Research Article

Exploring Aromaticity: From Linear Polyacene to Helicene

Anirban Panda[*]

Department of Chemistry, Jagannath Kishore College, Purulia, Post & Dist.: Purulia, PIN-723101, West Bengal, India

Abstract

We have computationally studied the aromaticity of a series of polyacenes, from linear to bent and/or helical polyacenes, keeping the total number of carbon atoms intact. The traditional structure-based aromaticity index (HOMA) has been correlated with the Clar 2-nomial for each polyacene. We have found that linear polyacenes are less aromatic than angular ones. Some other related parameters, like the HOMO-LUMO gap, the average NICS values, etc., are also computed to investigate the aromaticity involved in these types of systems. We have found that the structure-based aromaticity indices go parallel with the graph-based aromaticity indices.

Keywords: Aromaticity; Linear Polyacene; Helicene; HOMA; NICS

Email: anirban@jkcprl.ac.in (corresponding author)

1. Introduction

In the early 19th century, the term "aromaticity" was mostly employed to describe a certain class of organic substances in a chemical sense.[1,2] It is still crucial to the rationalization of the structure, stability, and reactivity of many molecules in the discipline of physical organic chemistry. The scientific community is still baffled by aromaticity because there is not a single definition for it and it has multiple dimensions. On the other hand, characteristics such as (i) planarity, (ii) total $(4n + 2)\pi$ electrons, (iii) stabilization energy,[3-4] (iv) bond length,[5] (v) magnetic exaltation,[6] (vi) preservation of π-electron delocalization after typical reactions,[7] and so on can be used to quantify aromaticity. All of the aforementioned traits are present in a completely aromatic system. Due to its multidimensional nature and lack of a single, definitive definition, aromaticity is quantified using a variety of indices. One such structural indices is the harmonic oscillator model of aromaticity (HOMA), which can accurately describe the variations in aromaticity in more complex systems.[8] The indices based on geometry When bond length alternation and rise, The geometry based quantifier HOMA quantifies the reduction in aromaticity with the increase in the bond length alternation and subsequent bond elongation.[9] Not only can aromaticity be illustrated by geometry based indices like HOMA but also a specified π-electron part in some greater π-electron structure may be affected by its structural environment.[8-10]

Beside HOMA index, nucleus independent chemical shift (NICS) is another widely used

index of aromaticity because of its simplicity and efficiency.[11-13] The extent of aromaticity can be established experimentally by the 1H NMR shift of aromatic and anti-aromatic compounds. This effect is a consequence of the π-electron ring current of aromatic systems under the influence of external magnetic field. NICS can be widely used to identify aromaticity, non-aromaticity, and anti-aromaticity of a single ring system and individual ring in polycyclic systems (local aromaticity).

In their landmark work on the "Nature of Chemical Bond," Pauling and Wheland succeeded in presenting a quantitative resonance theoretical picture of the graphitic network in a practical, chemically suitable, and quantitative form in 1939.[14] Nearly forty years later, Clar presented his theories in a brief pamphlet on "aromatic sextet" theory, which provides a qualitative explanation for the stability of conjugated systems.[15] The spectrum of benzenoid systems served as an illustration of his views on the aromatic sextet. Herndon and Hosoya have used the Clar structures for benzenoid hydrocarbons to parameterize valence bond computations, although Clar's concepts characterized the aromaticity of benzenoid hydrocarbons through the experimental method.[16] In 1976, Randić proposed the "conjugated circuit model" to analyze the aromaticity of conjugated polycyclic compounds, drawing inspiration from Clar structures.[17] Using the model, it was established that the Helicenes are relatively more stable than equivalent polyacenes.[18] Cyvin and Gutman have previously published a list of numerous formulas in their book[19] that may be used to count the number of Kekule structures K (B) for different kinds of benzenoid systems (B). In a different study,

