CHAPTER 3

A mini review article: Aromaticity in the light of magnetic criteria

3.1.

INTRODUCTION

The history of aromaticity, which is a fundamental concept in chemistry, began in 1825 when Michael Faraday[1] isolated benzene for the first time. However, the very first definition of aromaticity was given by Kekulé[2-3] in which he suggested oscillating structures where synchronous 1, 2-shifts of the three double bonds occur perpetually. Then after six decades, the works of Hückel[4-8] and Pauling[9] explained the role of delocalization of electrons in the stabilization of aromatic systems, using the quantum mechanics based Molecular Orbital (MO) approach and Valence Bond (VB) method respectively. Since then, the circular delocalization of electrons is taken as the genesis of aromaticity.

Aromaticity is developed as an important phenomenon for its close relation with chemical reactivity.[10] The increasing interest on aromaticity persuaded a need to attach a quantitative character to it. Consequently, a number of quantitative aromaticity indices have been anticipated starting from the famous $(4n+2)$ π- electron rule of Hückel to the latest Shannon Entropy index.[11] At present, the molecular property based criteria for aromaticity can be broadly divided into four basic categories such as magnetic,[12] structural,[13] electronic,[14] and energetic.[15] Electron density based indices such as para-delocalization index (PDI),[14] fluctuation index (FLU)[16] and multi-centre bond index (MCBI)[17] have also been introduced to characterize aromaticity. Later, Klein and co-workers correlated aromaticity of molecular benzenoids to a unique type of polynomial, [18] as Clar-2-nomial on the basis of Clar's concept of aromatic sextet .[19] Later on, this correlation has been extended for radical benzenoids[20] and more recently on polyacenes and beyond.[21] However, most of the indices do not provide direct measure of aromaticity, as the phenomenon is not directly observable.[22]

After a meticulous revision of structural, energetic and magnetic indices of aromaticity for many aromatic systems, Cyranski et al. concluded aromaticity as an abstract concept from philosophical point of view.[22] Whereas, from another perspective, the event of aromaticity can be regarded as multidimensional since it cannot be described definitely by any single property based index and all indices do not always give consistent results. Due to all these problems the quantification of aromaticity still remains a challenging and fundamental problem, and ought to be addressed through a precise phenomenological description.[23]

3.2.

CRITERIA FOR DEFINING AROMATICITY

3.2.1. Chemical behavior

Electrophilic aromatic substitution reactions are the characteristic reactions of the aromatic systems but it is difficult to define aromaticity with the help of the chemical behavior of the molecule. Since aromaticity is a property of the initial state, and reactivity is the property of the intermediate states so quantifying aromaticity with the help of chemical reactivity is not straightforward. The characteristic electrophilic aromatic substitution reaction also has many exceptions, for example, phenanthrene and anthracene which are aromatic molecules prefer addition of bromine rather than substitution. Also fullerenes (eg, C_{60} or C_{70}) are aromatic compounds but since they are devoid of any hydrogen, they do not undergo aromatic substitution reactions but only undergo addition reactions.[12]

3.2.2 Structural pattern

Aromatic systems are mainly planar systems. The characteristic property of an aromatic system is that its bond lengths are all equal and π-electrons are delocalized. The direct determination of bond lengths gives us valuable information regarding the extent of delocalization. In contrast, in antiaromatic molecules the alternating double and single bond lengths differ significantly, generally over 0.2 Å in length.[24] However, bond length equalization and the symmetry associated with it cannot be used as the only parameter for defining aromaticity because some systems possessing equal bond lengths are not aromatic. Again, borazine which is an isoelectronic system with benzene has roughly equal bond lengths and considered to be weakly aromatic in nature.[12] The degree of aromaticity in borazine has been a topic of some controversy[25] starting soon after its discovery in 1926 by Stock and Pohland.[26] The properties of borazine are in good accordance with a ring structure of six atoms which ''on-the-average'' correspond to a sp^2 hybridized-carbon.[27] Also, strain effects and other contributing factors provide hindrance in predicting aromaticity with the help of structural criteria.[24]

