odd\ no = Anti-Aromatic$$

where, πb = number of π bonds within the ring system, DNC = delocalized negative charge on carbon atoms of ring system.

3. Results and Analysis

3.1. Innovative Mnemonics for Prediction of the Hybridization State (sp^2 & sp^3) of Carbon Atom/Atoms in Organic Compounds Containing Negative Charge

Hybridization state of carbon atom bearing negative charge in organic compounds can be calculated from the total number of σ bonds around such carbon and number of localized negative charge on the carbon (T_{SLNC}) and subtract one (01) from this total value of T_{SLNC} to get the hybridization state (sp^2 & sp^3) of the carbon atom bearing negative charge in the organic compounds.

Innovative Formula: Power of the hybridization state, $(P_{Hyb}) = (T_{SLNC}) - 1$
where, P_{Hyb} = power on the hybridization state of the carbon atom bearing negative charge, $T_{SLNC} =$ (Total no of σ bonds around each carbon atom + LNC), LNC = localized negative charge.

All single (-) bonds are the σ bond, in a double bond (=) there is one σ and one π. 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.

In cyclopropenyl anion, cyclopentadienyl anion, and cycloheptatrienyl anion (Figure 1a, 1b, 1c), vertex carbon atom bearing a negative charge is in sp^2 hybridization state. Here in all cases, the vertex carbon atom is surrounded by 3 single bonds (σ bonds) around itself, because, here, the negative charge of the vertex carbon atom is treated as delocalized negative charge (DNC) and cannot be counted during prediction of the hybridization state of the vertex carbon atom. Hence, the power of the hybridization state, $(P_{Hyb}) = (T_{SLNC}) - 1 = 3-1 = 2 (sp^2)$, whereas rest carbon atoms also bear sp^2 hybridization state corresponding to 3σ bonds (2 single bonds and one double bond). The presence of all sp^2 hybridized carbons in cyclopropenyl anions, cyclopentadienyl anions, and cycloheptatrienyl anions make them planar.

But in phenyl carbanion (Figure 1d) vertex carbon atom bearing a localized negative charge (LNC=1) is surrounded by 2σ bonds (one single bond and one double bond) around itself. Hence, the power of the hybridization state, $(P_{Hyb}) = (T_{SLNC}) - 1 = (2+1)-1 = 2 (sp^2)$, whereas rest carbon atoms in the ring system also bear sp^2 hybridization state corresponding to 3σ bonds (2 single bonds and one double bond). The presence of all sp^2 hybridized carbons in phenyl carbanion make it planar.

In cyclobutenyl dianion and cyclooctatrienyl dianion (Figure 2a, 2b), both negative charges are treated as delocalized negative charge (DNC) and not counted during the prediction of the power of the hybridization state (P_{Hyb}). In this case, the power of the hybridization state of both carbons bearing negative charge (P_{Hyb}) = $(T_{SLNC}) - 1 = (3+0)-1 = 2 (sp^2)$, whereas rest carbon atoms in the ring systems also bear sp^2 hybridization state corresponding to 3σ bonds (2 single bonds and one double bond). The presence of all sp^2 hybridized carbons in both cyclobutenyl dianion and cyclooctatrienyl dianion make them planar.

In cyclohexadienyl anion (Figure 2c), vertex carbon atom (negative charge = 0) is surrounded by 4σ bonds (four single bonds) around itself. Hence, the power of the hybridization state, $(P_{Hyb}) = (T_{SLNC}) - 1 = (4+0)-1 = 3 (sp^3)$, whereas rest carbon atoms in the ring system contain sp^2 hybridization state including negative charge-based carbon atom (3 single bonds). The presence of sp^2 hybridized carbons along with one sp^3 hybridized carbon make it non-planar.
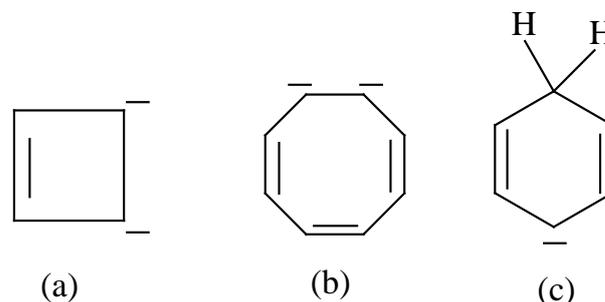

Figure 2. Structure of cyclobutenyl dianion (a), cyclooctatrienyl dianion (b) and cyclohexadienyl anion (c)