Klien et al. examined a qualitative resonance theoretical approach to explain the characteristics of π-electron spins on different kinds of graphitic network boundaries.[20,21] Klein's method took into account the pairing of adjacent neighboring (starred or unstarred) and non-neighboring (unstarred or starred) sites of various graphitic edges.[22] The numbers (χ_n^*) of starred sites of degree n and the numbers (χ_n^0) of unstarred sites of degree n were used to indicate the overall ground state spin:

$$S_{RT} = |2\chi_1^* + \chi_2^* - 2\chi_1^0 - \chi_2^0|/6 \qquad (1)$$

Later the resonance theoretically anticipated ground state spin was re-expressed in terms of the total numbers of starred and unstarred sites, or χ^* and χ^0.as

$$S_{RT} = |\chi^* - \chi^0|/2 \qquad (2)$$

The wide strip systems with two well-separated edges showed good agreement between the unrestricted HF computations and this variety of simple resonance theoretic predictions for edge localized electrons. In 2009 Misra and co-worker extended Eric Clar's ideas about "aromatic sextet" to a quantitative format in terms of "Clar 2-nomial" considering molecular benzenoids[22] and subsequently radical benzenoids.[23] Clar's theory has been effectively used to conjugated carbon nanostructures, such as carbon nanotubes,[24] nanoribbons,[25] etc., as a part of the theoretical development involved. By employing density functional theory calculations, Baldoni et al. were able to justify their use of the theory in obtaining edge energies, band gap, and edge-induced stresses of hydrogen terminated graphene nanoibbons.[26] King and Ormsby have

examined the electrical structure and magnetic characteristics of flawless single-walled carbon nanotubes using Clar's valence bond model in a different study.[24] Apart from graphene, defective graphene, carbon nanotubes, nanoribbon, and diverse types of fullerenes, verities of conjugated carbon nanostructure such as, fractal benzenoids, nano-tori, nano-cone was also defined by Clar's concepts.[27]

As the number of rings increases, linear polyacenes become more reactive, making it impossible to experimentally characterize the higher members.[15, 16] The inner rings are where major chemical processes preferentially take place. Another illustration of monotonic behaviour in the polyacene series is the progressive narrowing of the gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO).[28, 29] The aromaticity of each ring changes when a linear polyacene is converted to a bent polyacene.

In this work we have studied the nature of change of aromaticity with the change in the structure (from linear to angular) of polyacene molecules with same number of carbon atoms, namely, (1) naphthalene (2) anthracene and (3) phenanthrene; (4) tetracene, (5) benzanthracene, (6) benzo[c] phenanthrene, (7) pentacene, (8) benzo[a]naphthacene, (9) naphtha[1,2-α] anthracene and (10) Dibenzo [c,g] phenanthrene (Figure 1). We have studied the local aromaticity of individual rings in terms of structural aromaticity index HOMA, nucleus independent chemical shift, NICS(0) and NICS(I), and the graph based aromaticity index, Clar's Aromaticity Index (Clar 2-nomial). We have also compared the HOMO-LUMO gap, electronegativity and hardness of the linear and angular polyacene to study their aromatic nature in terms of these parameteres.

Figure 1. The polyacene compounds under study. For simplicity, the double bond and/or rings showing the delocalization of electrons are avoided. Only the schematic molecular
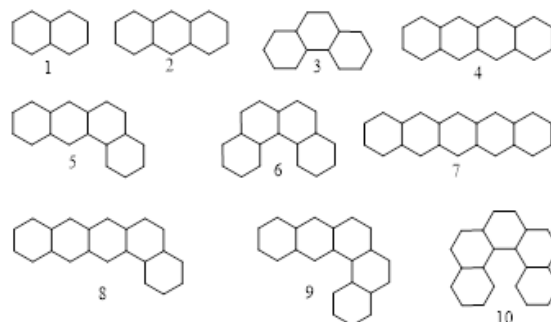
graphs are shown.

2. Theoretical and Computational Detail

The local aromaticity of polyacene compounds can be investigated using the Harmonic Oscillator Model of Aromaticity (HOMA) index.[30-36] It is one of the most accurate structural measures of local aromaticity. The HOMA index for each benzene ring in a polycyclic aromatic hydrocarbon molecule is defined as[30-35]

$$HOMA = 1 - \frac{\alpha}{6}\sum_{i=1}^{6}(R_0 - R_i)^2 \qquad (3)$$

where α and R are the constants characteristic of C-C bonds in a hydrocarbon π-system, R_i is the observed or calculated length of the ith C-C bond in a given benzene ring and the summation is made over the six π-bonds. A large positive HOMA value indicates a larger degree of local aromaticity in the ring concerned. We adopted the values α=257.7 and R_0=1.388 Å [37] to calculate HOMA indices.