3.2.3 Energetic criteria

Aromaticity has long been connected to the enhanced resonance energies (REs) and the aromatic stabilization energies (ASEs). Even the (4n+2) π- electron rule of Hückel is based on energetic criterion. The energetic measure of aromaticity and antiaromaticity is based on evaluations of energies relative to the reference systems such as conjugated polyenes or olefins.[24] However, determinations of (REs) and (ASEs) are quite difficult even for simple systems.[12] Since ASE itself is not physically observable, [28] direct experimental determination of ASE is difficult. However, starting from the pioneering work of Pauling and Sherman,[29] various efforts have been made to estimate ASE from experimental data. Also, introduction of isodesmic [30] and homodesmotic reactions, [31] has made it possible to calculate the ASE from the energies of reactants and products, obtained experimentally from calorimetric measurements.[32] In a recent work a phenomenological model is discussed to evaluate ASE without any reference state.[23]

3.2.4. Magnetic criteria

Primarily, aromaticity was restricted to all carbon, coplanar, delocalized conjugated π systems having (4n+2) π electrons according to Huckel's rule of aromaticity.[4-8] Presently aromaticity is not only confined to the organic systems, according to Boldyrev, "Aromaticity has in recent years become an important and powerful unifying concept to describe the stability and bonding in many chemical species beyond organic chemistry, including inorganic cations, anions, radicals, and clusters.",[33] three dimensional aromaticity involving σ-electrons and multidimensional aromaticity involving d-orbitals have been reported. Aromaticity has not been confined to ground states but it has been extended to transition states and excited states. There is possibly no direct way to calculate the aromaticity in a molecule experimentally.

Magnetic criteria are currently the most popular methods and constitute the most frequently used aromaticity indices. There are various criteria for defining aromaticity such as energy, structure, electron density based indices[34] and magnetic properties but we focus our discussions to magnetic properties only. Magnetic properties provide considerable insight into the concept of aromaticity. The anomalous diamagnetization of benzene has been related to the delocalization of π-electrons since the early days of quantum chemistry. The aromatic molecules demonstrate relatively strong diamagnetism when placed in a magnetic field; this is due to the generation of an opposing magnetic field by the induced ring currents. The magnetic criteria of aromaticity are dependent on the specific reaction of the aromatic compounds to externally applied uniform magnetic field which is placed perpendicular to the molecular plane. This contribution of π-electrons to the magnetic susceptibility component which is placed perpendicular to the molecular plane was chosen as an indicator of aromaticity. While the direction of an induced current in a loop is determined by the relative orientation of the magnetic field and the loop's movement but the direction of the current in a molecule also depends on the type of the system. Generally in a system containing 4nπ electrons, an external magnetic field induces a paratropic ring current (i.e. in the opposite direction relative to a classic loop) while a system containing (4n+2)π electrons shows a diatropic ring current(i.e. in the same direction as a classic loop).[35]

Magnetic properties are necessary but not sufficient to describe a system as aromatic or antiaromatic but magnetic criterion has an advantage over other criterion that we can compare the paratropic and diatropic ring currents to experimental values derived from NMR. Now, the concept of aromaticity is no longer confined to the organic domain but has been found in all-metal clusters systems and the existence of an σ-aromaticity.[36] The most popular and frequently used aromaticity indices are NMR chemical shifts, magnetic susceptibility anisotropy, Nucleus Independent Chemical Shift (NICS), Aromatic Ring Current Shielding (ARCS) and Current Density Analysis (CDA plots).[35]

