

## Preface

Aromaticity is a notion that appeared in the mid-nineteenth century to differentiate between unsaturated hydrocarbons and formally unsaturated benzene [1–3]. At the end of the nineteenth century it seemed that cyclicity was a necessary condition for differentiation between the two, but at the beginning of the twentieth century it turned out that the above assumption was not correct because cyclooctatetraene exhibited typical properties known for polyenes [4]. The essential property of benzene-like compounds, often identified with aromatic compounds, was low reactivity. Hence thermodynamic stability was defined as resonance energy [5, 6] and was the first quantitative measure of aromaticity. Many theoretical approaches were proposed later to estimate this quantity, and now the criterion is often considered to be the most fundamental [7]. Almost at the same time, magnetic susceptibility was used to describe aromaticity [8, 9]. Consequently, many concepts based on magnetism were developed, probably the most effective in assessment of aromaticity being nucleus independent chemical shift (NICS) [10] or Fowler's maps of ring currents [11]. The criterion served Schleyer as a basis for a definition of aromaticity: "Compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic. Cyclic delocalisation may also result in bond length equalization, abnormal chemical shifts and magnetic anisotropies, as well as chemical and physical properties which reflect energetic stabilisation"[12]. For a long time bond length alternation has been used as an indication of non-aromaticity, but a quantitative approach based on this criterion was only invented by A. Julg in 1967 [13]. This idea was extended in 1972 [14] and can be used to estimate both the local and global aromaticity of molecules. Actually there are many quantitative descriptors assumed to be, or even named as, aromaticity indices. To make the situation clearer, widely acceptable criteria were reported in Tetrahedron: [15]

A cyclic  $\pi$ -electron compound is aromatic if there appears a measurable  $\pi$ -electron delocalization in the ground state of the molecule. This is associated with:

1. An increase of stability related to the system without cyclic  $\pi$ -electron delocalization
2. Intermediate and unaltered bond lengths that are close to the mean value of the length for the typical single and double bonds
3. Inducing  $\pi$ -electron ring current when the molecule is exposed to the external magnetic field

An additional criterion, in our opinion a very important one, but which is not a property of the ground state, is reactivity. Generally, aromatic compounds undergo electrophilic substitution reactions (aromatic substitution) more easily than addition, which is often expressed as a typical tendency of these kinds of systems to retain their initial  $\pi$ -electron structure [16, 17].

Since aromaticity has been recognized as a multidimensional phenomenon [18, 19] two modern definitions take into account all the above-listed features. Krygowski, Katritzky et al. [15] proposed:

Those cyclic  $\pi$ -electron systems which follow all the features of aromatic character (including reactivity) are aromatic, while those which follow some but not all of them are partly aromatic.

In turn, Chen, Schleyer et al. [20] proposed that:

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.

So far, aromaticity has no unique and widely accepted definition. Despite this shortcoming, or maybe perversely due to it, the phenomenon has been a subject of an ever-increasing number of intense studies. What is the reason for that? The concept, although theoretical in nature, is of immense practical importance [15]. Its impact on modern organic chemistry can hardly be overestimated. Let the facts speak for themselves. Two thematic issues of Chemical Reviews have been devoted to aromaticity in the last decade [7, 20–53]. The 2001 May volume of the journal, which explicitly dealt with the topic [21–39], was recognized as being extremely successful. The Association of American Publishers awarded that work the Best Single Issue Prize in the “Professional and Scholarly Publishing Division” [40]. The 2005 October issue, dedicated more generally to electron delocalization in sigma and pi sense, was a consequence of that success [7, 20, 40–53]. In the meantime two excellent single review articles appeared: “Aromaticity as a cornerstone of heterocyclic chemistry” [54] and “Aromaticity of polycyclic conjugated hydrocarbons” [55]. Soon after, the December 2006 thematic issue of Chemical Reviews on “Designing the molecular world” [56] contributed with a number of highly recommended articles on the subject: “Twisted acenes,” [57] “Aromatic molecular-bowl hydrocarbons: synthetic derivatives, their structures, and physical properties,” [58] “Heterofullerenes,” [59] and “Renaissance of annulene chemistry” [60]. Conferences, symposia, and workshops organized all over the world gathered scientists representing different fields of science and having different experience and skills. Let us note just few of those events: European Science Foundation Exploratory Workshop: New Perspectives on Aromaticity, organized in Exeter (2004) [61–74] or ISNA – International Symposium on Novel Aromatic Compounds [75, 76], arguably the most important and influential conference in the field, which is now organized every two years, with the next meeting to be held in Luxembourg 2009 [75, 77–94].