The electronegativity (χ) and hardness (η) in terms energy of HOMO and LUMO can be written as

$$\chi = -\frac{E_{HOMO} + E_{LUMO}}{2} \qquad (4)$$

and

$$\eta = E_{HOMO} - E_{LUMO} \qquad (5)$$

All the molecular geometries have been optimized using restricted B3LYP functional and 6-31+G(d,p) basis set.

The NICS values of the non-chemical probe 'Bq" are computed on the ring plane

[NICS(0)]. Nonetheless, the influence of the π-system's interaction with the σ-skeleton of the relevant ring is intrinsically included in the NICS(0) values. Therefore, NICS values are also computed 1 Å atop the ring [NICS(1)] of the systems under study to assess the local aromaticity. The aromaticity index NICS of the polyacenes has been estimated by using UB3LYP/GIAO methodology with 6-31+G(d,p) basis set. The GIAO method [38] was used to perform calculations of NICS values at the centre of the rings (NICS(0)). All the calculations have been done using Gaussian09 suite of programme.[39]

A brief discussion on Quantitative Clar Theory is due here. The theory, developed by Klein et. al., is essentially based on valence structures[40] with conjugated π –network in each site that is indicated to either a Clar sextet or a double bond.[41] Thus a Clar structure is a classical electronic structure that contain Clar sextet in one ring and an arrow is interconnected to the adjacent ring containing two double bonds. Thus the Clar structure describes the π-network identified by graph B and subsequently one can construct the Clar polynomial P of various systems following the earlier work[22,23,40]

$$P_B(x,y) \equiv \sum_C^B x^{s_B(C)} y^{a_B(C)} \quad (6)$$

The terms x and y in this polynomial denote the contribution of Clar sextets and the arrow that connects them to their neighboring ring, respectively. The varied weights of the several Clar structures connected to Clar structure C can be added to form the total. The number of Clar sextets in C and the number of rings next to the Clar sextet into which a Clar sextet can move with the least amount of bond rearrangement—that is, the degree of mobility to the Clar sextet—are indicated by the symbols s_G (C) and $a_G(C)$ in Clar structures. In keeping with our prior work, we employ the

variables x = 2 and y = 1 in this work.[22,23] We discuss the Clar aromaticity index adopting a similar treatment as was done in our previous work for quantifying local aromaticity. Klein et al. have shown that the Clar aromaticity Index (*CAI*) for a hexagonal ring κ of a benzenoid B can be expressed as

$$CAI_B(\kappa) = \sum_C^B s_B(C,\kappa) x^{s_B(C)} y^{a_B(C)} / P_B(x,y) \quad (7)$$

$$CAI'_B(\kappa) = \sum_C^B a_B(C,\kappa) x^{s_B(C)} y^{a_B(C)} / P_B(x,y) \quad (8)$$

where $s_B(C,\kappa)$ is 1 or 0 depending on whether κ is in Car sextet in C or not. Also, $a_B(C,\kappa)$ counts the number of naphthalenes which contains $\kappa \subseteq C$ along with two other double bonds of naphthalene contained in C. Here $CAI'_B(\kappa)$ plays the role of secondary aromaticity index arising from the migration of the sextet to neighboring ring. It can be easily seen that $a_B(C,\kappa)$ is either 0 or 1. These local invariants and the global invariants are connected via $\sum_\kappa^B s_B(C,\kappa) = s_B(C)$ and $\sum_\kappa^B a_B(C,\kappa) = a_B(C)$ which follows

$$\langle s \rangle_B = \sum_\kappa^B CAI_B(\kappa) \quad \text{and} \quad \langle a \rangle_B = \sum_\kappa^B CAI'_B(\kappa) \quad (9)$$

Hence one can think of expressing local aromaticity of any ring of the polyacene by a linear combination of sextetness ($CAI_B(\kappa)$) and sextet mobility ($CAI'_B(\kappa)$) for that particular ring. Taking into account the non-local contributions as considered in Ref. 22, one can express the Clar aromaticity index (CAI) in terms of three-parameter expression such as

$$CAI(m) = C_1 CAI_G(m) + C_2 CAI'_G(m) + C_3 \frac{1}{1 + (n_m / 6)}$$

(10)

where n_κ is the number of benzene ring which are adjacent to ring κ. The relevance for introducing the third term can be understood

when one fits the aromaticity index against the non-local contributions from the neighbouring sites.