3.2.4.1. NMR chemical shifts

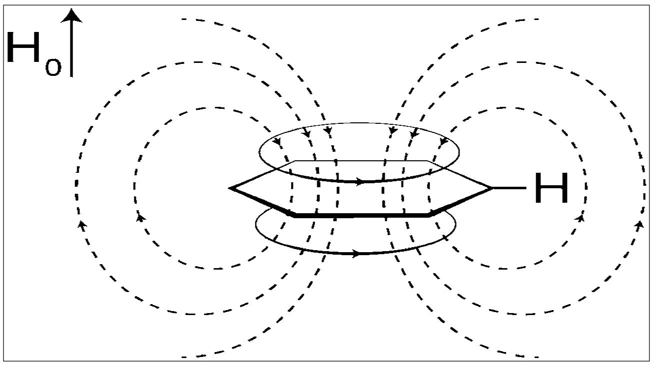

Figure 3.1. Representation of the Ring Current Model in the case of benzene. [35]

The most widely used NMR chemical shifts method is the ^{1}H-NMR method. According to the Ring Current Model (RCM),[37] for a (4n+2) π electrons system, the diatropic ring current will form an induced magnetic field which is opposite in direction to the applied external magnetic field at the centre of the ring as depicted in the above diagram (Figure 3.1). While outside the ring the curved lines of the magnetic field are in the same direction as the applied external field. Thus protons that are inside the ring experience an upfield shift while protons that are outside experience a downfield shift. In the case of a 4nπ electron system, a paratropic ring current is induced, so here the induced magnetic field is in the same direction as the external field at the centre of the ring while outside the ring it is in the opposite direction to the external field, thus here the internal protons experience a downfield shift while the external protons experience an upfield shift, that is the effect is exactly the opposite. Thus, the chemical shifts of protons have been used to characterize aromatic and antiaromatic compounds. The ring current picture has proven to be powerful in justifying the magnetic properties of π electron systems quantitatively. The concept is so visual "that one can almost *feel* when a molecule is subjected to a magnetic field." The ring current is connected to the concept of aromaticity experimentally through anisotropy of magnetic susceptibility or through exaltation of magnetic susceptibility or by chemical shifts methods in a Nuclear Magnetic Resonance experiment and also individual ring current intensities which can be computed.[38]

The rings of most aromatic systems are too small to accommodate inner protons, so the chemical shifts of hydrogen at the bridging positions provide better information regarding the aromaticity and antiaromaticity of the systems. However, this criterion is not general for aromatic systems that are devoid of hydrogen like for example C_{60} and the oxocarbons (30) and ^{13}C chemical shifts in aromatic hydrocarbons are not deshielded.[24]

Other NMR chemical shifts methods are Li^+ and ^3He chemical shifts method. Chemical shifts of ^7Li were used to investigate the electron delocalization. Aromatic and antiaromatic compounds of Li^+ complexes show significant shielding and deshielding respectively of the ^7Li NMR signals due to the induced ring currents. ^7Li chemical shifts obtained by modern computations technique match well with the ^7Li NMR chemical shifts that are obtained experimentally. So, one of the advantages of using Li^+ NMR chemical shifts as a computational tool is that it can be compared with the experimental Li NMR data of Li^+ complexes.[24] However, a major drawback is that the ring currents are relatively small. Also, the number of Li^+ complexes is limited therefore the use of Li^+ NMR chemical shifts as a magnetic criterion is also limited. An extension of the use of NMR to assess aromaticity was developed mainly by Mitchell.[39]

3.2.4.2. Magnetic susceptibility anisotropy

This method provides another magnetic criterion of aromaticity. The tensor normal to the aromatic ring is much larger than the average of other tensors and this difference is termed as exaltation. Magnetic susceptibility exaltation (λ) is the difference between the observed bulk magnetic susceptibility value and the susceptibility that is evaluated on the basis of an increment system ($\lambda=\chi_m-\chi_{m'}$). The exaltation of magnetic susceptibility is mainly due to the induced ring currents and is a widely employed magnetic criterion especially for the characterization of metal clusters. In the 1996 review article entitled "What is aromaticity", Schleyer and Jiao suggested that "compounds which exhibit significant exalted diamagnetic susceptibility are aromatic. Those compounds with exalted paramagnetic susceptibility may be antiaromatic."[24]

However, this method is applicable for planar or nearly planar aromatic molecules and is not applicable in the case of spherical systems. Also, in some cases, high magnetic anisotropy does not necessarily imply aromaticity. In addition, the contribution to the magnetic susceptibility component which is perpendicular to the molecular plane provides a more consistent aromaticity criterion than that which is dependent solely on magnetic anisotropy.[40] This method was popular earlier, but recently it is not much in use because it is difficult to quantify aromaticity using this method. Nowadays, computational methods are more developed and provide a better qualitative and quantitative understanding of the magnetic properties.

