

CHAPTER 1

Aromaticity

1.1.

INTRODUCTION

1.1.1. Genesis of the Concept of Aromaticity

The term “aromatic” was employed by chemists as early as in the beginning of the 19th century which was used to depict organic substances with a pleasant odor and distinguished them from the straight chain aliphatic compounds. The term “aromaticity” then became intrinsically linked with benzene after it was first isolated and characterized by Michael Faraday in the year 1825.¹ However, the foremost definition of aromaticity was given by Kekulé² where he described benzene as “a regular arrangements of the six carbon atoms” in which he suggested oscillating structures where synchronous 1, 2-shifts of the three double bonds occur continually. Emil Erlenmeyer³ recommended the use of the word "aromatic" for the compounds possessing similar properties to benzene and was the first one to attach reactivity criteria to aromaticity. The deciding reactivity criterion for aromaticity as proposed by him was that the compound should be inclined more towards substitution reactions than towards addition ones. In 1867, Dewar predicted the structure of benzene as one of seven possible isomers⁴ and alleged that his experiments involving benzene supported the structure as deduced by Kekulé. Based on the structure constructed by Kekulé, Robinson and Armit in 1925 represented the benzene by a ring. After the inception of valence bond theory in 1928,⁵ the stabilization of the aromatic systems was attributed to the delocalization of π - electrons. A breakthrough in defining the aromaticity of a substance was accomplished by Hückel in 1931. "Hückel's rule" of cyclic $4n+2$ π -electron systems enables aromatic and anti-aromatic compounds to be differentiated on the basis of the number of π -electrons. However, this rule is firmly applicable only to conjugated monocyclic systems so an extension of this rule to polycyclic systems was successfully accomplished by Clar in 1972 in the book “*The Aromatic Sextet*”.⁶ Clar's rule defines the aromatic π -sextets as six π -electrons localized in a single benzene-like ring divided from adjoining rings by formal CC single bonds which was vital for characterization of properties of polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, anthracene or phenanthrene. The concept of aromaticity was further extended to heteroatoms such as furan, thiophene and pyrrole and to annulenes and their respective ions as tropylium ions.

The confinement of the concept of aromaticity to the domain of organic chemistry was broken by the inception of the concept of metalloaromaticity by Calvin and Wilson in the year 1945.⁷ The opposite pattern of aromatic character to conventional Hückel systems was observed by Heilbronner⁸ where a monocyclic array of orbitals in which there is a single out-of-phase overlap (an odd number of out-of-phase overlaps) is stabilized (aromatic) with $4n$ electrons, whereas with $4n+2$ electrons it is destabilized (antiaromatic). The name assigned was Möbius aromaticity which was derived from the topological resemblance of an arrangement of orbitals to a Möbius strip. Discovery of cyclononatetraenyl anion by Katz⁹ paved the inclusion of aromatic anions to the realm of aromaticity. Baird's rule further stretches the boundary of aromaticity to the lowest triplet excited state of planar cyclic structures where it is also observed that the Huckel's rule of aromaticity is reversed.¹⁰ Three dimensional aromaticity was first introduced by Aihara in planar boron clusters in the year 1978.¹¹ The most recent advancement in the field of aromaticity was the characterization of the first all-metal aromatic cluster Al_4^{2-} by Boldyrev, Wang et al.¹² Quoting Boldyrev's words "*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.*",¹³ three dimensional aromaticity involving σ -electrons and multidimensional aromaticity involving d -orbitals (δ -aromaticity) or even ϕ - (including f -orbitals) have been reported.¹⁴ The chronological advancement in the field of aromaticity is listed in Table 1.1 and illustrated in Figure 1.1.