In cyclobutenyl anion, cyclopentenyl anion and cyclohexenyl anion (Figure 3a, 3b, 3c), there is a presence of sp^3 hybridized carbon atom/atoms along with all sp^2 hybridized carbon atoms makes them non-planar.
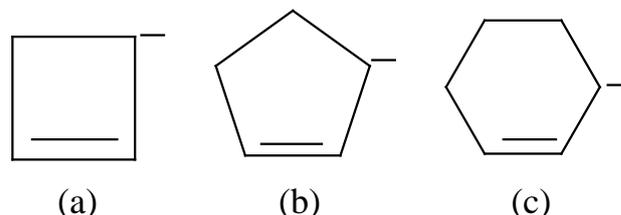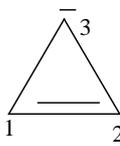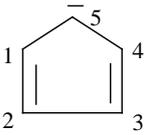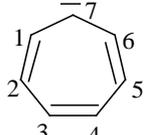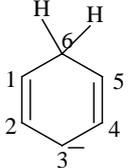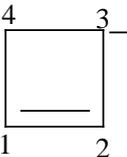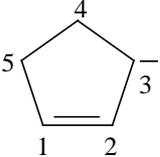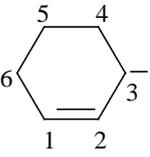

Figure 3. Structure of cyclobutenyl anion (a), cyclopentenyl anion (b) and cyclohexenyl anion (c)

Prediction of the hybridization state of organic compounds containing negative charge-based carbon atom/atoms have been highlighted in Table 1.

Table-1. Hybridization state of Organic Compounds with the help of LNC

Organic Compounds (planar/non-planar)	Number of σ bonds around the carbon atom/atoms bearing negative charge (T_S)	Number of localized negative charge (LNC)	Total Number of σ bonds around the carbon atom/atoms and localized negative charge (T_{SLNC})	Power on the hybridization state of the carbon atom/atoms (P_{Hyb}) = (T_{SLNC}) – 1 (Corresponding hybridization state)
Cyclopropenyl anion (Planar)	3σ bonds (around C_3)	0	03	02 (sp^2 C_3)
	3σ bonds (around C_1 & C_2)	0	03	02 (sp^2 - C_1 & C_2)
Cyclopentadienyl anion (Planar)	3σ bonds (around C_5)	0	03	02 (sp^2 - C_5)
	3σ bonds (around C_1, C_2, C_3, C_4)	0	03	02 (sp^2 - C_1, C_2, C_3, C_4)
Cycloheptatrienyl anion (Planar)	3σ bonds (around C_7)	0	03	02 (sp^2 – C_7)
	3σ bonds (around C_1, C_2, C_3, C_4, C_5, C_6)	0	03	02 (sp^2 - C_1, C_2, C_3, C_4, C_5, C_6)
Phenyl carbanion (Planar)	2σ bonds (around C_1)	01	03	02 (sp^2 - C_1)
	3σ bonds (around C_2, C_3, C_4, C_5, C_6)	0	03	02 (sp^2 - C_2, C_3, C_4, C_5, C_6)
Cyclobutenyl dianion (Planar)	3σ bonds (around C_3 & C_4)	0	03	02 (sp^2 - C_3 & C_4)
	3σ bonds (around C_1 & C_2)	0	03	02 (sp^2 – C_1 & C_2)
Cyclooctatrienyl dianion (Planar)	3σ bonds (around C_7 & C_8)	0	03	02 (sp^2 - C_7 & C_8)
	3σ bonds (around C_1, C_2, C_3, C_4, C_5, C_6)	0	03	02 (sp^2 - C_1, C_2, C_3, C_4, C_5, C_6)
Cyclohexadienyl anion (non-planar)	3σ bonds (around C_3)	0	03	02 (sp^2 - C_3)
	4σ bonds (around C_6)	0	04	03 (**sp^3 – C_6**)
	3σ bonds (around C_1, C_2, C_4, C_5)	0	03	02 (sp^2 - C_1, C_2, C_4, C_5)
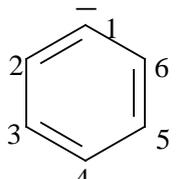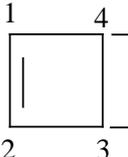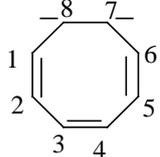
Organic Compounds (planar/non-planar)	Number of σ bonds around the carbon atom/atoms bearing negative charge (T_S)	Number of localized negative charge (LNC)	Total Number of σ bonds around the carbon atom/atoms and localized negative charge (T_{SLNC})	Power on the hybridization state of the carbon atom/atoms (P_{Hyb}) = (T_{SLNC}) – 1 (Corresponding hybridization state)
Cyclobutenyl anion (non-planar)	3σ bonds (around C_3)	0	03	02 (sp^2 - C_3)
	4σ bonds (around C_4)	0	04	03 (**sp^3 – C_4**)
	3σ bonds (around C_1, C_2)	0	03	02 (sp^2 - C_1, C_2)
Cyclopentenyl anion (non-planar)	3σ bonds (around C_3)	0	03	02 (sp^2 - C_3)
	4σ bonds (around C_4 & C_5)	0	04	03 (**sp^3 – C_4 & C_5**)
	3σ bonds (around C_1, C_2)	0	03	02 (sp^2 - C_1, C_2)
Cyclohexenyl anion (non-planar)	3σ bonds (around C_3)	0	03	02 (sp^2 - C_3)
	4σ bonds (around C_4, C_5, C_6)	0	04	03 (**sp^3 – C_4, C_5, C_6**)
	3σ bonds (around C_1, C_2)	0	03	02 (sp^2 - C_1, C_2)