It is interesting to note that ring currents and aromaticity are theoretical properties and neither are measurable quantities but both NMR chemical shifts and magnetic susceptibility exaltation methods are experimentally measurable quantities that result from ring currents.

3.2.4.3. Current Density Analysis Plots (CDA)

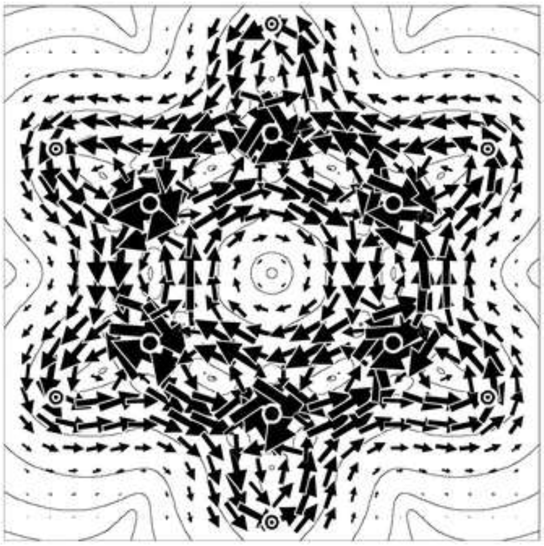

Figure 3.2. Plot of the current density induced in the molecular plane of the benzene by a perpendicular external magnetic field.[56]

This method is purely a computational method. It is the visualization of the ring currents with the help of arrows and the direction of the arrows gives us the idea of whether the ring current is diatropic or paratropic. Clockwise direction represents paratropic ring current while anticlockwise direction represents diatropic ring current. Also the size of the arrows indicates the strength of the ring current. The CDA plot of benzene ring is depicted in the above figure (Figure 3.2).

According to the Ring Current Model (RCM)[37] in the presence of an external magnetic field, a diatropic ring current is generated in aromatic systems and a paratropic ring current is generated in antiaromatic systems. Thus, the aromaticity of a planar or a nearly planar compound when placed in an external magnetic field perpendicular to the molecular plane can be obtained directly, either by calculating the intensity of the current or by calculating the current density in a given system. New computational methodologies are now developed that provide a visual representation of the current density field induced in a molecule. These current density maps provide relevant information and help in understanding features of aromatic compounds.

The main advantage of this method is that it provides pictorial representation of the ring currents in the systems. However, the major drawback of this method is that it is very difficult to quantify and also the pictures that are obtained through this method are not easily separable into their individual components. Also, in some cases, high magnetic anisotropy does not necessarily imply aromaticity. In addition, second order magnetic properties; such as polarizability, magnetizability, and nuclear shielding were not calculated accurately by the original methods which can generally be obtained by the integration of first order current density. The most popular CDA methods are: Continuous Transformation of Current Density – Diamagnetic Zero (CTOCD-DZS) [41-43] also known as the ipsocentric method.[44-46]