The question has been posed: how does aromaticity change if in a carbocyclic  $\pi$ -electron system one or if a few CH units are replaced by heteroatom(s)? What can be expected? Undoubtedly, these kinds of changes are associated with changes in electron structure due to different electronegativity, e.g.,  $\chi(\text{Csp}^2) = 2.75$  as compared with  $\chi(\text{Nsp}^2) = 3.94$ ,  $\chi(\text{B}) = 2.04$ ,  $\chi(\text{S}) = 2.56$ ,  $\chi(\text{P}) = 2.19$  (Tables 6.5 and 6.7 in [95]) and should be reflected in  $\pi$ -electron delocalization. In consequence, many properties typical of aromaticity may change, sometimes dramatically.

This volume consists of seven contributions, which present various kinds of heteroaromatic compounds and various aspects of their chemistry, physical chemistry, and structural chemistry. The aromaticity of these compounds is, however, the crucial point of these contributions and makes this notion more understandable.

The first chapter by M. A. R. Matos and Joel F. Liebman deals with recent advances in the experimental thermochemistry of nitrogen, oxygen, and sulfur derivatives of indane and indene. Analyses are based on enthalpies of formation in gaseous phase, and are mostly concerned with aromatic stability and strain destabilization in cases where molecules contain a saturated fragment. At the end there is a table of enthalpies of formation of indanes and related dibenzoannulated species. The table also presents enthalpy differences between indane/indene analogs and their five-membered fragments, which are fused to benzene. The differences are a rough estimation of enthalpy of formation of benzene but also contain the contribution resulting from conjugation between the benzene ring and a fused fragment.

Chapter 2 by László Nyulászi and Zoltán Benkő deals with the chemistry and physical organic chemistry of aromatic phosphorus heterocycles and is divided into four subchapters dealing with three-, four-, five-, and six-membered rings, in which there may be more than one phosphorus atom. The chapter begins with a clear presentation of the electronic structure that phosphorus may achieve in molecules with CP bonds. For cyclopentadiene and phosphole eight aromaticity indices are collected. Almost all of them indicate that phosphole is more aromatic than cyclopentadiene. It is also shown that even small structural effects (substituent, bonding modes) can have a substantial impact on the chemistry of the reported systems.

Chapter 3 by Marcin Stepień and Lechosław Latos-Grażyński deals with  $\pi$ -electron delocalization in relation to tautomerism and chemical properties in porphyrines and porphyrinoids. An important and very interesting problem discussed here is that for the title systems aromaticity may be concerned either locally (for one or a few rings) or for a whole macrocycle. The body of the chapter is based on analyses of  $^1\text{H}$  NMR and UV/Vis spectroscopies and takes into account the relations between  $\pi$ -electron delocalization and tautomeric equilibria.

In the next chapter by Ibon Alkorta and José Elguero, applying computational approaches presents interrelations between aromaticity and chemical and physico-chemical properties of heterocycles. The following problems and properties are considered: tautomerism, conformation analysis, acid–base equilibria, H-bonding and proton transfer, energetics, reactivity, IR-, NMR-, and MW-spectroscopies. At the end is a discussion of problems related to supramolecules and macrocycles.

Alexandru T. Balaban in the fifth chapter considers six-membered rings with one heteroatom and even some metallobenzene derivatives. Thus, analysis of the

role of heteroatom becomes more precise. There is a comparison of the aromaticity of 18 charged and neutral species with indicated values of NICS. Since the formation of the title compounds results from replacement of a CH fragment by an appropriate heteroatom or its substituted derivative, the original “aromaticity constants” (that may also be considered “relative electronegativities” of these groupings) of the first row atoms are presented.

Alžbeta Krutošáková and Tibor Gracza present in the sixth chapter recent studies of heteroanalogs of pentalene dianion in which the CH fragment is replaced by O, NH, S, Se, and Te atoms. Mostly the syntheses of these kinds of compounds or their derivatives are presented, but the distinction between particular representatives is well outlined.

Chapter 7, by Jacek Młochowski and Mirosław Giurg deals with aromatic and related selenaheterocycles and their applications. The chapter presents firstly the chemical properties of selenaheterocyclic rings: tautomerism, reactions on the carbon atom and on the heteroatom, and finally ring transformations. Next are presented the syntheses of selenaheterocyclic compounds like selenphanes, isoselenazoles, selenazoles, selenadiazoles, and selenoporphyrines. Finally, an outline of the applications of selenaheterocycles is presented.

The role of the concept of aromaticity in the field of heterocyclic chemistry can hardly be overestimated. It is considered to be a cornerstone of heterocyclic chemistry [54]. We believe that the presented selection of recent achievements in the field supports this opinion very well.

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