3. Results and Discussions

In this study we have calculated the aromaticity index HOMA, NICS(0) and NICS(1) of different linear polyacene under consideration and their corresponding angular isomer (1-10). The values of HOMA, NICS (0) and NICS (1) for individual rings and their average are shown in **Table 1**.

Table 1. The values of HOMA, NICS(0), NICS(1) and their average of the compounds

Compound	Ring	A	B	C	D	E	Average
1	HOMA	0.76	0.76				0.76
	NICS(0)	−8.50	−8.49				−8.50
	NICS(1)	−10.37	−10.37				−10.37
2	HOMA	0.60	0.68	0.60	---		0.63
	NICS(0)	−7.52	−11.19	−7.52	---		−8.74
	NICS(1)	−9.53	−12.55	−9.53	---		−10.54
3	HOMA	0.84	0.42	0.84	---		0.70
	NICS(0)	−8.81	−5.50	−8.81	---		−7.71
	NICS(1)	−10.68	−7.97	−10.68	---		−9.78
4	HOMA	0.51	0.59	0.59	0.51		0.55
	NICS(0)	−6.73	−11.02	−11.02	−6.73		−8.88
	NICS(1)	−8.85	−12.39	−12.39	−8.85		−10.62
5	HOMA	0.72	0.25	0.87	0.68		0.63
	NICS(0)	−8.65	−3.59	−10.35	−8.32		−7.73
	NICS(1)	−10.51	−6.37	−12.0	−10.23		−9.78
6	HOMA	0.76	0.30	0.30	0.76		0.53
	NICS(0)	−9.35	−6.73	−6.73	−9.35		−8.04
	NICS(1)	−10.92	−8.64	−8.64	−10.92		−9.78
7	HOMA	0.47	0.53	0.54	0.53	0.47	0.51
	NICS(0)	−5.86	−10.73	−12.22	−10.73	−5.84	−9.08
	NICS(1)	−8.09	−12.14	−13.50	−12.26	−8.33	−10.86
8	HOMA	0.55	0.65	0.60	0.16	0.88	0.57
	NICS(0)	−7.22	−11.99	−10.33	−2.65	−8.48	−8.13
	NICS(1)	−9.33	−13.22	−11.94	−5.62	−10.29	−10.08
9	HOMA	0.68	0.69	0.30	0.53	0.78	0.60
	NICS(0)	−8.08	−11.03	−4.28	−6.93	−8.31	−7.73
	NICS(1)	−11.24	−11.99	−6.92	−9.30	−12.92	−10.47
10	HOMA	0.81	0.44	0.58	0.44	0.81	0.62
	NICS(0)	−8.39	−6.09	−6.34	−6.09	−8.39	−7.06
	NICS(1)	−11.29	−7.84	−9.06	−7.68	−11.29	−9.43

The most significant Kekulé resonance structure for describing the characteristics of polycyclic aromatic hydrocarbons (PAHs) is, in accordance with Clar's idea, the one having the greatest number of disjoint aromatic π-sextets, or benzene-like moieties. Six π-electrons located in a single benzene-like ring and isolated from neighbouring rings by formal C-C single bonds have been referred to as aromatic π-sextets. Considering naphthalene (**1**) being a well-studied case, we discuss the aromaticity of anthracene and others (**2-10**). All the possible Clar structures are shown in **Figure 2**. It is evident that for anthracene the π-electrons are distributed over the three rings equally i.e. all the rings should have equal aromaticity. But from the HOMA and NICS values we conclude that the middle ring is