3.2.4.4. Nucleus Independent Chemical Shift (NICS)

It is the most popular method for quantifying the magnetic properties of molecules mainly due to its simplicity and efficiency. NICS has been popularized by Schleyer and his co-workers.[47] NICS is defined as the negative value of the absolute magnetic shielding. NICS method uses a ghost atom namely Bq (named after the ghost Banquo from Shakespeare's Macbeth), it is devoid of any electrons, protons and neutrons. Initially it was placed at the centre of the system [NICS (0)], then later at a distance of 1 Å above the plane [NICS (1)].This ghost atom is like a sensor for the magnetic environment at the position at which it is placed. The ghost atom senses this magnetic environment and reports the chemical shielding values through the use of computational technique like GIAO. [48-49] The NICS values were reported with reversed signs, in agreement with NMR chemical shift convention. Positive NICS value indicates a paratropic magnetic field whereas a negative NICS value indicates a diatropic magnetic field, thus a negative NICS value would mean that a system is aromatic and a positive NICS value would correspond to an antiaromatic system. In some cases, the negative value indicates the 3D-aromaticity of the molecule.[50] The chemical shift is used as an indicator of the direction and magnitude of the induced magnetic field. From Figure 3.3 it can be noted that NICS corresponds well with the aromatic stabilization energy.[24]

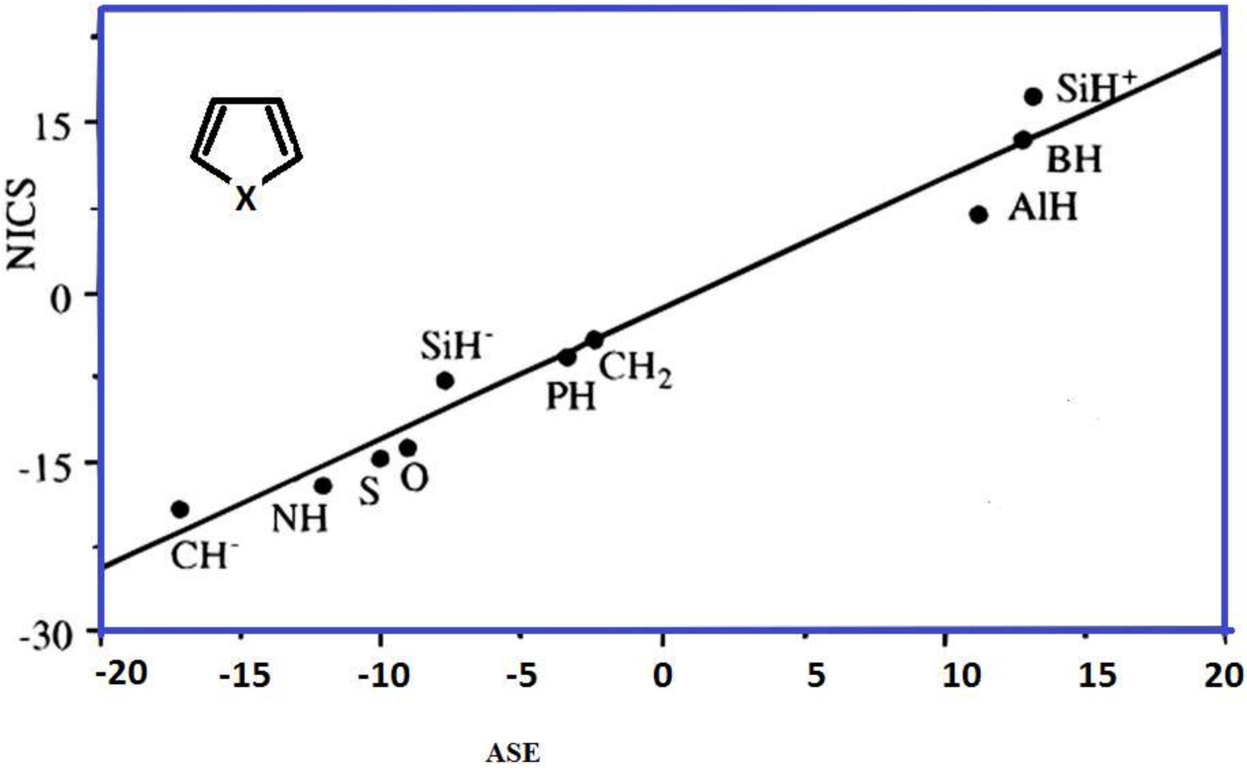

Figure 3.3. Plot of NICS (0) (ppm) *vs*. the ASE (kcal mol^{-1}) for a set of five-membered ring heterocycles, C_4H_4X (X = as shown).[24]