3.2. Innovative Mnemonics for Prediction of Aromatic and Anti-aromatic Behavior of Organic Compounds Containing Negative Charge

Innovative Formula: Evaluation of 'A' Value to predict aromatic and anti-aromatic nature of organic compounds containing negative charge.

$$A = \pi b + DNC + 1(constant) = even\ no = Aromatic$$

$$A = \pi b + DNC + 1(constant) = odd\ no = Anti - Aromatic$$

where, πb = number of π bonds within the ring system, DNC = delocalized negative charge on carbon atoms of the ring system.
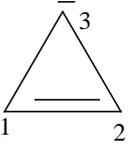
Any compound that lacks at least one of the three features (cyclic/planar/conjugated) is to be treated as non-aromatic. Non-aromatic compounds may be acyclic or non-planar or non-conjugated.
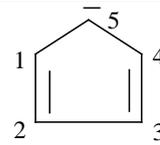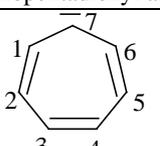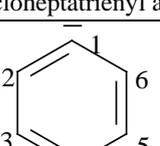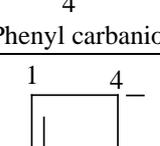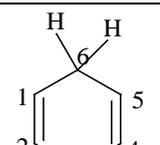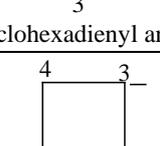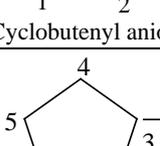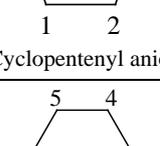
In cyclopropenyl anion, cyclopentadienyl anion and cycloheptatrienyl anion (Figure 1a, 1b, 1c), vertex carbon atom bearing negative charge is in sp^2 hybridization state discussed earlier. Here in all cases, vertex carbon contains delocalized negative charge (DNC) and can be counted during prediction 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 + DNC + 1(constant) = 1+1+1 = 3 (odd no) = anti-aromatic; 'A' value for cyclopentadienyl anion = πb + DNC + 1(constant) = 2+1+1 = 4 (even no) = aromatic and 'A' value for cycloheptatrienyl anion = πb + DNC + 1(constant) = 3+1+1 = 5 (odd no) = anti-aromatic. In phenyl carbanion (Figure 1d), all carbon atoms are sp^2 hybridized including negative charge bearing carbon atom, makes it planar. Here, 'A' value = πb + DNC + 1(constant) = 3+0+1 = 4 (even no) = aromatic.

Adequate examples for the prediction of aromatic, anti-aromatic and non-aromatic behavior of organic compounds containing negative charge-based carbon atom/atoms have been highlighted in Table 2.

Table 2. Aromatic, anti-aromatic, and non-aromatic behavior of organic compounds with the help of DNC

Organic Compound (cyclic, planar, conjugated)	πb value [πb =number of π bonds within the ring system]	Number of localized negative charge (DNC)	A value [A = πb + DNC +1(constant)] (even No /odd No)	Remark on Nature of compound (Aromatic/Anti Aromatic)
Cyclopropenyl anion	1	1	1 + 1 + 1 = 3 (odd No)	Anti-Aromatic

Structure	πb value	Number of localized negative charge (DNC)	Number of sp³ hybridized carbon atom/atoms	Remark on Nature
Cyclopentadienyl anion	2	1	2 + 1 + 1 = 4 (even No)	Aromatic
Cycloheptatrienyl anion	3	1	3 + 1 + 1 = 5 (odd No)	Anti-Aromatic
Phenyl carbanion	3	0	3 + 0 + 1 = 4 (even No)	Aromatic
Cyclobutenyl dianion	1	2	1 + 2 + 1 = 4 (even No)	Aromatic
Cyclooctatrienyl dianion	3	2	3 + 2 + 1 = 6 (even No)	Aromatic
Organic Compound (cyclic, non-planar)	πb value [πb =number of π bonds within the ring system]	Number of localized negative charge (DNC)	Number of sp³ hybridized carbon atom/atoms	Remark on Nature of compound (Non-Aromatic)
Cyclohexadienyl anion	2	1	01 (sp³ – C₆) (non-planar)	Non-Aromatic
Cyclobutenyl anion	1	1	01 (sp³ – C₄) (non-planar)	Non-Aromatic
Cyclopentenyl anion	1	1	02 (sp³ – C₄ & C₅) (non-planar)	Non-Aromatic
Cyclohexenyl anion	1	1	03 (sp³ – C₄, C₅ and C₆) (non-planar)	Non-Aromatic
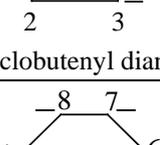
4. Conclusion

It may be expected that these three-time economic innovative mnemonics will help the student of chemical education at undergraduate, senior undergraduate and post-graduate level to predict the aromatic and anti-aromatic behavior of organic compounds containing negative charge bearing carbon atom/atoms along with non-aromatic nature. Experiments, *in vitro,* on 100 students, showed that by using these formulae students can save up to 2-3 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-based teaching methodologies including three formulae in the field of Aromaticity in organic chemistry.

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