more aromatic than those at the sides.[42] Although it is observed that the higher aromaticity of the central ring of the molecule as indicated by NICS agrees with the stronger ring currents around the inner rings of acenenes.[43] On the other hand phenanthrene which is an isomer of anthracene contains two aromatic sextet in the terminal and consequently they have higher values of NICS and HOMA than central one. The average HOMA value of phenanthrene is higher than that of anthracene. This can be explained as anthracene contains one Clar sextet in its resonance structure but phenanthrene contains two sextets. On the other hand average NICS values show opposite trend, this is because of the sextet migration is impossible for phenanthrene.[22]
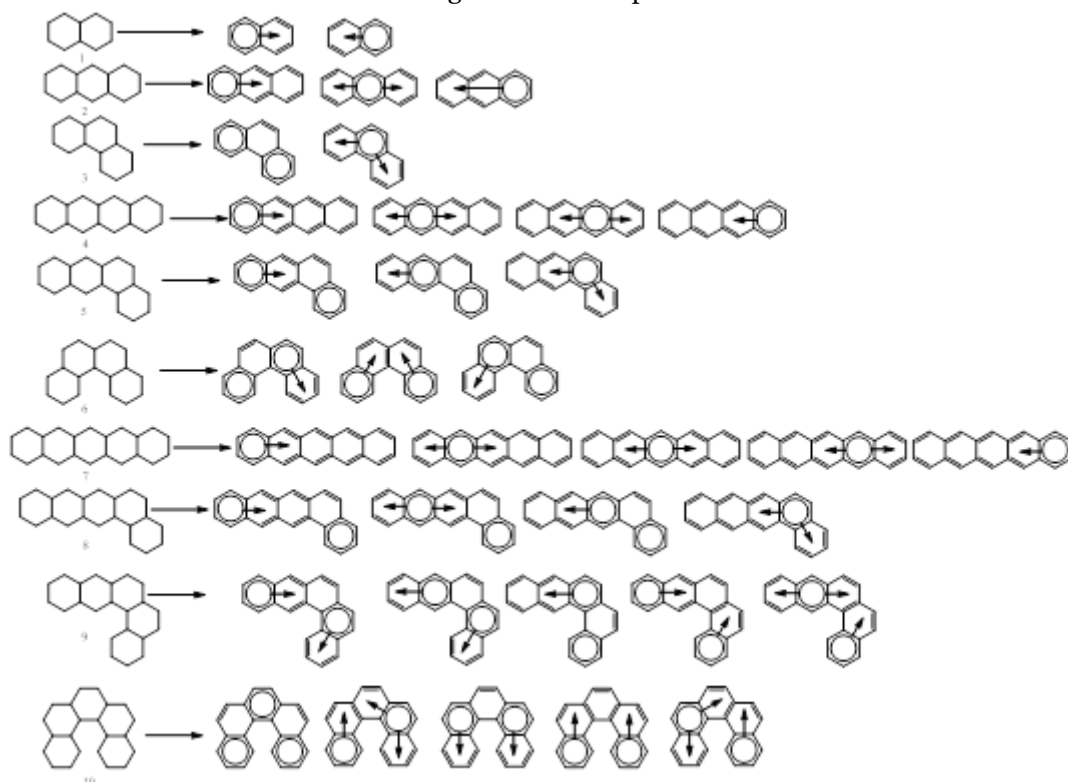
Figure 2. Representation of nine poly aromatic hydrocarbons and their Clar structures with the corresponding ring labels. Clar's aromatic π-sextets are indicated with circles

For four membered polyacenes, we can see that the average NICS values decrease when it goes to angular isomer. This fact can be explained as, in linear polyacenes, the sextet

can migrate from one ring to another, i.e., the sextets are not localized in linear polyacene. Therefore, the average NICS value is much lower for **5 and 6** than for linear polyacenes **4**.

Similarly, for the hydrocarbons with five hexagons, the average NICS values for angular polyacenes are less than that of the corresponding linear one, **7**.

Table 2. The Clar 2-nomials of the selected compound and the Clar Aromaticity Index of the respective rings of the compounds.