According to an article in 2005 by Schleyer and his coworkers, "NICS has several advantages over many other aromaticity criteria: (i) NICS does not require reference standards, increment schemes, or calibrating (homodesmotic) equations for evaluation. (ii) Unlike λ which depends on the square of the ring area, NICS only shows a modest dependence on the ring size. It does depend on the number of electrons. The 10 π electron systems give significantly higher values than those with six π electrons, for example, the cyclooctatetraenedication and dianion. (iii) Importantly, in several sets of related molecules, NICS correlates well with other aromaticity indexes based on energetic, geometric, and other magnetic criteria (iv) NICS can becomputed easily using standard quantum chemical programs such as Gaussian 09, Gaussian 98, Gaussian 03, ADF, and deMon."[12]

After their initial publication, Schleyer and his co-workers noted the problem in using NICS for 3-membered systems due to the local shielding effects of the neighboring σ-bonds. So they introduced two modifications in the following year. [51] The first modification was that the bq was raised 1 Å above the molecular plane, which was termed as NICS (1). Since σ-contributions are short ranged, so NICS (0) has greater σ-contributions, so by raising the bq by 1 Å, the σ-contributions are effectively reduced. Secondly, the total NICS value was separated into σ and π contributions. Since aromaticity results from π contributions, so NICS (1) is a better aromaticity criterion than NICS (0).

However, the major drawback of NICS is that it reports only a single value at a given position, without any information regarding the magnetic field. Also, there are other magnetic shielding contributions from the local circulation of electrons in bonds, lone pairs and interior electrons, so the reliance on the π-system is not pure. In fact the σ framework of the CC and CH bonds affects the chemical shifts of organic molecules, as a result of this; the NICS value is non-zero for non-aromatic, saturated and unsaturated hydrocarbon rings. Sometimes NICS is considered as a local index rather than a global, aromatic index because contributions from remote parts of molecule are small. Later refinement of the original NICS technique offered better understanding of the aromatic systems which include the Dissected NICS technique which consists of the LMO-NICS method and the CMO-NICS method.[12] Other modifications like NICS rate and NICS scan are also known.

The major difficulty in quantifying aromaticity may be due to the fact that aromaticity is not a property of the ground state energy of molecules but is rather dependent on the excited π electron state. So a recent and a fresh approach, i.e., Quantitative Structure Aromaticity Relationships (QSArR) in relating aromaticity with physico-chemical molecular properties such as chemical hardness and electronegativity are reflected in the works of Putz. His works focuses on the connection of aromaticity with a reactivity index. If successfully applied, "It may provide both conceptual new insight on the aromaticity concept as well as generalization of the chemical reactivity theory and principles grounded on structural indices as electronegativity and chemical hardness that have been intensively considered in the last decades within density functional theory and quantum chemistry." [52-54]

3.3.

CONCLUSIONS

Aromaticity is now no longer confined to the domain of organic chemistry and various inorganic clusters are found to be aromatic considering the delocalization of the π electrons as the genesis of aromaticity. The ease with which aromaticity bridges the gap between traditional aspects of organic chemistry and latest discoveries in inorganic chemistry are truly fascinating. Aromaticity is not a physically observable quantity so defining it precisely is still a challenge. Quantification of aromaticity is a major challenge to the theoretical and the computational chemists till date. Whether aromaticity is a multidimensional phenomenon or it can be defined by a universal single unique criterion is a debatable topic. The journey of aromaticity from Kekulés definition of benzene has been extensive and the recent developments in this field provide a considerable better insight into the concept. It is aptly said by Schleyer that, “aromaticity has been a time-dependent phenomenon.” The perception of aromaticity is different in terms of its properties and characteristics to chemists with diverse backgrounds.[55] The magnetic criterion for defining the concept of aromaticity has become very prominent surpassing the other criteria. Various developments in this field have occurred in the recent years and most of the developments were in the magnetic domain. So we can conclude by saying that the magnetic criterion is the most important criterion and provides a plethora of opportunities of future work on aromaticity.

3.4.