Table 1.1. Chronological salient contributions to the advancement of the concept of aromaticity

Contributors	Year	Works
M. Faraday	1825	Benzene isolation
A. Kekulé	1865	Cyclic formula of benzene
Erlenmeyer	1866	Reactivity criteria for aromaticity
J. Dewar	1867	Dewar benzene formula
R. Robinson and T. W. Armitt	1925	Aromatic π -sextet
E. Hückel	1931	Hückel molecular orbital theory
Evans, Warhurst	1938	Transition state stabilization by aromaticity
Calvin, Wilson	1945	Aromaticity in metal systems
S. Winstein	1959	Homo-aromaticity
E. Heilbronner	1964	Möbius annulene
T. J. Katz	1965	Aromatic anions
A. L. Chung and M. J. S. Dewar	1965	Anti-aromaticity
Osawa	1970	Superaromaticity
E. Clar	1972	Clar aromatic sextet
Baird	1972	Triplet aromaticity
Aihara	1978	Three-dimensional aromaticity
M. J. S. Dewar	1979	σ -aromaticity
P. v. R. Schleyar	1979	In plane and double aromaticity
H. W. Kroto, R. F. Curl, and R. E. Smalley	1985	Buckminsterfullerene C ₆₀
Boldyrev and Wang	2001	All-metal aromaticity
P. v. R. Schleyar	2005	d-orbital aromaticity
Boldyrev and Wang	2007	δ -aromaticity
Tsipis	2008	f-aromaticity

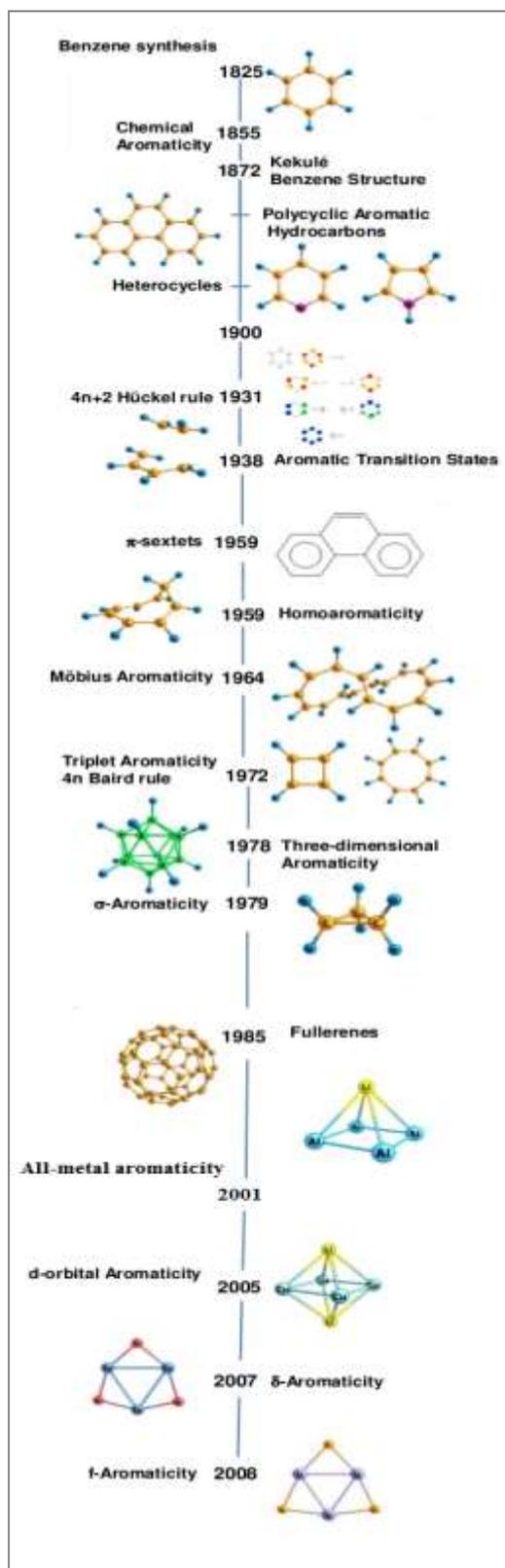


Figure 1.1. Chronological advancement of aromaticity.

The works of Hückel⁵ and Pauling¹⁵ 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. In a VB-type approach to the archetypical aromatic molecule benzene, the circular topology of benzene facilitates a resonance between the wave functions of two complementary sets of localized bond which leads to an extra stabilization of the aromatic moiety. On the other hand, resonance integral or interaction matrix element in circular, planar conjugated hydrocarbons with $4n+2$ π -electrons were considered to be the reason behind the additional stabilization in benzene by the MO approach.^{5,16} Goldstein and Hoffmann later provided a generalization to other pericyclic topologies.¹⁷