Compound	Polynomial	CAI(α)					
		A	**B**	**C**	**D**	**E**	**Average**
1	$2xy$	0.71	0.71				0.71
2	$2xy + xy^2$	0.60	0.58	0.60			0.59
3	$x^2 + xy^2$	0.71	0.60	0.71			0.67
4	$2xy^2 + 2xy$	0.52	0.52	0.52	0.52		0.52
5	$2x^2y + xy^2$	0.63	0.59	0.47	0.79		0.62
6	$2x^2y + x^2y^2$	0.77	0.54	0.54	0.77		0.66
7	$3xy^2 + 2xy$	0.48	0.47	0.47	0.47	0.48	0.47
8	$x^2y^2 + 2x^2y + xy^2$	0.54	0.55	0.50	0.39	0.82	0.56
9	$x^2y^3 + 3x^2y^2 + x^2y$	0.63	0.66	0.44	0.59	0.75	0.61
10	$x^3 + 2x^2y^2 + 2x^2y^3$	0.77	0.57	0.48	0.57	0.77	0.63

The average HOMA values of individual rings are greater where the sextets are localized. The trend is nicely followed in case of hydrocarbons with ring size 5. However, the average HOMA values for four membered rings differ to some extent from this trend. In this case, the structure **6** with more sextets shows a lower HOMA value compared to that estimated for structure **5** with fewer sextets**.** This observation may be explained on the basis of the strain involved with the structures. Qualitatively, it is evident that the strain involved in the structure **6** is more due to the bent involved in the structure compared to that involved in structure **5**. Thus, the geometry of the system gets distorted, compromising its aromaticity.

A discussion on the Clar Aromaticity Index (*CAI*) and its relation to other Aromaticity Indexes are is due here. The Clar 2-nomials of all the molecules under investigation and the Clar Aromaticity Indexes of individual rings of each system are given in **Table 2**. It is evident from the given data, that in general, the average *CAI* increases from linear to bent systems. Since the average *CAI* is determined per ring unit, the aromaticity increases per ring with an increase in the extent of bending. This explains the impelling cause for a linear polyacenes to become a helical one. The advantage of using the *CAI* over other indices is that, unlike *CAI*, other indices do not give such a nice correlation between the helicity and corresponding aromaticity of the chosen molecule. All *CAI* values are calculated using Eqn. (10). Equating HOMA values in Eqn. (10) for all chosen molecules, and subsequently doing a least square analysis, one gets the following constants: C_1 = 0.58; C_2 = 0.18; C_3= 0.38. An almost linear correlation exists between the HOMA values and CAI, as shown in **Figure 3**.

HOMA Vs *CAI*
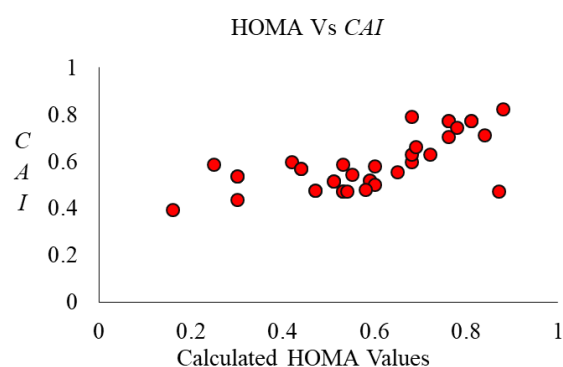
Figure 3. Comparison diagram of HOMA versus Clar Aromaticity Index values calculated using the constants as discussed in the text. The constants are derived after a least square analysis taking HOMA values into consideration.

We have also calculated the HOMO-LUMO gap ($\triangle E_{HL}$), electronegativity (χ), and hardness of the polyacenes ($\boldsymbol{\eta}$) (See Table 3). It has been observed that, in general, the gap is greater for the angular polyacenes than the corresponding linear polyacenes. A large $\triangle E_{HL}$ implies that the angular hydrocarbons are comparatively harder than their linear counterparts. The higher the hardness, the higher the resistance to reaction. In other words, the angular polyacenes are less reactive and have more kinetic stability. Thus, increasing helicity gives more aromatic stability as well as less reactivity. As far as electronegativity values are concerned, the electronegativity of the linear polyacenes, barring compound **6**, has a higher value than that of the angular one. Since the absolute electronegativity is a good measure of the molecular ability to attract electrons to itself, the trend in the electronegativity values of the hydrocarbons goes more or less parallel with the trend obtained from the hardness values. The exception for molecule **6** may be attributed to the strain involved in the structure, as discussed previously.

Table 3. The energy values of HOMO, LUMO, HOMO-LUMO gap ($\Delta E_{HOMO\text{-}LUMO}$), Electronegativity and Hardness of the compounds in eV unit.