REFERENCES

1. Faraday, M. M.*Phil.Trans.Roy.London.* **1825,** *115*, 440-446.
2. Kekulé, A. *Bull.Soc.Chim.Paris* **1865,** *3*, 98-100.
3. Kekulé, A. *Ann.Chem.Pharm* **1866,** *137*,129-196.
4. Hückel, E. *Z. Phys.* **1930,** *60*,423–456.
5. Hückel, E. *Z. Phys.* **1931**, *70*, 204–86.
6. Hückel, E. *Z.Phys.* **1932,** *76*,628-648.
7. Hückel, E. *Z.Electrochem, Angew.Phys.Chem.* **1937,** *43*, 752-788.
8. Hückel, E. *Z.Electrochem, Angew.Phys.Chem* **1995,** *61*,866-890.
9. Pauling, L; Wheland, G.W. *J.Chem.Phys.* **1933**, *1*, 362-374.

10. (a) Balaban, A. T.; Oniciu, D.C.; Katritzky, A.R. *Chem. Rev* **2004**, **104***(5)*, 2777-2812. (b) Chattaraj, P. K.; Sarkar, U.; and Roy, D. R. *J. Chem. Educ*., **2007**, *84*, 354.(c) Chattaraj, P.K.; Roy, D. R.; Elango, M.; and Subramanian, V. *J. Phys. Chem.A* **2005**, *109*, 9590.
11. Noorizadeh, S.; Shakerzadeh, E. *Phys.Chem.Chem.Phys.* **2010**, *12(18)*, 4742-4749.
12. Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem.Rev* 2005, *105(10)*, 3842-3888.
13. Krygowski, T. M.; Cyrański, M. K. *Chem. Rev* 2001, **101***(5)*, 1385-1420.
14. Poater, J.; Duran, M.; Solà, M.; Silvi. B. *Chem.Rev* **2005**, *105(10)*, 3911-3947.
15. Cyrański, M. K. *Chem. Rev* 2005, **105***(10)*, 3773-3811.
16. Matito, E.; Duran, M.; Solà, M. *J. Chem. Phys.* 2005, **122***(1)*, 014109.
17. (a)Bultinck, P.; Ponec, R.; Van Damme, S. *J. Phys. Org. Chem* 2005, *18(8)*, 706-718. (b) Roy, D.R.; Bultinck, P.; Subramanium, V.; Chattaraj, P.K. *J. Mol. Struc (THEOCHEM)* 2008, *854(1-3)*, 35-39.
18. Misra, A.; Klein, D. J.; Morikawa, T. *J. Phy. Chem. A* **2009,** *113(6)*,1151-1158.
19. Clar, E. The Aromatic Sextet. Wiley & Sons: New York, **1970**.
20. Misra, A.; Schmalz, T. G.; Klein, D. J. *J. Chem. Inf. Model* **2009,** *49(12)*, 2670-2676.
21. Bhattacharya, D.; Panda, A.; Misra, A.; Klein, D. J. *J.Phys.Chem.A* **2014,** *118(24)*, 4325-4338.
22. Cryański, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P.v.R. *J.Org.Chem* **2002,** *67(4)*, 1333-1338.
23. Paul, S.; Goswami, T.; Misra, A *AIP Advances* **2015**,*5*, 107211.
24. Schleyer, P.v.R.; Jiao, H. *Pure & Appl.Chem.***1996,** *68* 209-218.
25. Islas, R.; Chamorro, E.; Robles, J.; Heine, T.; Santos J.C.; Merino, G. Borazine: to be or not to be aromatic *Struct.Chem.* 2007, *18*, 833.
26. Stock, A.; Pohland, E. Borwasserstoffe, IX.: B3N3H6. *Chem. Ber.*1926, *59B*, 2215.
27. Bhattacharya, D.; Shil, S.; Misra, A.; Bytautasc, L.; Klein, D.J. *Phys. Chem. Chem. Phys.* 2015, *17*, 14223.
28. Mo, Y.; Peyerimhoff, S. D. *J.Chem.Phys.*1998, *109(5)*, 1687-1697.
29. Pauling, L.; Sherman, J. *J. Chem. Phys.* 1933, *1(8)*, 606-617.
30. Hehre, W. J.; Radom, L.; Schleyer,P. v. R.; Pople, J.A. Ab Initio Molecular Orbital Theory, Wiley &Sons: New York, **1986**.
31. Hehre, W. J.; McIver, R.T.; Pople, J.A.; Schleyer,P. v. R. *J. Am. Chem. Soc*. **1974**, *96(22)*, 7162-7163.
32. Pedley, J. B.; Naylor, R. B.; Kirby, S. P.; Thermodynamical Data of Organic Compounds, Chapman & Hall: London, **1986**.
33. Jose, M. M.; Boldyrev, A. I.; Merino, G.; Ugalde, M.J. *Chem.Soc.Rev.* 2015, *44*, 6519.
34. Poater, J.; Fradera, X.; Duran, M.; Solá, *Chem-Eur.J.***2003**, *9(2)*, 400-406.
35. Poranne, G. P.; Stranger, A. *Chem.Soc.Rev.* 2015, *44*, 6597.
36. (a) Dewar, M. J. S.; McKee, M.L *Pure Appl. Chem.*1980, *52*, 1431 – 1441. (b)Dewar, M. J. S. *Bull. Soc. Chim.Belg.* 1979, *88*, 957 – 967.
37. Pople, J. A. *Mol, Phys.*, **1958**, *1*,175-180.
38. Gomes, A. N. F.; Mallion, R. B. *Chem.Rev.* **2001**, *101*, 1349-1384.
39. Mitchell, R. H. *Chem.Rev.* **2001**, *101*, 1301-1315.