1.1.2 Criteria for defining aromaticity

A basic definition of aromaticity based on its criteria can be qualitatively described as, *“Aromaticity is a manifestation of electron delocalization in closed circuits, either in two or in three dimensions. This results in energy lowering, often quite substantial, and a variety of unusual chemical and physical properties. These include a tendency toward bond length equalization, unusual reactivity, and characteristic spectroscopic features. Since aromaticity is related to induced ring currents, magnetic properties are particularly important for its detection and evaluation”*.¹⁸ 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. On the basis of available literature, the basic criteria for the quantification of aromaticity can be divided into the following categories: (a) Reactivity: electrophilic aromatic substitution reactions are the characteristic reactions of the aromatic systems, (b) Structure: 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, (c) Energy: aromatic systems have enhanced Resonance Energies (REs) and the Aromatic Stabilization Energies (ASEs), (d) Magnetic Criteria: Magnetic properties are currently the most popular and frequently used criterion for defining aromaticity, 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 (Figure 1.2). The magnetic criteria of aromaticity are reviewed in detail in Chapter 3.

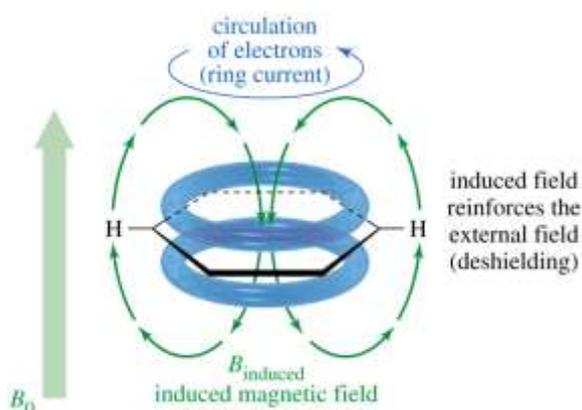


Figure 1.2. Demonstration of relatively strong diamagnetism of archetypical aromatic benzene molecule when placed in a magnetic field due to the generation of an opposing magnetic field by the induced ring currents.

Although aromaticity being the most widely used concept in Chemistry for a long time, the designation of aromaticity is still not unequivocally settled and any of its definition is not unique enough. So quantification of aromaticity is still a major issue to the theoretical and the computational chemists. 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 a challenge till date. Whether aromaticity is a multidimensional phenomenon or can it be defined by a universal single unique criterion is an arguable topic. Aromaticity is perceived differently by chemists of diverse backgrounds in terms of its characteristics and properties. The journey of aromaticity from Kekulé's 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.*"¹⁹ So, even after two centuries of its existence, this colossal concept is still continually flourishing with increasing vigor and stable novel molecules are enriching the domain of aromaticity.

1.2

EXO-CYCLIC AROMATICITY

Exo-cyclic delocalization at the expense of aromaticity was first used to explain the stability of experimentally observed small ring allenes²⁰ but after that this domain of aromaticity has remained untouched for a long period of time. In this thesis, a new domain of aromaticity is explored where novel aromatic molecules are theoretically modeled which gains extra stability due to the generation of aromaticity via the back-donation of the substituted ligands attached to the ring (Figure 1.3). The well known back-donation of the π -electrons of the Fluorine ligand to the vacant p_z of Boron is tweaked upon while designing these highly stable aromatic systems. The concept of $2p-2p$ orbital interaction or back-donation of fluorine has been well identified in the organic and inorganic domain.²¹⁻²³ Both the inductive effect and the resonance or the back-donation effect play a vital role when the non-bonded pair of electrons of fluorine interact with the vacant orbital of the boron atom to which it is attached. The tendency of back-donation by fluorine has been established to be greater than that of the other halogen atoms such as chlorine and bromine, where the order of back-donation is found to be $F > Cl >> Br$.²⁴ The degree of back-donation decreases with the increase in the atomic sizes of the halogens since the $2p-2p$ interaction is more favorable as compared to the interaction between $3p$ and $4p$ orbital of chlorine and bromine respectively with the vacant $2p$ orbital of boron due to mismatch in the size of the orbitals.