Compound	E_{HOMO}	E_{LUMO}	$\Delta E_{HOMO\text{-}LUMO}$(eV)	Electronegativity (χ) (eV)	Hardness (η) (eV)
1	−0.22364	−0.04965	−4.73	3.72	4.73
2	−0.20225	−0.07197	−3.55	3.73	3.55
3	−0.22102	−0.04926	−4.67	3.68	4.67
4	−0.18858	−0.08765	−2.75	3.76	2.75
5	−0.20578	−0.06904	−3.72	3.74	3.72
6	−0.21766	−0.06289	−4.21	3.82	4.21
7	−0.17941	−0.09914	−2.18	3.79	2.18
8	−0.19252	−0.08534	−2.92	3.78	2.92
9	−0.20081	−0.07552	−3.41	3.76	3.41
10	−0.21246	−0.06107	−4.12	3.72	4.12

4. Conclusion

In this work, we have studied the aromatic character of the linear and their corresponding angular polyacenes. A total of ten molecules have been investigated. The aromaticity indexes, like Nuclear Independent Chemical Shift (NICS) values and Harmonic Oscillator Model of Aromaticity (HOMA) values, are calculated using standard software. In addition, we have establised Clar's 2-nomial for each molecule under investigation and estimated Clar Aromaticity Index (CAI) values as described by Misra et al.[22] Out of these three indexes, the Clar Aromaticity Index gives more acceptable data for the global aromatic character of conjugated hydrocarbons. It has been shown that the linear molecules are less

aromatic than the angular ones. This explains the stability of helical hydrocarbons. The other calculated parameters, like the HOMO-LUMO gap, electronegativity values, and hardness of the molecules, support the observation. However, a more quantitative measurement for a larger helical system (N-helicenes) is needed to establish the present observation on a larger farm foundation.

Acknowledgement:

I am thankful to Jagannath Kishore College, Purulia for providing me with Computational Support and Library facility.

References

[1] Kekulé , A. *Bull. Soc. Chim. Fr.* 1865, **3**, 98.

[2] Erlenmeyer, E. *Ann. Chem. Pharm.* 1866, **137**, 327.

[3] Pauling, L. *The Nature of the Chemical Bond and Structure of Molecules in Crystals*; Cornell University Press: Ithaca, 1960.

[4] Cyran´ski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem.* 2002, **67**, 1333.

[5] Bird, C. W. *Tetrahedron* 1985, **41**, 1409.

[6] Flygare, W. H. *Chem. ReV.* 1974, **74**, 653.

[7] Breslow, R. *Angew. Chem., Int. Ed. Engl.* 1968, **80**, 573.

[8] Krygowski, T. M.; Zachara, J. E.; Szatylwicz, H. *J. Org. Chem.* 2004, **69**, 7038.

[9] Krygowski, T. M.; Cyran´ski, M. K. *Chem. ReV.* 2001, **101**, 1385.

[10] Krygowski, T. M.; Cyran´ski, M. K. *Phys. Chem. Chem. Phys.* 2004, **6**, 249.

[11] Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. ReV.* 2005, **105**, 3842.

[12] Schleyer, P. v. R.; Manoharan, M.; Jiao, H.; Stahl, F. *Org. Lett.* 2001, **3**, 3643.

[13] (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* 1996, **118**, 6317. (b) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta R.; Schleyer, P. v. R. *Chem. Rev.,* 2005, **105**, 3842 and references therein.

[14] Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1939.

[15] Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, UK, 1964; Vols. I and II.

[16] Clar, E. *The Aromatic Sextet*; Wiley: London, UK, 1972.

[17] Randić, M. *Chem. Phys. Lett.* 1976, **38**, 68.

[18] Randic,M.; Gimarc,B.M.; Trinajstic, N. On the Aromatic Stabilities of Polyacenes and Helicines. *Croacita Chemica Acta.* **1986**, 59(2), 345.

[19] Cyvin, S. J.; Gutman, I. Kekule Structures in Benzenoid Hydrocarbons; Springer Verlag: New York, **1986**.

[20] Ivanciuc, O.; Bytautas, L.;Klein, D. J.;Mean-field resonating-valence-bond theory for unpaired π-electrons in benzenoid carbon species. J. Chem. Phys. 2002, 116, 4735-4748.