40. Benassi, R.; Lazzeretti, P.; Taddei, F. *J.Phys.Chem.* 1975, *79(8)*, 848-851.
41. Coriani, S.; Lazzeretti, P.; Malagoli, M.; Zanasi. R. *Theor.Chim.Acta.* **1994**, *89*,181-192.
42. Lazzeretti, P.; Malagoli, M.; Zanasi, R. *Chem.Phys.Lett.* **1994**, *220*, 299-309.
43. Zanasi, R. *J.Chem.Phys.* 1996, *105*, 1460-1469.
44. Steiner, E.; Fowler, P.W. *J.Phys.Chem.A* 2001, *105*, 9553-9562.
45. Steiner, E.; Fowler, P.W. *Chem.Commun.* **2001**, 2220-2221.
46. Steiner, E.; Fowler, P. W.; Havenith, R. W .A. *J.Phys.Chem.A* 2002, *106*, 7048-7056.
47. Schleyer, P. v. R; Maerker, C.; Dransfeld, A.; Jiao,H.; Hommes, N. J. R. *J.Am.Chem.Soc.* **1996**, *118*, 6317-6318.
48. London, F. *J. Phys. Radium.* **1937**, *8*, 397.
49. (a) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497.(b) Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1995**, *99*, 606.(c) Schreckenbach, G.; Ziegler, T. *Theor. Chem. Acc.* **1998**, *99*, 71.
50. Chattaraj, P.K. Aromaticity and Metal Clusters,Taylor & Francis/CRC Press: Florida, **2010**.
51. Schleyer, P. v. R; Jiao, H.; Hommes, N.J.R.; Malkin,V. G.; Malkina, O. *J.Am.Chem.Soc.* **1997**, *119*,12669-12670.
52. Putz, M. V. *MATCH Commun. Math. Comput. Chem*. **2010**, *64*, 391-418.
53. Putz, M. V. *Int. J. Mol. Sci.* 2010, *11*, 1269-1310.
54. Tarko, L.; Putz, M. V. *J.Math.Chem,***2010**, *47(1)*,487-495.
55. Schleyer, P. v. R. *Chem.Rev.* 2001, *101*, 1115-1118.
56. Bultinck, P. General discussion. *Faraday Discussions* **2007**, 135, 367-401.