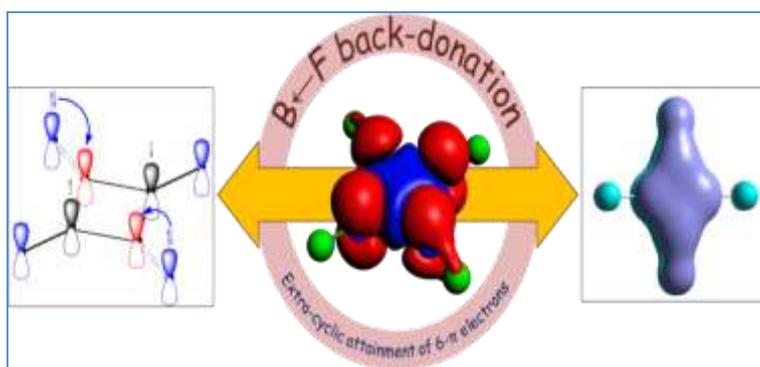


Figure 1.3. Illustration of exo-cyclic aromaticity.

The concept of exo-cyclic aromaticity is further explored to understand and analyze the stability and aromaticity of modeled novel heteroatomic molecular systems where aromaticity in the heteroatomic central ring is achieved through back donation of electrons from the substituted ligands.

1.3

ALL-METAL AROMATIC CLUSTERS

Thorn and Hoffmann²⁵ predicted in 1979 that some theoretical metallocycles should display delocalized bonding and thereby some aromatic behaviors. In the same year, the term “metalloaromaticity” was introduced by Bursten and Fenske²⁶ to explain metal complexes of cyclobutadiene - aromatic compounds comprising of a metal atom coordinated to C₄H₄, which can be considered as the archetypal Hückel antiaromatic ($4n \pi$ electrons) molecule. However, a coordinated C₄H₄ often behaves as if it were aromatic instead of antiaromatic. The first organometallic compound including an aromatic cycle entirely composed of metal atoms was synthesized by Robinson et al.²⁷ in the year 1995. Despite of an increasing development in the field of synthesizing aromatic compounds with metal atoms being a part of the aromatic ring, the concept of aromaticity was not extended into gas-phase metal clusters and bulk metal alloys until very recently in 2001 when a series of bimetallic clusters, LiAl₄⁻, NaAl₄⁻, and CuAl₄⁻, in the gas phase and obtained their photoelectron spectra.¹² The theoretical studies revealed that the most stable isomers of these bimetallic clusters all contain a square-planar Al₄²⁻ dianion, which was established to be aromatic moiety. Thus, aromaticity was extended to an all-metal isolated Al₄²⁻ dianion and to bimetallic all-metal LiAl₄⁻, NaAl₄⁻, and CuAl₄⁻ clusters. Since then aromaticity has been reported in a large number of gaseous all-metal or metalloid clusters: XAl₃⁻ (X = Si, Ge, Sn, Pb),²⁸⁻³⁰ M₄²⁻ (M = Ga, In, Tl, Sb, Bi),³¹⁻³⁴ T₅⁶⁻ (T = Ge, Sn, Pb),^{35,36} M₄²⁺ (M = Se, Te),³⁷⁻⁴¹ M³⁻ (M = Al, Ga),⁴²⁻⁴⁵ Al₆²⁻,⁴⁶ Hg₄,^{31,34} M₅⁻ (M = Sb, Bi),⁴⁷⁻⁴⁹ Au₅Zn⁺,⁵⁰ Cu₃³⁺,⁵¹ Cu₄²⁻,⁵² [Fe(X₅)]⁺ (X = Sb, Bi).⁵³

Apart from the metal systems, the annular system N₄²⁻ is also found to be aromatic.⁵⁴ Kuznetsov et al. first studied the M₃²⁻ clusters and explained their stability and aromaticity.⁵⁵ These stable anionic clusters X₃²⁻ (X = Mg;⁵⁵ Zn, Cd, Hg ;⁵⁶ Be⁵⁷), exhibits exclusively pi-aromaticity with no sigma component whatsoever as opposed to other metal clusters like Al₄²⁻ where both σ - and π - aromaticities are present.²⁸ Some of these anionic cluster molecules are of “fleeting” type⁵⁸ and are at the most kinetically stable. Moreover,

there exists a likelihood of “bond-stretch isomerism” in these systems depending on which specific local minima (and/or the global minimum) they are present in.⁵⁹ Among different M_3^{2-} clusters, research on Be_3^{2-} cluster (Figure 1.4) is prominent due to its interesting nature of stability, reactivity, aromaticity, structural variety and bond stretch isomerism. Bond Stretch Isomerism (BSI) occurs when the isomers differ in the lengths of certain bonds. The idea of bond stretch isomerism was first proposed by Hoffmann and co-workers in the year 1972 where they had referred to separate stable configurations whose structures vary only in the length of one (or more) chemical bond(s) where the isomers were shown to occupy different minima on their potential energy surface.⁶⁰⁻⁶² In addition to all these properties Be_3^{2-} is a comprehensively studied system due to the presence of few electrons and accordingly different sophisticated computations are possible.