[21] Klein, D. J.; Bytautas, L. Graphitic Edges and Unpaired π-Electron Spins. J. Phys. Chem. A 1999, 103, 5196−5210.

[22] Misra A, Klein D. J., Morikawa T. *J. Phys. Chem. A* 2009, **113**, 1151.

[23] Misra, A.; Schmalz, T. G.; Klein, D. J. Clar Theory for Radical Benzenoids. *J. Chem. Inf. Model.* **2009**, 49, 2670−2676.

[24] Ormsby, J.L.;King, B.T. Clar Valence Bond Representation of π -Bonding in Carbon Nanotubes. J. Org. Chem. 2004, 69, 4287-4291.

[25] Wassmann, T.; Seitsonen, A.P.;MarcoSaitta, A.;Lazzeri, M.;Mauri, F. Clar's Theory, Pi-electron Distribution, and Geometry of Graphene Nanoribons. J. Am Chem. Soc. 2010, 132, 3440−3451.

[26] Baldoni, M.; Selli, D.; Sgamellotti, A.; Mercuri, F. Electronic Properties and Stability of Graphene Nanoribbons: An Interpretation Based on Clar Sextet Theory. J. Phys. Chem. C 2009, 113, 862−866.

[27] Klein, D. J.;Balaban, A.T.; Clarology for Conjugated Carbon Nano-Structures: Molecules, Polymers, Graphene, Defected Graphene, Fractal Benzenoids, Fullerenes, NanoTubes, Nano-Cones, Nano-Tori, etc. J. Org. Chem. 2011, 5,27-61.

[28] Hess, B. A. Jr.; Schaad, L. J. *J. Am. Chem. Soc.* 1971, **93**, 2413.

[29] Aihara, J. *J. Phys. Chem. A* 1999, **103**, 7487.

[30] Kruszewski J.; Krygowski, T. M. *Tetrahedron Lett.,* 1972, 3839.

[31] Krygowski, T. M.; Ciesielski, A.; Bird C. W.; Kotschy, A. *J. Chem. Inf. Comput. Sci.,*1995, **35**, 203.

[32] Krygowski, T. M.; Cyrański, M.; Ciesielski, A.; Świrska B.; Leszczyński, P. *J. Chem. Inf. Comput. Sci.,* 1996, **36**, 1135.

[33] Cyrański, M. K.; Stepień B.T.; Krygowski, T. M. *Tetrahedron,* 2000, **56**, 9663.

[34] Krygowski T. M.; Cyrański, M. K. *Chem. Rev.,* 2001, **101**, 1385.

[35] Krygowski T. M.; Cyrański, M. K. *Phys. Chem. Chem. Phys.,* 2004, **6**, 249.

[36] Mohajeri A.; Ashrafi, A. *Chem. Phys. Lett.,* 2008, **458**, 378.

[37] Portella, G.; Poater, J.; Bofill, J. M.; Alemany P.; Solà, M. *J. Org. Chem.,* 2005,**70**, 2509.

[38] Wolinski K, Hilton JF, Pulay P. *J. Am. Chem. Soc.* 1990, **112**, 8251.

[39] Bhattacharaya D.; Panda A.; Misra A.; Klien D. J.; Clar theory extended for polyacenes and beyond. *J. Phys. Chem. A* **2014,** *118*, 4325-4338.

[40] Klein, D. J.;Balaban, A.T.; Clarometic Carbon Nanostructures. *J.Phys.Chem. C* **2011,** *113*, 19123-19133.

[41] (a) Krygowski, T. M.; Cyranski, M. K.; Czarnocki, Z.; Ha¨felinger, G.; Katritzky, A. R. Tetrahedron 2000, **56**, 1783. (b) Portella, G.; Poater, J.; Bofill, J. M.; Alemany, P.; Sola, M. *J. Org. Chem.* 2005, **70**, 2509.. (c) Zhigalko M. V.; Shishkin O. V.; Gorb, L.; Leszczynski, J. *J. Mol. Struct.: THEOCHEM* 2004, **693**, 153.

[42] (a) Erich Steiner, E.; Fowler, P. W. *Int. J. Quantum Chem* 1996, **60**, 609. (b) Steiner, E.; Fowler, P. W.. Havenith R. W. A. *J. Phys. Chem. A,* 2002, **106**, 7048.