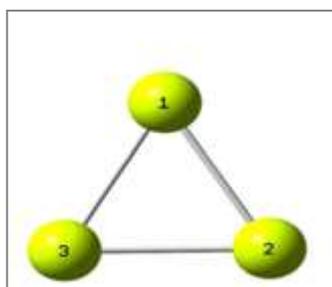


Figure 1.4. Optimized structure of Be_3^{2-}

1.4

AROMATIC NUCLEOBASES

Every multicellular organism includes the DNA which is a significant functional molecule that has evolved to programme and pass on information through generations which play fundamental roles in carrying genetic information in all living things on Earth. DNA has a double helix structure which consists of the four nucleobases adenine (A), cytosine (C), guanine (G) and thymine (T), which is stored within as the primary code and it is the linear sequential arrangement of these four canonical bases that makes up the genetic code (Figure 1.5). They are non-polar and due to their aromaticity, planar. The flat shape of the nucleobases is particularly important when considering their roles as the building blocks of DNA. With respect to the electronic nature of the molecule, aromaticity portrays a closed shell, conjugated system comprising of alternating single and double bonds in a ring. This

arrangement permits pi electron delocalization around the ring, thereby increasing the molecule's stability by resonance.

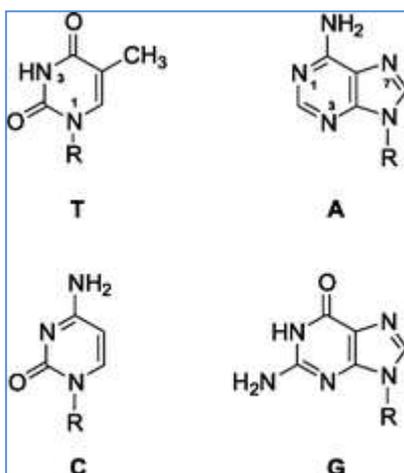


Figure 1.5. The structure and schematic representation of four nucleobases adenine (A), cytosine (C), guanine (G) and thymine (T).

1.5.

OBJECTIVES OF THE THESIS

1. 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. Magnetic criteria are currently the most popular methods and constitute the most frequently used aromaticity indices since magnetic properties provide considerable insight into the concept of aromaticity. Here we make an attempt to review the concept of aromaticity in the light of magnetic criteria in detail.
2. A new domain of aromaticity is explored where novel aromatic molecules are theoretically modeled which gains extra stability due to the generation of aromaticity via the back-donation of the substituted ligands attached to the ring. The well known back-donation of the π -electrons of the Fluorine ligand to the vacant p_z of Boron is tweaked upon while designing these highly stable novel

aromatic systems where the aromaticity is achieved through exo-cyclic conjugation.

3. The concept of exo-cyclic aromaticity is further explored to understand and analyze the stability and aromaticity of modeled novel heteroatomic molecular systems where aromaticity in the heteroatomic central ring is achieved through back donation of electrons from the substituted ligands and to establish the manifestation of exo-cyclic aromaticity in novel designed three-membered heterocyclic moieties.
4. To illuminate the underlying rationale behind the occurrence of bond stretch isomerism in the anionic all-metal aromatic Be_3^{2-} cluster. The primary force behind the presence of two different isomers of the Be_3^{2-} molecule may be the Renner-Teller effect which identifies the prospective of a triatomic molecule present in a degenerate electronic state to split into two when the molecule is bent.
5. In the last part, we make an attempt to provide theoretical elucidation of methylation of aromatic DNA nucleobase cytosine which is an extensively studied DNA modification and its subsequent oxidation processes involving aromatic nucleobases. Here we try to monitor the processes of cytosine modifications using conceptual Density Functional Theory (DFT) based study to compute quantum chemical parameters.

1.6.

REFERENCES

1. Faraday, M. M. *Phil.Trans.Roy.London.* **1825**, 115, 440.
2. (a) Kekulé, A. *Bull.Soc.Chim.Paris* **1865**, 3, 98-100. (b) Kekulé, A. *Ann.Chem.Pharm*, **1866**, 137,129.
3. Erlenmeyer, E. *Ann. Chem. Pharm.* **1866**, 137, 327.

4. Dewar, J (1867). "On the Oxidation of Phenyl Alcohol, and a Mechanical Arrangement adapted to illustrate Structure in the Non-saturated Hydrocarbons". Proc. R. Soc. Edinb. 6: 82–86.
5. (a) Hückel, E. *Z. Phys* **1931**, 70, 204. (b) Hückel, *Z.Phys.* **1932**, 76,628-648. (c) Hückel, E. *Z.Electrochem,Angew. Phys. Chem.* **1937**, 43, 752-788. (d) Hückel, E. *Z.Electrochem, Angew.Phys.Chem* **1995**, 61,866-890.
6. Clar, E. *The Aromatic Sextet*. Wiley & Sons: New York, **1970**.
7. Calvin, M.; Wilson. K. *J. Am. Chem. Soc.* **1945**, 67, 2003.
8. Heilbronner, E. *Tet Lett* **1964**, 5, 1923.
9. Katz, T. H; Garratt, P. J. *J. Am. Chem. Soc.* **1963**, 85, 2852.
10. (a) Colin, B. N. *J. Am. Chem. Soc.* **1972**, 94, 4941. (b) Henrik, O, *Nat Chem*, **2012**, 4, 969.
11. Aihara, J. *J. Am. Chem. Soc.* **1978**, 100, 3339.
12. Li, X.; Kuznetsov, A.; Zhang, H.; Boldyrev, A. Wang, L. *Science* **2001**, 291, 859.
13. Jose, M. M.; Boldyrev, A. I.; Merino, G.; Ugalde, M. J. *Chem.Soc.Rev.* **2015**, 44, 6519.
14. Tsipis, A.; Kefalidis, C.; Tsipis, C. *J. Am. Chem. Soc.* **2008**, 130, 9144.
15. Pauling, L; Wheland, G.W. *J. Chem. Phys.* **1933**, 1, 362.
16. Pauling, L. In *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press: Ithaca, New York, 1960.
17. Goldstein. M.J.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, 93, 6193.
18. Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R.; *Chem. Rev.* **2005** 105 (10), 3842.
19. Schleyer, P.V.R. Introduction: Aromaticity. *Chem. Rev.* **2001**, 101, 1115.
20. Fernández, I.; Dyker, C. A.; DeHope, A.; Donnadiou, B.; Frenking, G.; Bertrand, G. *J. Am. Chem. Soc.* **2009** 131, 11875.
21. Gutowsky, H. S.; McCall, D. W. *J. Phys. Chem.* **1953**, 21, 279.
22. Onak T. P.; Landesman, H; Williams R E.; Shapiro, I paper presented to the Division of Inorganic Chemistry, 135th National Meeting of the American Chemical Society, Boston, Mass, April 1959.
23. Cotton, F. A.; Wilkinson, G. "*Advanced Inorganic Chemistry*," Interscience, London, 1966, 256.
24. Olah, G. A.; Mo, Y. K.; Halpern, Y. *J. Am. Chem. Soc.* **1972**, 94, 3551.
25. Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, 3, 39.
26. Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1979**, 18, 1760.
27. Li, X.-W.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, 117, 7578.
28. Li, X.; Zhang, H. F.; Wang, L. S.; Kuznetsov, A. E.; Cannon, N. A.; Boldyrev, A. I. *Angew Chem Int Ed* **2001**, 40, 1867.
29. Díaz-Cervantes, E.; Poater, J.; Robles, J.; Swart, M.; Solà, M. *J. Phys. Chem. A* 2013, 117, 40, 10462.
30. Kuznetsov, A. E.; Boldyrev, A. I.; Li, X.; Wang, L. S. *J Am Chem Soc* **2001**, 123, 8825.
31. Twamley, B.; Power, P. P.; *Angew Chem Int Ed* **2000**, 39, 3500.
32. Cisar, A.; Corbett, J. D. *Inorg Chem* **1977**, 16, 2482.
33. Critchlow, S. C.; Corbett, J. D. *Inorg Chem* **1984**, 23, 770.

34. Tuononen, H. M.; Suontamo, R.; Valkonen, J.; Laitinen, R. S. *J Phys Chem A* **2004**, *108*, 5670.
35. Todorov, I.; Sevov, S. C. *Inorg Chem* **2004**, *43*, 6490.
36. Todorov, I.; Sevov, S. C. *Inorg Chem* **2005**, *44*, 5361.
37. Gillespie, R. J.; Barr, J.; Kapoor, R.; Malhotra, K. C. *Can J Chem* **1968**, *46*, 149.
38. Gillespie, R. J.; Barr, J.; Crump, D. B.; Kapoor, R.; Ummat, P. K. *Can J Chem* **1968**, *46*, 3607.
39. Barr, J.; Gillespie, R. J.; Kapoor, R.; Pez, G. P. *J Am Chem Soc* **1968**, *90*, 6855.
40. Couch, T. W.; Lokken, D. A.; Corbett, J. D. *Inorg Chem* **1972**, *11*, 357.
41. Burford, N.; Passmore, J.; Sanders, J. C. P. In: Liebman, J. F.; Greenburg, A. (eds) From atoms to polymers. Isoelectronic analogies. VCH, New York, 1989, p 53.
42. Li, X.; Wang, X. B.; Wang, L. S. *Phys Rev Lett* **1998**, *81*, 1909.
43. Wu, H.; Li, X.; Wang, X. B.; Ding, C. F.; Wang, L. S. *J Chem Phys* **1998**, *109*, 449.
44. Baeck, K. K.; Bartlett, R. J.; *J Chem Phys* **1998**, *109*, 1334.
45. Kuznetsov, A. E.; Boldyrev, A. I. *Struct Chem* **2002**, *13*, 141.
46. Kuznetsov, A. E.; Boldyrev, A. I.; Zhai, H. J.; Li, X.; Wang, L. S. *J Am Chem Soc* **2002**, *124*, 11791.
47. Gausa, M.; Kaschner, R.; Lutz, H. O.; Seifert, G.; Meiwes-Broer, K. H. *Chem Phys Lett* **1994**, *230*, 99.
48. Gausa, M.; Kaschner, R.; Seifert, G.; Faehrmann, J. H.; Lutz, H. O.; Meiwes, K. H. B. *J Chem Phys* **1996**, *104*, 9719.
49. Zhai, H. J.; Wang, L.S.; Kuznetsov, A. E.; Boldyrev A. I. *J Phys Chem A* **2002**, *106*, 5600.
50. Tanaka, H.; Neukermans, S.; Janssens, E.; Silverans, R. E.; Lievens. P. *J Am Chem Soc* **2002**, *125*, 2862.
51. Alexandrova, A. N.; Boldyrev, A. I.; Zhai, H. I.; Wang, L. S. *J Phys Chem A* **2005**, *109*, 562 .
52. Wannere, C. S.; Corminboeuf, C.; Wang, Z. X.; Wodrich, M. D.; King, R. B.; Schleyer, P. v. R. *J Am Chem Soc* **2005**, *127*, 5701.
53. Lein, M.; Frunzke, J.; Frenking, G. *Angew Chem Int Ed* **2003**, *42*, 1303.
54. Van Zandwijk, G.; Janssen, R. A. J.; Buck, H. M. *J Am Chem Soc* **1990**, *112*, 4155.
55. Kuznetsov, A. E.; Boldyrev, A. I. *Chem. Phys. Lett.* **2004**, *388*, 452.
56. Yong, L.; Chi, X. *Theochem* **2007**, *818*, 93.
57. Roy, D. R.; Chattaraj , P. K. *J Phys Chem A* **2008**, *112*, 1612.
58. Hoffmann, R.; Schleyer, P. v. R.; Schaefer, H. F., III. *Angew Chem Int Ed* **2008**, *47*, 7164.
59. (a) Parkin, G. *Acc Chem Res* **1992**, *25*, 455. (b) Parkin, G. *Chem Rev* **1993**, *93*, 887.
60. Stohrer W. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779.
61. Stohrer W. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 1661.
62. Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, *110*, 4506.